

THE JOURNAL OF PHYSICAL CHEMISTRY

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SYMPOSIUM ON SOLUTIONS OF ELECTROLYTES, NEW HAVEN, CONN., JUNE 16-18, 1954

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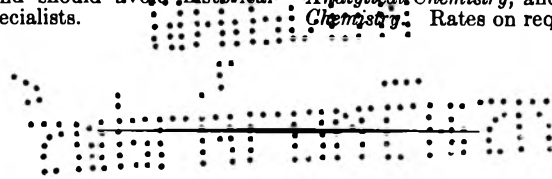
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ELECTROLYTES: FROM DILUTE SOLUTIONS TO FUSED SALTS

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The properties, particularly the conductance of electrolyte solutions in different solvents, including water, are critically reviewed in the light of current theories. These theories account rather successfully for the properties of electrolytic solutions in all solvents. Concentrated solutions are best looked upon as solutions of solvent in fused salt. The concentrations at which the theories of dilute solutions begin to fail in a significant manner remain uncertain.

Foreword

It is the purpose of this paper to interpret existing experimental data in the light of current theories and, conversely, to evaluate current theories in the light of existing data. In what follows we shall deal largely with the conductance of electrolytic systems. The reason for doing this is twofold: first, conductance is the one property of such systems that can be measured with precision over a wide range of conditions such as solvent, solute, concentration and temperature; second, both time and printer's ink are limited so far as this symposium is concerned. Our discussion will relate largely to systems at ordinary temperatures since adequate data are lacking at other temperatures.

I. Underlying Theoretical Relationships

From the theories of Debye and Hückel,¹ Onsager² and Bjerrum³ have been derived equations which, along with the law of mass action, account rather satisfactorily for the properties of dilute electrolyte solutions. These equations are

$$-\log f = \beta\sqrt{C} \quad (1)$$

$$\Lambda/\gamma = \Lambda_0 - (\Lambda_0\alpha + \beta)\sqrt{C\gamma} \quad (2)$$

$$\frac{C\gamma^2 f^2}{1-\gamma} = K \quad (3)$$

and

$$K^{-1} = \frac{4\pi N}{1000} \left(\frac{e^2}{DkT} \right)^3 Q(b) \quad (4)$$

Here C is the equivalent concentration, f is the activity coefficient, γ is the degree of dissociation, Λ is the equivalent conductance, Λ_0 is the limiting conductance and α and β are constants whose val-

ues are fixed by the dielectric constant and viscosity of the solvent, the number of unit charges on each of the ions and the absolute temperature. K is the constant of the ion-ion pair equilibrium.

In equation 4, N is Avogadro's number, e is the unit of charge, D is the dielectric constant of the solvent, k is Boltzmann's constant, T is the absolute temperature and

$$b = e^2/aDkT \quad (5)$$

where a is the distance between charges when the ions are in contact. Values of $Q(b)$ have been computed by Bjerrum for values of b from 1 to 15, and by Fuoss for values from 15 to 80. For a completely dissociated electrolyte, $\gamma = 1$ in equations 1 and 2, while equations 3 and 4 become inapplicable.

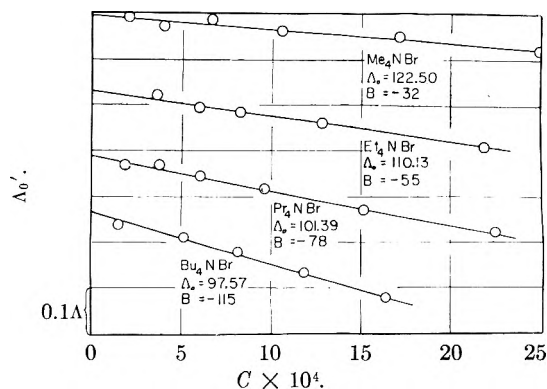
All the above equations are based on the assumption that the solutions are dilute and, therefore, they apply more nearly the lower the concentration. They are also approximate equations inasmuch as, in their development, certain terms of higher order have been neglected. They are also underlain by the assumption that the interaction between ions due to Coulombic forces may be described in terms of the macroscopic dielectric constant D . In equation 2 the further assumption is made that Stokes' law is applicable to the motion of ions in a viscous medium.

In what follows we shall examine the applicability of these equations in the light of available experimental data. We shall attempt to determine to what extent observed deviations are due to neglected terms and, so far as possible, what other factors may be involved. We shall attempt to determine the conditions such as concentration, dielectric constant, and the like, under which the equations are applicable. Finally, we shall con-

(1) P. Debye and E. Hückel, *Physik. Z.*, **24**, 305 (1923).

(2) L. Onsager, *ibid.*, **28**, 27 (1927).

(3) N. Bjerrum, *Kgl. Danske Vidensk. Selskab*, **7**, No. 9 (1926).

Fig. 1.— Λ_0' - C plots for quaternary ammonium bromides.

sider such data as we have that may throw some light on the state of electrolytes in solutions of high concentration.

II. Completely Dissociated Electrolyte Solutions

1. **Deviations from Onsager's Equation.**—There are only two pure solvents, water and liquid hydrogen cyanide, in which 1,1 electrolytes are completely dissociated into their ions and concerning which necessary data are available. Therefore, it is only in these two solvents that we are able to determine how the equivalent conductance of free ions depends on their concentration in a pure solvent. It should be noted, however, that such studies may be carried out with suitable solvent mixtures.

Onsager,² Onsager and Fuoss⁴ and Fuoss⁵ have pointed out that a more complete conductance equation should contain terms of order higher than \sqrt{C} . Such terms appear in the following equation, assuming complete dissociation

$$\Lambda = \Lambda_0 - (\Lambda_0\alpha + \beta)\sqrt{C} + BC + D'C \log C \quad (6)$$

where B and D' are constants which, thus far, have not been successfully evaluated on a theoretical basis.

There are many electrolyte systems for which D' appears to be zero and the conductance is adequately described as a function of concentration by the simple equation

$$\Lambda = \Lambda_0 - (\Lambda_0\alpha + \beta)\sqrt{C} + BC \quad (7)$$

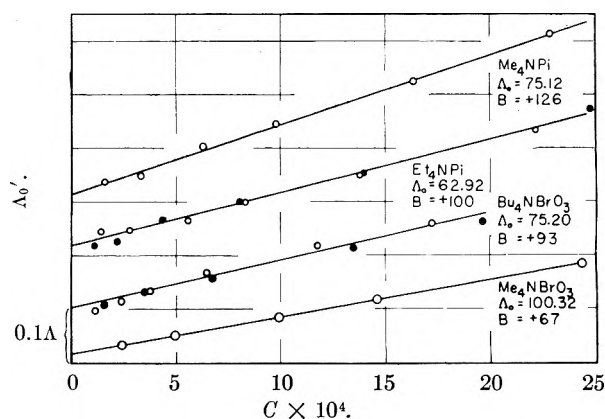
In evaluating the term BC , it is convenient to write (7) in the form

$$\frac{\Lambda + \beta\sqrt{C}}{1 - \alpha\sqrt{C}} \equiv \Lambda_0' = \Lambda_0 + BC \quad (8)$$

The coefficient B of equation 8 is not identical with that of equation 7; the relation is: $B_7 = B_8(1 - \alpha\sqrt{C})$. For water at 25°, $\alpha = 0.23$ and over the concentration range within which the two equations are valid, the differences in B are within the limit of experimental error, about 0.01% in the value of Λ . From a plot of Λ_0' vs. C , the slope yields the value of B . Since this value is the change in Λ_0' per unit of concentration change, it will be dependent on the value of Λ_0 . In comparing values of B for different salts in a given solvent or for a given salt in different solvents, it is well to normal-

(4) L. Onsager and R. M. Fuoss, *This Journal*, **36**, 2689 (1932).

(5) R. M. Fuoss, *Physik. Z.*, **35**, 59 (1934).

Fig. 2.— Λ_0' - C plots for bromates and picrates.

ize equation 8 by dividing through by Λ_0 . This leads to the equation

$$\Lambda_0'/\Lambda_0 = 1 + B'C \quad (9)$$

where

$$B' = B/\Lambda_0 \quad (10)$$

Mr. E. Lowell Swarts has recently carried out an extensive investigation in the Brown Laboratories for the purpose of learning how B is dependent on the nature of the ions of the electrolyte. In Fig. 1, are shown plots of Λ_0' vs. C for a series of quaternary ammonium bromides in water at 25°. It will be noted that all plots are linear for concentrations up to about $2 \times 10^{-3} N$. Deviations of experimental values from the straight line are generally within 0.01 Λ -unit. All deviations are negative and B becomes more negative as the size of the quaternary ammonium ions increases. In Fig. 2 are shown Λ_0' vs. C plots for quaternary ammonium salts of large anions. Here B is positive and is the greater the larger the negative ion. Again, all plots are linear up to $2.5 \times 10^{-3} N$.

TABLE I

VALUES OF B' FOR SALTS IN WATER AT 25°

	I ⁻	Br ⁻	Cl ⁻	NO ₃ ⁻	BrO ₃ ⁻	Pi ⁻
Me ₄ N ⁺	-0.81	-0.26	+0.13	+0.12	+0.67	+1.68
Et ₄ N ⁺	-1.05	- .50	+1.59
<i>n</i> -Pr ₄ N ⁺	-2.39	- .77
<i>n</i> -Bu ₄ N ⁺	-2.79	-1.18	-1.27	+1.24
<i>i</i> -Am ₄ N ⁺	-1.68
Na ⁺	+1.03	+0.56	+2.05

Values of B' for various salts are presented in Table I. Examination of this table will show that the value of B' is a specific property of the ions. For example, B' becomes more negative as we go from chloride to iodide and from tetramethyl- to tetrabutylammonium halide. For salts having a positive deviation, B' is greater as the positive ion is smaller for the picrates but the reverse holds for bromates. This is apparent from the plots for the two picrates and the two bromates in Fig. 2.

As Onsager² has pointed out, if ion association occurs, the measured conductance will be less than predicted by the simple equation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C} \quad (11)$$

For this reason, some writers have ascribed a negative deviation from Onsager's equation to ion association. This conclusion, however, is not

warranted. Deviation due to association is not linear over any considerable concentration range and we should expect the deviation to become smaller (negatively) as the positive ions become larger, which is not the case. Fuoss and Kraus⁶ found that, in mixtures of dioxane and water, tetraisoamylammonium nitrate is completely dissociated for mixtures of dielectric constant greater than about 44. As we shall see presently, we have recently verified the results of Fuoss and Kraus and have found that other electrolytes exhibit a similar behavior.

2. When does Onsager's equation begin to fail?

We may now inquire as to the nature of the deviations at higher concentrations. For sodium iodide, the Λ_0' vs. C plot is linear within 0.05% from $2 \times 10^{-4} N$ to $5 \times 10^{-3} N$ and $B = 131.7 \Lambda_0$ for this salt is 127.24. At higher concentrations, BC reaches very large values. For $C = 1.0$, $BC = 131$. In other words, at this concentration the linear deviation term has a value greater than Λ_0 . For tetrabutylammonium iodide, $B = -290$. If the deviation from Onsager's equation continued linearly to higher concentrations, this electrolyte would have zero conductance at a concentration of about 0.3 N . Actually, for this salt, the deviation from Onsager's equation does not remain linear at concentrations greater than about $2.5 \times 10^{-3} N$.

Now the linear term of equation 7 has the same theoretical basis as has the term $(\Lambda_0\alpha + \beta) \sqrt{C}$; if one term fails at higher concentrations, should not the other terms fail also? In other words, does Onsager's equation fail at high concentrations because the underlying assumptions are no longer valid? The only alternative that we have is that the general equation should contain terms in C of order higher than the first power. Precise data between 1×10^{-4} and 0.1 N might resolve this question.

3. Liquid Hydrogen Cyanide.—Hydrogen cyanide has a dielectric constant of 118 at 18°. The only data that we have for this solvent are those of Coates and Taylor.⁸ While the precision of these measurements is understandably lower than that of similar measurements in water, the data, nevertheless, enable us to find the magnitude of the deviation from Onsager's equation. Plots of Λ_0' vs. C are linear for all salts and B is positive for all. In Table II are shown values of B' in HCN and H₂O. In general, the values of B' for salts in this solvent are markedly larger than they are for the same salts in water; B' has the lowest value for tetramethylammonium iodide and the largest for sodium picrate. There is a rough parallelism between the B' values in HCN and in water, but there are numerous inversions. These may in part be due to lack of precision.

4. The $D'C \log C$ Term.—While there is a theoretical basis for the introduction of this term into the conductance equation, it cannot be said that it has been shown that this term affects ob-

TABLE II
VALUES OF Λ_0 , B AND B' FOR SOME SALTS IN HCN AT 18°

Salt	Λ_0	B	B' , HCN	B' , H ₂ O
Me ₄ NCl	382.6	+1730	+4.53	+0.12
Me ₄ NBr	383.0	+1700	+4.44	-0.26
Me ₄ NI	387.7	+190	+0.49	-0.81
Et ₄ NI	357.2	+510	+1.43	-1.05
Me ₄ NPi	310.6	+1130	+3.64	+1.68
Et ₄ NPi	282.2	+1400	+4.96	+1.59
NaI	345.1	+430	+1.25	+1.03
NaPi	267.8	+1200	+4.67	+2.05

servations significantly. In the first place, it seems to be definitely absent in the case of many salts. For solutions of sodium iodide,⁷ for example, the plot of Λ_0' vs. C is strictly linear up to $5 \times 10^{-3} N$. It is difficult to see how this linear plot could hold so closely over so large a concentration range if a term of the form of $D'C \log C$ were present in the conductance equation. Indeed, if any term other than linear were present, it would have to be in a high power of C .

The deviation curves of potassium salts, particularly salts of oxygen acids, frequently exhibit a minimum at concentrations between about 3×10^{-3} and $5 \times 10^{-4} N$. These minima may often be fitted by an equation of the form of

$$\Lambda_0' = BC + D'C \log C \quad (12)$$

This equation has a minimum at a concentration C_m which satisfies the equation

$$\log C_m = -(B/D' + 0.43) \quad (13)$$

and $\Lambda_0 = \Lambda_0'$ at the concentration

$$C^* = 2.7 C_m \quad (14)$$

Baker^{7,9} has obtained conductance values for a number of potassium salts which could be fitted by means of equation 12, but this equation does not apply at concentrations much above C^* . Numerous measurements in the Brown Laboratories have been carried out with a variety of potassium salts which have yielded deviation curves with minima, but the measurements were not reproducible in the region of the minima. In some cases, we were able to eliminate the minima but not consistently so. In numerous instances, it was observed that the resistance of the solution drifted toward lower values on the initial addition of salt. These peculiar effects were seldom observed with sodium salts and never with quaternary ammonium salts.

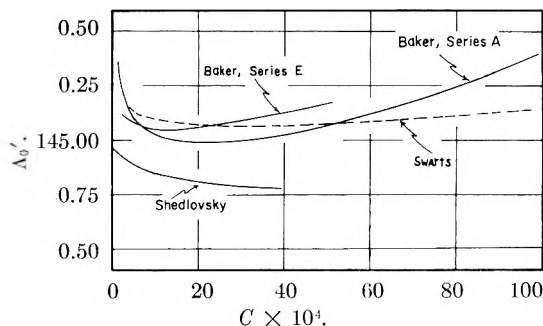


Fig. 3.— Λ_0' - C plots for potassium nitrate.

(6) R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

(7) E. G. Baker, Thesis, Brown University (1951).

(8) G. E. Coates and E. G. Taylor, *J. Chem. Soc.*, 1495 (1936). See also J. Lange, J. Bergå and N. Konopik, *Monatsh.*, **80**, 709 (1949).

(9) (a) E. G. Baker and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **37**, 726 (1951); (b) "Electrochemical Constants," National Bureau of Standards, Department of Commerce, Washington D. C., 1953, p. 27.

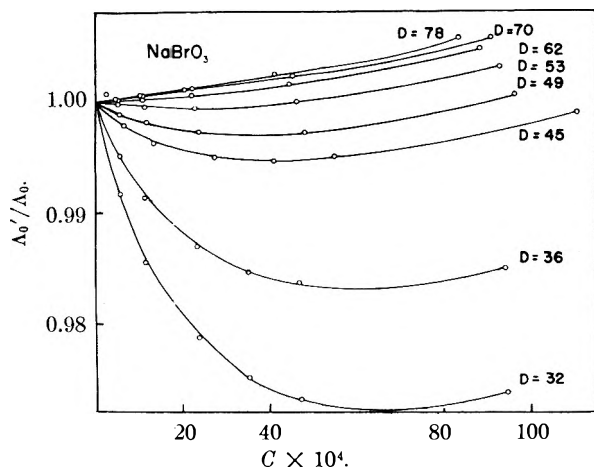


Fig. 4.— Λ_0'/Λ_0 - C plots for NaBrO_3 in dioxane-water mixtures.

By way of example, Λ_0' vs. C plots are shown in Fig. 3 for potassium nitrate. Three of these plots relate to different salt samples measured in the Brown Laboratories. One is a plot of Shedlovsky's data¹⁰ for potassium nitrate. It may be noted that Baker's data⁹ from series E may be very closely fitted by equation 12.

It is, of course, possible that for some salts, B/D' has a value so large that the minimum lies at concentrations inaccessible to measurement. In such cases, the $D'C \log C$ term would have rather large values between 1×10^{-4} and $1 \times 10^{-2} N$ unless D' were very small. It is doubtful, however, that a satisfactory fit could be had in the region where the deviation is a linear function of C . The logarithmic term seems definitely excluded for salts for which B is negative.

III. Ion Association

1. **Evaluation of B .**—If the equivalent conductance of the free ions is known as a function of their concentration, it is always possible, in principle, to evaluate the dissociation constant K of the ion pair equilibrium by combining this relation with equations 1 and 3. In the method of Fuoss⁸ for the evaluation of K , it is assumed that the free ions conform to Onsager's equation 2. As we have just seen, this equation does not hold precisely in aqueous solutions and one may suspect that it does not hold for other solvents. Now, if ion association takes place in a given solvent, it is not possible to evaluate the constant B of the linear deviation term because ion association causes a conductance decrease and this effect cannot be separated from effects due to other causes. However, it is possible to evaluate B for mixtures of water with solvents of lower dielectric constant and values of B and B' can be obtained as a function of dielectric constant. Once the functional relation between B' and D has been determined in mixtures where the salt is completely dissociated, the value of B' may be approximated for other mixtures by extrapolating to lower dielectric constants.

Mr. Robert W. Martel has carried out such an investigation with solutions of several salts in dioxane-water mixtures at 25°. Values of B'

(10) T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

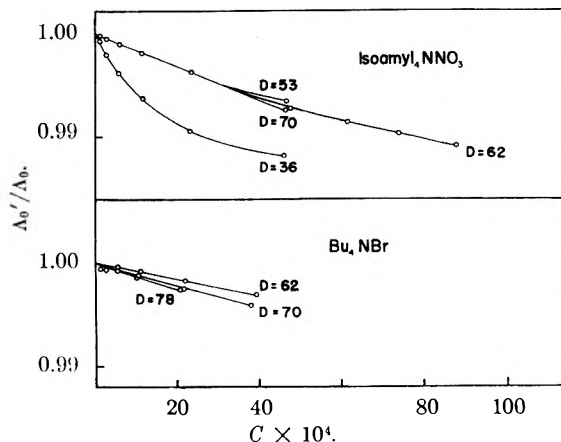


Fig. 5.— Λ_0'/Λ_0 - C plots for Am_4NNO_3 and Bu_4NBr in dioxane-water mixtures.

were determined from Λ_0'/Λ_0 vs. C plots for water and for mixtures of decreasing dielectric constant until ion association sets in. Such plots for sodium bromate are shown in Fig. 4 and, for tetraisoamylammonium nitrate and tetrabutylammonium bromide, in Fig. 5.

For sodium bromate in pure water, B' is positive; with decreasing dielectric constant, B' decreases and becomes negative. The value of B' is equal to the slope of the plots at low concentrations. It will be noted that the deviation increases sharply in going from a dielectric constant of 53.3 to 48.9. This is due to the fact that ion association occurs in the mixture of lower dielectric constant.

For tetraisoamylammonium nitrate, B' has the same value from pure water to 30% dioxane mixtures ($D = 53.3$). For this salt, the Λ_0'/Λ_0 vs. C plots of Fig. 5 practically coincide for these mixtures and appear as a single line in dilute solutions. For the 50% mixture ($D = 35.9$), negative deviation is markedly greater than it is for mixtures of greater dielectric constant due to ion association at these lower values of D . For the butyl salt, $-B'$ decreases slightly as D decreases.

In Fig. 6 are shown values of B' for four salts as a function of dielectric constant. For sodium bromate and tetrabutylammonium iodide, B' increases (negatively), almost linearly, as D decreases; for tetraisoamylammonium nitrate, B' does not change and for tetrabutylammonium bromide, $-B'$ decreases slightly as D decreases. Values of B' and B are shown in Table III, columns 3 and 4, for tetrabutylammonium iodide, tetraisoamylammonium nitrate, sodium bromate and tetrabutylammonium bromide.

2. **Evaluation of Dissociation Constants.**—Plots of B' vs. D are not far from linear. If such plots are extrapolated to values of D where association occurs, the value of B' for the mixture may be approximated. Thus, since $B = B'\Lambda_0$, the deviation BC from Onsager's Equation may be computed. The conductance equation of the free ions may then be written

$$\Lambda - BC \equiv \Lambda^* = (\Lambda_0\alpha + \beta)\sqrt{C} \quad (15)$$

According to the procedure of Fuoss¹¹ equation 2 is assumed to yield conductance values of the free

(11) R. M. Fuoss, *ibid.*, **57**, 488 (1935).

ions as a function of concentration. According to the present method, it is assumed that the conductance of the free ions is given by equation 15.

Since the deviations from Onsager's equation are negative, values of K computed by the present method are larger than those computed by that of Fuoss.

In Table III, columns 5 and 6, are given values of K_a and K_F respectively, as computed according to the present method and that of Fuoss. It will be noted that K_a is always greater than K_F and that the difference is the greater the larger the value of K . For most of the salts, the degree of association, $1 - \gamma$, ranged between 0.1 and 0.3%. For the most concentrated solutions of sodium bromate for $D = 31.5$, the association reached a value of 1.15%.

TABLE III

CONSTANTS OF SALTS IN DIOXANE-WATER MIXTURES

D	A_0	B	B'	K_a	K_F
Tetrabutylammonium iodide					
78.48	96.27	-279	-2.9
66.10	70.70	-239	-3.4
53.38	53.81	-252	-4.7	...	0.19
40.20	43.78	-285	-6.5	0.36	.095
35.85	41.67	-304	-7.3	.128	.060
Tetraisoamylammonium nitrate					
78.48	89.27	-150	-1.68
70.33	74.84	-134	-1.79
61.86	63.11	-113	-1.79
53.28	54.01	-94	-1.74	...	0.47
35.85	42.55	-77	-1.8	0.113	.092
Sodium bromate					
78.48	105.75	59	0.56
70.33	90.37	48	.53
61.86	77.27	21	.27
53.28	66.43	-17	-0.26	...	3.2
48.91	61.76	-37	-.60	0.88	0.52
44.54	57.66	-52	-.90	.43	.28
35.85	50.72	-96	-1.9	.130	.098
31.53	47.99	-145	-3.0	.072	.054
Tetrabutylammonium bromate					
78.48	97.56	-127	-1.30
70.33	80.89	-94	-1.16
61.86	67.66	-53	-0.78

It may be pointed out, in this connection, that values of K cannot be evaluated with any degree of assurance for highly dissociated salts in pure solvents. It is probable that when K is less than 1×10^{-3} , the values obtained by the Fuoss method are not greatly in error. For large values of K , no method yet devised can yield an assured value of this constant. Further investigation of mixtures of water with solvents of lower dielectric constant would be of interest.

IV. Bjerrum's Theory

In the light of the measurements of Fuoss and Kraus⁶ with solutions of tetraisoamylammonium nitrate in dioxane-water mixtures, equation 4 of Bjerrum accounts remarkably well for the relation between the dielectric constant of the solvent medium and the dissociation constant of the elec-

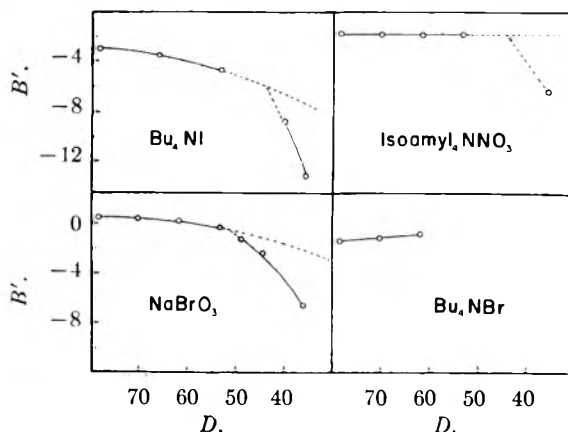


Fig. 6.— B' - D plots for salts in dioxane-water mixtures.

trolyte. If values of K for sodium bromate in Table III are plotted against values of D , a curve is obtained which rises sharply with increasing dielectric constant and approaches infinity at a value of D in the neighborhood of 52. This is in accord with Bjerrum's theory. We have not made a comparison on a quantitative basis because, at best, for large values of K , numerical values are uncertain. However, we cannot escape this conclusion that, in accordance with theory, for each salt there is a limiting value of the dielectric constant above which association does not occur.

According to Bjerrum's theory, the quantity a of equation 5 is the distance of closest approach of a pair of ions. While the values of a as derived from equation 5 are of the right order of magnitude, they are probably too large. We have precise values of the distance between charges in ion pairs from dielectric measurements of salts in benzene. From the polar moments,¹² the distance between charges is obtained by dividing the moments by the value of the unit charge. For tetraisoamylammonium thiocyanate and tetrabutylammonium perchlorate, the distances are, respectively, 3.23 and 2.96 Å. From dissociation constants, Fuoss and Kraus have found the value 6.4 Å. for tetraisoamylammonium nitrate. It would seem that values of a as so derived are about twice the distance between centers of charge. Naturally, the distance between charges may be affected somewhat by the solvent.

The properties of an electrolyte solution cannot be precisely described in terms of a macroscopic dielectric constant. Values of the dissociation constant for tetrabutylammonium picrate in ethylene chloride, ethylidene chloride and *o*-dichlorobenzene,¹³ are, respectively, 22.6×10^{-5} , 4.54×10^{-5} and 1.71×10^{-5} . The dielectric constants of these solvents are, respectively, 10.23, 10.00 and 9.927. For tetrabutylammonium nitrate the constant is 11.8×10^{-5} in ethylene chloride and 0.46×10^{-5} in *o*-dichlorobenzene; for tetraethylammonium nitrate the constant is 7.4×10^{-5} in ethylene chloride and 0.75×10^{-5} in ethylidene chloride. The constant for tetraisoamylammonium

(12) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, part 4, 585 (1936).

(13) F. Accascina, E. L. Swarts, P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **39**, 917 (1953).

nitrate for a dioxane-water mixture of dielectric constant $10^{(6)}$ is 2.5×10^{-4} ; in ethylene chloride,¹⁴ it is 1.20×10^{-4} .

On the basis of existing data, it would appear that while Bjerrum's theory reproduces the dissociation constant as a function of dielectric constant rather successfully for a given type of solvent, such as dioxane-water mixtures, it yields only approximate values as we go from solvent to solvent. Obviously, the effective dielectric constant is to some extent dependent on constitutional factors of the ions as well as of the solvent molecules.

V. Triple Ions

Observable phenomena are much more varied and complex in solvents of low than they are in solvents of high dielectric constant, such as water. This is not due to the failure of any of the underlying laws which are applicable to dilute solutions. It is due to the fact that, as the dielectric constant decreases, new ionic and molecular species make their appearance, all of which are in equilibrium with one another. The many and varied properties of electrolyte solutions have their origin in interactions resulting from the charges on the ions, whether the ions be entirely free or whether they be associated with one another in any one of many different ways.

In water, we have to deal only with Coulombic interactions between ions separated by distances that are large with respect to their size or that of the solvent molecules. As the dielectric constant decreases (to a value of 35 to 50), short range interactions must be taken into account; ion pairs, or ion dipoles, are formed. As the dielectric constant falls to a value in the neighborhood of 20, interactions take place between ions and ion dipoles, triple ions are formed. In solvents of yet lower dielectric constant, dipoles interact with one another to form quadrupoles and more complex structures and these, in turn, interact with simple ions to form new ionic species.

Fuoss and Kraus¹⁵ have developed a theory for the interaction between ions and ion dipoles, somewhat analogous to the theory of Bjerrum for the short range interactions between ions. They have applied this theory to their conductance measurements with solutions of tetraisoamylammonium nitrate in dioxane-water mixtures of low dielectric constant. The theory gives a good account of the conductance through the minimum. On the basis of this theory, triple ions of this salt are not stable in those mixtures having dielectric constants above 23. Fuoss¹⁶ has derived expressions for the conductance temperature coefficient. This theory has been applied with considerable success to solutions to tetrabutylammonium nitrate and picrate in anisole¹⁷ over the temperature range from -33 to 95° . The validity of the triple ion equilibrium has been well established for solutions in a variety of solvents.

(14) L. M. Tucker and C. A. Kraus, *J. Am. Chem. Soc.* **69**, 545 (1947).

(15) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

(16) R. M. Fuoss, *ibid.*, **56**, 1837 (1934).

(17) G. X. Bien, C. A. Kraus and R. M. Fuoss, *ibid.*, **56**, 1860 (1934).

VI. Solutions in Benzene

1. **Dilute Solutions.**—Our knowledge of solutions in benzene is more extensive than that of solutions in any other solvent with the possible exception of water. At the same time, the properties of benzene solutions are more varied than are those in any other solvent. In benzene, we have conductance measurements from $1 \times 10^{-6} N$ to $2 N$; we have molecular weight measurements from near $1 \times 10^{-4} N$ to 0.75 molal; and we have polarization data down to $2 \times 10^{-5} N$. We have values of the dipole moments for the ion dipoles of many salts and we know the distance between the centers of charge in these dipoles.

Aqueous solutions of different salts of strong acids and bases have practically the same properties. Constitutional factors are unimportant; about the only observable difference is that of ion mobilities. On the other hand, in solutions of salts in solvents of very low dielectric constant, constitutional factors play a dominant role.

As an example, let us consider the properties of tetraisoamylammonium thiocyanate in benzene at 25° . The dissociation constant¹⁸ of the ion pair equilibrium is approximately 5.6×10^{-18} . At a concentration of $1 \times 10^{-6} N$, only two parts per million of the electrolyte exists in the form of free ions; the remainder is present as ion dipoles, whose polarization¹² is 5050 cc., dipole moment, 15.4 Debye units and distance between centers of charge 3.23 Å. A minimum occurs in the conductance at a concentration of $1.4 \times 10^{-5} N$ due to triple ion formation. The constant¹⁸ of the triple ion equilibrium is 7.1×10^{-6} . On the basis of polarization measurements,¹² quadrupole formation begins to appear at concentrations as low as $4 \times 10^{-5} N$. At higher concentrations, the quadrupoles interact to form more complex structures. At $C = 1.7 \times 10^{-3} N$, the molecular weight corresponds to that of 4.35 formula weights per mole.¹⁹

2. **Conductance.**—In Fig. 7, are plotted values of $\log \Lambda$ vs. $\log C$ for tetraisoamylammonium thiocyanate in benzene at 25° . In the same figure is shown a similar plot for tetrabutylammonium thiocyanate in order to illustrate the form of the conductance curve at somewhat higher concentrations.²⁰ In the same figure is shown a plot of the association number of the amyl salt²¹ on the same scale of $\log C$.

At lower concentrations, the number of ions per mole of salt is proportional to the equivalent conductance of the solutions; at higher concentrations, it is greater because of the increasing viscosity of the solution. To a first approximation, the conductance of a solution is inversely proportional to its viscosity. At $C = 1.03 N$, the viscosity of the tetraamyl salt solution is 9.76 times that of benzene and the conductance is 0.36. On the basis of the viscosity of benzene and the conductance-viscosity product of this salt in ethylene chloride, the value of Λ_0 in benzene should be approximately 90. Thus about 4% of the electrolyte

(18) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 3614 (1933).

(19) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934).

(20) L. E. Strong and C. A. Kraus, *ibid.*, **72**, 166 (1950).

(21) D. T. Copenhafer and C. A. Kraus, *ibid.*, **73**, 4557 (1951).

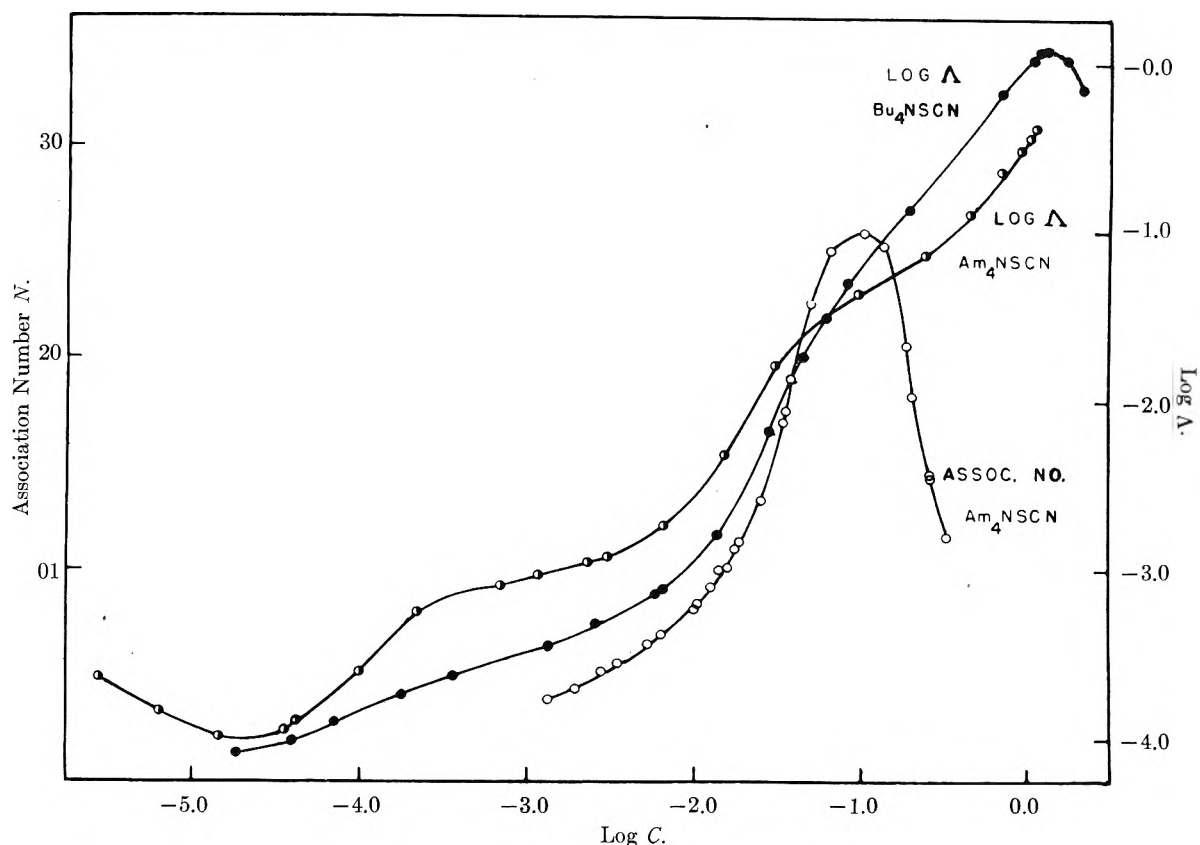


Fig. 7.—Plots of association numbers *versus* $\log C$ for Am_4NSCN and of $\log \Lambda$ *versus* $\log C$ for Am_4NSCN and Bu_4NSCN in benzene.

should be present in the ionic form. As may be seen from Fig. 7, tetrabutylammonium thiocyanate is a better conductor than the corresponding amyl salt at higher concentrations. The conductance passes through a maximum of 1.16 at 1.35 N . We do not know the viscosity but it is probably of the order of 20 times that of benzene. On this basis, the electrolyte might be dissociated by as much as 20%.

3. Association Numbers.—To account for the increasing conductance of tetraisoamylammonium thiocyanate with concentration from a minimum value of 1×10^{-4} at 1.4×10^{-5} to a value of 0.40 at a concentration of 1.14 N , we need to consider the various equilibria in these solutions as indicated by molecular weight determinations. In Fig. 7, are shown values of the association numbers, n (formula weights per mole), as a function of $\log C$. According to polarization measurements, ion dipoles begin to associate to quadrupoles at 4×10^{-5} N . At 1.74×10^{-3} N , the association number of tetraisoamylammonium thiocyanate is already 4.35, far beyond the quadrupole stage. As shown on the figure, the association number increases greatly with increasing concentration to reach a maximum value of 26 at 0.14 N . Thereafter association decreases rapidly to a value of 11.5 at a concentration of 0.49 N . The molecular weight that corresponds to a given association number is a mean value; the solution contains molecular species ranging all the way from, perhaps, simple dipoles to aggregates containing many more formula weights than the average value, n .

We have seen that the conductance increase at the minimum may be accounted for on the basis of interaction of simple ions with ion dipoles with the formation of triple ions. As quadrupoles are formed, we should expect them to interact with simple ions to form a new ionic species and a further conductance increase would result. As more molecular species are formed with increasing concentration, the fraction of salt present in ionic form increases and the conductance increases accordingly. It is not improbable that the larger aggregates are multiply charged.

While the conductance increase may be accounted for fairly satisfactorily at lower concentrations, perhaps up to the maximum value of n , it seems probable that other factors come into play at higher concentrations, above $C = 1.0$, for example. As may be seen from the plot of n *vs.* $\log C$, the association number falls off rapidly at concentrations above that of maximum n . It may be noted, however, that the conductance increase in this concentration range is much smaller for the amyl than for the butyl salt. For tetrabutylammonium thiocyanate, n reaches a maximum value of 32 at $C = 0.31$ N , a concentration much higher than that of the amyl salt. At the highest concentration measured for the amyl salt, the conductance is 0.40. At the same concentration, for the butyl salt, the conductance is 1.08, approximately two and one-half times that of the amyl salt.

In this connection, it may be pointed out that salts of large ions and relatively small polar mo-

ments are much poorer conductors than corresponding salts of larger moments. Their association numbers are also much smaller. Thus, the dipole moment of tetraisoamylammonium picrate is 18.3 D , that of the corresponding tertiary salt is 13.3 D . For the quaternary salt, the value of n is 1.40 at $C = 0.0041$; that of the tertiary salt at this concentration is approximately 1.06 and it is only 2.64 at $C = 0.72$. At 0.0132 N , the conductance of the quaternary salt is 0.0108; the conductance of the tertiary salt at a concentration of 0.015 is 3.1×10^{-6} . The conductance of the tertiary salt increases greatly at higher concentrations, reaching a maximum value of 0.047 at $C = 1.08$. The quaternary salt could not be measured at high concentration because of limited solubility.

At lower concentrations, the conductance of solutions of electrolytes in benzene is largely determined by the size and structure of their ions and the dipole moment of their ion pairs. At high concentrations, solutions of all electrolytes are rather good conductors.

VII. Concentrated Solutions

1. **Aqueous Solutions.**—At high concentrations, the viscosity of all electrolyte solutions increases with increasing concentration. Since the conductance of a solution is roughly proportional to the reciprocal of viscosity, the conductance may fall to very low values when the viscosity is large. Accordingly, in studying the conductance of concentrated solutions, the value of the conductance-viscosity product, $\Lambda\eta$, is employed.

Concentrated aqueous electrolyte solutions would be of great interest because in this solvent the solute exists completely as free ions at all concentrations. It would be of interest to know how $\Lambda\eta$ might vary as water was added to a fused salt. There is only one inorganic salt with which the necessary measurement might be made, lithium chlorate, which melts at 129°. Some conductance data are available²² for highly concentrated solutions of this salt but, unfortunately, viscosity data are lacking.

In Fig. 8, are shown plots of $\Lambda\eta$ against moles of salt per mole of water for four salts; these are the only salts for which both conductance and viscosity data are available at high concentrations. The

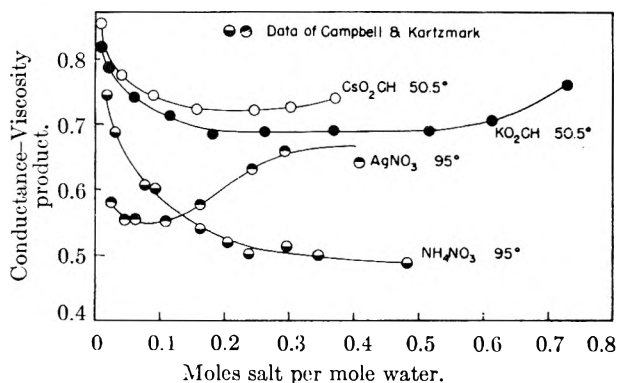


Fig. 8.—Plots of $\Lambda\eta$ versus moles salt per mole water for salts in water.

(22) W. M. Burgess, Thesis, Brown University, 1926.

two uppermost plots are for cesium and potassium formates.²³

The solubility limit for the first salt is two moles of water per mole of salt; for potassium formate it is somewhat over one mole of water per mole of salt. These salts were measured at 50.3°. Silver nitrate and ammonium nitrate²⁴ have been measured at 95°. The limiting concentration for both these salts is two moles of water per mole of salt.

In dilute solutions, the value of $\Lambda\eta$ falls off in accordance with Onsager's equation, since the value of η differs little from that of water. The curve for the formates begins to flatten out at about 10 moles of water per mole of salt (about 4 N) and changes little thereafter until it begins to rise again at their highest concentrations. For cesium formate, the rise comes at about 3 moles of water per mole of salt and for potassium formate at about 1.5 moles. Although similar, the curves for the two formates differ markedly.

The plot for silver nitrate differs markedly from that of the formates just discussed. The $\Lambda\eta$ product falls off sharply to a minimum at 12 moles of water per mole of salt. After passing the minimum, the value of $\Lambda\eta$ levels off; above a ratio of about 2.5/1 of water to salt, the course of the plot is uncertain. The plot of $\Lambda\eta$ for ammonium nitrate falls off gradually and continuously with increasing concentration to a value of about 0.5 at two moles of water per mole of salt. It is possible that hydrogen bonding takes place between the ammonium and the nitrate ions.

In any case, the course of the $\Lambda\eta$ values for different salts varies markedly. Just what is going on in these solutions we cannot say, but we should bear in mind that ions are hydrated and the degree of hydration must necessarily change at sufficiently high concentrations.

2. **Solutions in Butanol.**—In Fig. 9, are shown plots of Seward's measurements²⁵ with solutions of tetrabutylammonium picrate in butanol over the complete concentration range from dilute solution to fused salt. Equivalent conductances and values of $\Lambda\eta$ are plotted vs. weight per cent. of salt. Measurements were carried out at 91°; the melting point of the salt is 90° and the dielectric constant of butanol at that temperature is 9.8. The dissociation constant of the salt is 3.2×10^{-4} . The limiting equivalent conductance, Λ_0 , of the salt is 71.5 and the equivalent conductance of the fused salt is 0.778. The viscosity of the fused salt is 581×10^{-3} and that of butanol is 6.09×10^{-3} .

The conductance decreases continuously from dilute solution to fused salt without the appearance of a minimum, which would seem to indicate that triple ion formation does not occur. The Λ plot passes through a pronounced minimum at 5.04 wt. % of picrate, which corresponds to 0.84 mole % and a concentration of 0.083 molar. At concentrations above that of the minimum, $\Lambda\eta$ increases rapidly and, from 40 to 100%, the value of $\Lambda\eta$ is very nearly a linear function of weight per

(23) M. J. Rice and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **39**, 802 (1953).

(24) A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.*, **30**, 128 (1952).

(25) R. P. Seward, *J. Am. Chem. Soc.*, **73**, 515 (1951).

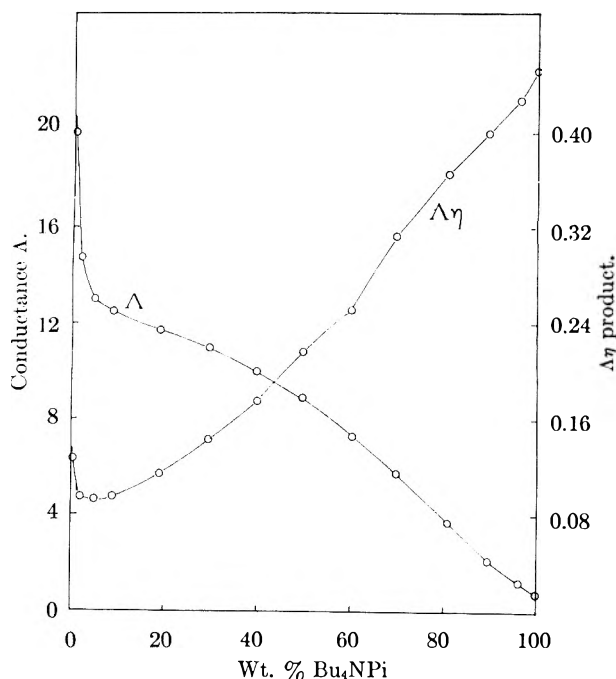


Fig. 9.—Plot of Λ and $\Lambda\eta$ versus weight per cent. of salt for Bu_4NPI in butanol.

cent. of salt. At 40 wt. % the mole fraction is 0.1, the concentration is 0.75 N and the solution contains 9 moles of solvent per mole of salt.

The conductance at the minimum is 18% of Λ_0 . The decrease in the value of $\Lambda\eta$ from the lowest concentration to the minimum is mainly due to the increasing association of ions to ion pairs; this follows from the value of the dissociation constant. *Per contra*, the increase in $\Lambda\eta$ at higher concentrations can only be due to dissociation of ion pairs. We have so little knowledge concerning concentrated solutions, particularly as regards the $\Lambda\eta$ product, that it is not possible to postulate a mechanism to account for the increase of dissociation above the minimum. It seems, however, that, in some way, interaction takes place whereby a greater proportion of salt is converted to free ions as concentration increases. We do not know to what extent the assumption of a macroscopic dielectric constant may lead us astray. Up to about 0.1 N , the conductance phenomena in benzene may be reasonably well accounted for on the basis of the formation of more complex molecular and ionic species with increasing concentration, the interaction between which leads to increased conductance much as in the case of triple ions. It would seem that the laws of dilute solutions do not apply to butanol solutions at concentrations above 0.083 N . There appears to be need for more extensive investigation of concentrated solutions in solvents of different dielectric constant, particularly, evaluation of the conductance-viscosity product and its dependence on concentration.

3. Solutions in Bromine.—Some results have been reported for solutions of salts in bromine^{26,27} which indicate that if the concentration of salts in

(26) G. W. Moessen and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **38**, 1023 (1952).

(27) M. J. Rice and C. A. Kraus, *ibid.*, **39**, 1118 (1953).

this solvent could be carried to sufficiently high values, the conductance-viscosity product would reach values such as might be expected of fused salts. Recently, Mr. Philip L. Mercier has measured the conductance and the viscosity of solutions of triisoamylammonium chloride in bromine at 25° from dilute solutions to fused salt. He has also determined the vapor pressure of these solutions up to the fused salt. The chloride ion of triisoamylammonium chloride forms a very stable complex with one molecule of bromine; the salt melts at 38° and the supercooled liquid may be handled without difficulty.

In Fig. 10, are shown plots of equivalent conductance and viscosity as a function of mole fraction of salt assumed to have the formula: $i\text{-Am}_3\text{NHCl}\cdot\text{Br}_2$. As may be seen from the figure, the conductance rises from very low values to a maximum of 4.23 at a concentration at which 12 moles of bromine are present per mole of salt. With increasing concentration, the conductance falls continuously to a value of approximately 0.080 for the fused salt. The viscosity is also shown in Fig. 10 as a function of mole fraction of salt. The viscosity of bromine is 0.009435; that of the fused salt is 5.63 or 600 times that of bromine.

In Fig. 11, is shown a plot of $\Lambda\eta$ values as a function of mole fraction of salt. The ordinates of this plot are the products of the ordinates of the two plots of Fig. 10. For the fused salt, $\Lambda\eta = 0.439$, a value much the same as that of salts in ordinary solvents. Thus, for Am_4NSCN , in ethylene chloride, $\Lambda_0\eta = 0.523$. With increasing bromine content of the system, $\Lambda\eta$ reaches a maximum value of 0.504 for one mole of bromine per mole of salt. The product falls to a value of 0.439 for 2.5 moles of bromine per mole of salt. With increasing bromine content of the system, the product decreases to very small values for the more dilute solutions.

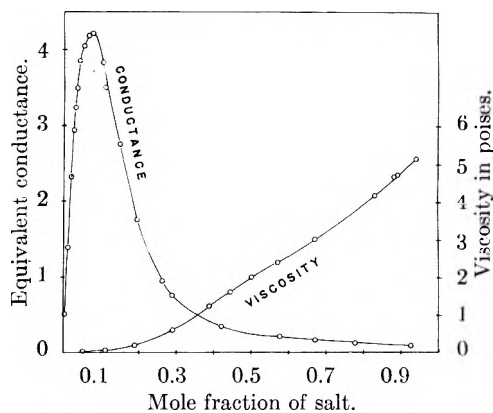


Fig. 10.—Plots of Λ and η versus mole fraction salt for Am_3NHCl in bromine.

It is apparent that up to 2.5 moles of bromine per mole of salt, the $\Lambda\eta$ product changes but little; in this region, the salt exists completely as ions. The decrease in the value of $\Lambda\eta$ in solutions of higher bromine content must be due to the formation of ion pairs.

In Fig. 11, is also shown a plot of vapor pressure lowering (actually vapor density lowering) $(p_0 - p)/p_0$ as a function of mole fraction of salt. It is

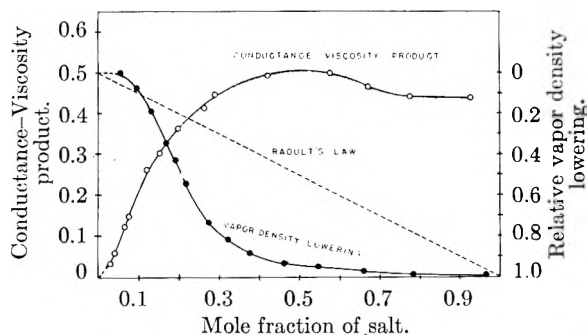


Fig. 11.—Plots of $\Delta\eta$ and vapor density lowering versus mole fraction salt for Am_3NHCl in bromine.

seen that, beginning with a solution containing about 10 moles of bromine per mole of salt, the vapor pressure decreases rapidly. For the mole fraction 0.99, the value found is 0.7% that of bromine. This great lowering of the vapor pressure of the solution with respect to that of the solvent may be due, at least in part, to the interaction of the negative ion with bromine molecules.

The broken line of Fig. 11 represents the vapor pressure change due to a normal solute in accordance with Raoult's law. It will be noted that the experimental curve crosses the broken line at a mole fraction of approximately 0.1 and, thereafter, rises well above it. This effect may be accounted for on the hypothesis that at higher bromine content of the solution, ion dipoles associate to form quadrupoles and perhaps more complex structures much as they do in benzene. This is not surprising in view of the relatively low dielectric constant of bromine, 3.09.

VIII. Conclusion

The laws of dilute electrolyte solutions, based on the theories of Debye and Hückel, Onsager, and Bjerrum, along with the law of mass action, account rather satisfactorily for the conductance and some other properties of dilute solutions in a great variety of solvents. While some refinements remain to be made in various details of the mathematical expressions derived from these theories, the theories themselves appear to be adequate within the limits postulated for their applicability. Highly concentrated electrolyte solutions are largely, or completely, dissociated into their ions. As of now, one of the outstanding problems in the field of electrolytes appears to lie in the transition region between dilute and concentrated solutions. It seems unlikely that the solution of this problem will be found in the mere extension of the laws of dilute solutions as we now know them.

Acknowledgment.—This Author wishes to acknowledge his indebtedness to Messrs E. Lowell Swarts, Robert W. Martel and Philip L. Mercier for permission to make use of the results of their investigations²⁸ prior to their publication.

DISCUSSION

R. M. Fuoss (Yale University).—The distinction between "free" and "associated" ions is arbitrary. No problem arises, of course, when ions are at large distances from each

(28) These investigations were carried out under the auspices of the Office of Naval Research.

other or when they are in contact. But just when do two approaching ions cease being counted as free ions? Bjerrum in 1926 proposed a simple (and entirely adequate) definition: for $r \gg \epsilon^2/2DkT$, ions are considered unassociated. In order to eliminate the sharp cut-off, a pair distribution function was later proposed (R. M. Fuoss, *Trans. Faraday Soc.*, 30, 967 (1934)) which showed that ions have in general a high probability of being either near each other or else far apart, and that the population of the transition distances is small as long as certain conditions on concentration and the ratio $\epsilon^2/aDkT$ are satisfied (R. M. Fuoss, *J. Amer. Chem. Soc.*, 57, 2604 (1935)).

F. T. GUCKER (Indiana University).—In your paper you discuss the $C \log C$ term. Could Professor Fuoss or Onsager tell us how they are progressing with the theoretical calculation of the coefficients of this term which they discussed at the Debye Symposium at Cornell?

R. M. FUOSS (Yale University).—Frequent mention has been made of the $c \log c$ terms in the conductance equation. Some comment on their origin and nature seems appropriate. Both in the electrophoresis and relaxation terms in the Onsager coefficient, the integral

$$\text{Ei}(\kappa a) = \int_{\kappa a}^{\infty} e^{-t} \frac{dt}{t}$$

appears when the expansion is carried to powers of concentration higher than $c^{1/2}$. In the final conductance equation, this function appears with a multiplier of order κ^2 , i.e., concentration to the first power. In order to show the limiting behavior of the function, Onsager and Fuoss (*J. Phys. Chem.*, 36, 2740 (1932)) included the formula

$$\text{Ei}(x) = -0.5772 - \ln x + x - x^2/2.2! + \dots$$

in their discussion of electrophoresis. It was not intended that this expansion be used for computation. The hazards of using it are best illustrated by a graph. The solid line in

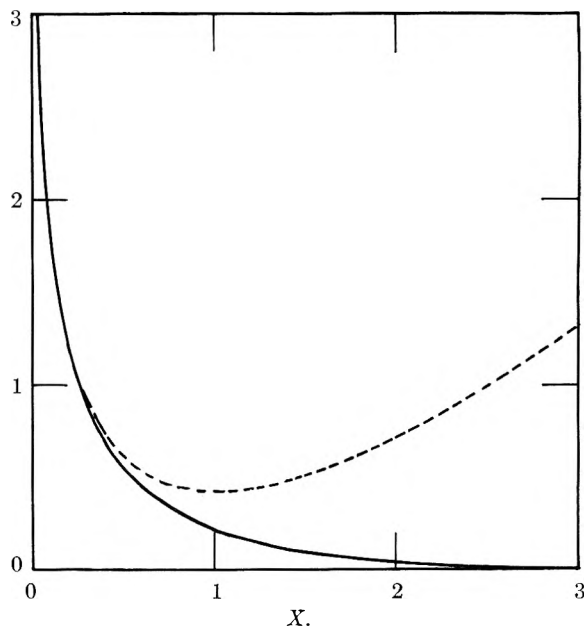


Fig. A.—Solid curve, exponential integral; dotted curve, approximation.

Fig. A is $\text{Ei}(x)$: note that $\text{Ei}(0) = \infty$ and that $\text{Ei}(\infty) = 0$. The dotted curve is the function

$$f(x) = -0.5772 - \ln x + x$$

For $0 < x < 0.2$, $f(x)$ is an excellent approximation for $\text{Ei}(x)$, but for $x > 0.3$, $f(x)$ begins to deviate more and more from $\text{Ei}(x)$ and after the minimum at $x = 1$ diverges to infinity. For a 1-1 electrolyte at $c = 0.010$, $\kappa a = 0.14$ for an ion size $a = 4.3 \times 10^{-8}$ cm. and at $c = 0.10$, $\kappa a = 0.46$. It is therefore clear that the " $c \log c$ " approximation may not be used in the range of even moderate concentrations. To state the situation in a slightly different way, the $c \log c$ approximation is numerically reliable only in the range of variables

where the $c \log c$ terms themselves are relatively insignificant compared to the $c^{1/2}$ terms. The explicit function must be used when the $c^{1/2}$ approximation is inadequate. It is tabulated as $[-Ei(-x)]$ in Jahnke-Einde's "Funktionentafeln" (Teubner, Leipzig, 1933), pp. 83-86.

LARS ONSAGER (Yale University).—Conduction in fused salts presents a difficult theoretical problem, but we may try to analyze the data. The temperature coefficients correspond to activation energies in the same 3-6 kcal./mole for univalent ions; the activation energies for the motion of ions in water fall in the same range. To explain this coincidence, we may interpret the energy required to form a hole as electrostatic field energy, and the field in the hole is determined by the charge of the ion.

H. S. FRANK (University of Pittsburgh).—Further in the direction of what the last two speakers have pointed out, the coarse-grained or "cage" structure (short-range) of liquids, including water, gives a way of defining association. Since this short-range structure makes a clear distinction between pairs of ions which are nearest neighbors and ones which are not nearest neighbors, it is meaningful to call the former associated and the latter non-associated. Even in the case of lithium iodide mentioned by Professor Onsager, it seems unlikely that the probability that an iodide ion can displace a water molecule touching a lithium ion is identically zero. The rare cases in which this occurred would give associated pairs of lithium iodide. In many other cases such associated pairs would presumably occur a good bit more frequently.

J. H. WANG (Yale University).—There appears to be some evidence conflicting with Professor Onsager's suggestion that diffusion and viscous flow in both aqueous and fused salt solutions involve the same activation mechanism, *i.e.*, the creation of vacancies or "holes" in the liquid system. If

the creation of vacancies is the activation mechanism of viscous flow, the viscosity of the liquid should increase with increased external pressure. But Bridgman has shown that for liquid water near 0° the viscosity actually decreases when the external pressure is increased continually from 1 to 1000 kg./sq. cm. This observation shows that the activation mechanism for diffusion or viscous flow in aqueous solutions may involve essentially a "breaking" or distorting of the hydrogen bonds in the water lattice instead of the creation of vacancies. Consequently I do not think that we can conclude that diffusion or viscous flow in aqueous and fused salt solutions involves the same activation mechanism from the mere fact that the corresponding activation energies are of the same order of magnitude.

LARS ONSAGER (Yale University).—Not only must the hole be so large that the ion can move, but the electrostatic potential must be such that it will have a low potential energy in its new location.

SOL ZAROMB (Massachusetts Institute of Technology).—Would you attribute the observed decrease in association in concentrated solutions to a counterbalancing of interionic forces? For example, if we assume a homogeneous dielectric constant ϵ throughout the entire medium, then a univalent negative ion j , located at distances of 5 and 6 Å. from two univalent positive ions at its left and right, respectively, would be subject to an electrostatic force $\sum_i \frac{e^2 \vec{r}_{ij}}{\epsilon \bar{r}_{ij}^3}$ equivalent to a separation of 9 Å. from a single positive ion, where e is the ionic charge and \vec{r}_{ij} is the vector distance between j and an i -th positive ion.

C. A. KRAUS.—I am unable to suggest a mechanism that would account for the reversal of the association process in concentrated solutions which would be anything more than a restatement of observed facts in terms that are less understandable than simple words.

RELATIVE CHEMICAL POTENTIALS OF ELECTROLYTES AND THE APPLICATION OF THEIR GRADIENTS

BY HERBERT S. HARNED

Contribution No. 1222 from the Department of Chemistry of Yale University, New Haven, Conn.

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Following some general remarks on the present state of knowledge of the relative chemical potentials of electrolytes, some recent determinations of activity coefficients of systems containing two electrolytes in concentrated solutions will be discussed. The theory of irreversible processes emphasizes the role of the gradient of the chemical potential as a "force" in causing the motions of the components of the solutions. Recent results on the diffusion coefficients of electrolytes in aqueous solutions will be employed to assess the importance of this role.

Three fourths of a century have passed since Gibbs¹ defined the quantity which has come to be called the "chemical potential" and developed its manifold uses in reversible thermodynamics. If the denotation, "chemical potential," has a meaning analogous to gravitational or electrical potential, its gradient should act as a force. Therefore, it is not strange to find the gradient of the chemical potential in company with the gradients of the electrical potential and temperature appearing as a so-called "force" in Onsager's² theory of reciprocal relations in irreversible processes and in irreversible thermodynamics.

The first extremely important generalization of solution thermodynamics was to show that all experimental mechanisms used to determine equilibria in solutions measure the same quantity. Explicitly, determinations of the lowering of the freezing point, rise in boiling point, lowering of the

vapor pressure, osmotic pressure, solubility and electromotive forces of suitable cells may all be used to determine the relative chemical potential of an electrolyte, now usually denoted the relative partial molal free energy of the electrolyte, or what ultimately amounts to the same thing the relative partial molal free energy of the solvent. From 1887 when van't Hoff's first papers appeared to the present time thousands of experimental contributions have been devoted to this subject and the most accurate results have been compiled, largely as activity coefficients, in various treatises. Accuracy in the determinations of activity coefficients has proved difficult to obtain and knowledge of them as a function of electrolyte concentration, nature of the medium, the temperature and the pressure is still fragmentary.

The study of irreversible processes in electrolytic solutions has proceeded simultaneously with these thermodynamic investigations. Owing to the accuracy of evaluating the gradient of the electrical

(1) J. W. Gibbs, "Collected Works," Yale University Press, New Haven, Conn., 1948.

(2) L. Onsager, *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).

potential and the sensitivity of the alternating current bridge, conductance measurements of electrolytes can be carried out with great accuracy. The conductance method is a general one and as employed with consummate skill over the years by Kraus and his colleagues has pioneered our knowledge of electrolytes in non-aqueous solvent solutions.

For the irreversible process of salt diffusion at constant temperature, the movement of the electrolyte in one direction and its replacement by the solvent, the gradient of the chemical potential is one of the propelling "forces." Although Fick's laws of diffusion were proposed in 1855, only recently have the measurements of diffusion coefficients been sufficiently accurate to test the current theories of this phenomenon. Indeed, for its full explanation in dilute solutions, accurate values of limiting conductances are required in addition to precise values of the activity coefficients as functions of the concentrations of the solutes.

In the sequel as illustrations of both reversible and irreversible processes, we shall restrict the discussion to some recent results on the thermodynamics of mixed electrolytes in concentrated solutions, to measurements of the diffusion coefficients of electrolytes in dilute aqueous solutions and to the diffusion coefficients of calcium chloride over a wide range of concentrations.

The Activity Coefficient of Hydrochloric Acid in Solutions of Chlorides of Different Valence Types at Constant Total Ionic Strength.—From measurements of the electromotive forces of cells of the type



containing hydrochloric acid and potassium, sodium, lithium chlorides, Harned^{3a} and Hawkins^{3b} found that at constant total molalities varying from 1 to 6 *M* the logarithm of the activity coefficient of hydrochloric acid varied linearly with its concentration. Later Harned⁴ surveyed the existing data on these 1-1 electrolyte mixtures. Since no experimental method was known to determine the activity coefficient of the salt in these acid mixtures, Harned assumed that its logarithm also varied linearly and represented the situation by the equations

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12}\mu_2 \quad (1)$$

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21}\mu_1 \quad (2)$$

$$\mu_1 + \mu_2 = \text{constant} = \mu \quad (3)$$

In these equations γ_1 and γ_2 are the activity coefficients of the acid and salt, respectively, in the mixtures, $\gamma_{1(0)}$ and $\gamma_{2(0)}$, their activity coefficients in pure water, μ_1 and μ_2 their concentrations expressed as ionic strengths and α_{12} and α_{21} , the linear constants at a given total ionic strength. If relations (1) and (2) are valid, their introduction into the Gibbs-Duhem equation leads to the simple result

$$\alpha_{21} = \alpha_{12} + \frac{2}{2.303} (\phi_{2(0)} - \phi_{1(0)}) \quad (4)$$

Thus, if α_{12} is determined, knowledge of the osmotic coefficients, $\phi_{1(0)}$, $\phi_{2(0)}$ of the acid and salt, respec-

tively, in their pure aqueous solutions, permits the calculation of α_{21} .⁵

A valuable contribution to the subject has been made by Glueckauf⁶ who has shown by means of fundamental cross differentiation equations

$$\nu_1 \left(\frac{\partial \ln \gamma_1}{\partial m_2} \right)_{m_1} = \nu_2 \left(\frac{\partial \ln \gamma_2}{\partial m_1} \right)_{m_2} \quad (5)$$

that if equations 1 and 2 are valid, then for 1-1 electrolyte mixtures, the sum ($\alpha_{12} + \alpha_{21}$) is not a function of the total ionic strength. This necessary condition can be used to test Harned's assumption of the linear variation of logarithm of the activity coefficient $\log \gamma_2$, in the acid solutions. In Table I are recorded the values of ($\alpha_{12} + \alpha_{21}$) obtained by Harned for hydrochloric acid-alkali metal chloride and hydrobromic acid-alkali metal bromide solutions. The constancy of these values of ($\alpha_{12} + \alpha_{21}$), particularly at the ionic strengths greater than one is good evidence for the linear variation rule for both electrolytes in these solutions. The

TABLE I

THE SUM OF PARAMETERS OF EQUATIONS 1 AND 2 FOR THE SYSTEMS HX-MX, IN WATER ($\mu = m_1 + m_2$)

System	t/μ	0.5	$-(\alpha_{12} + \alpha_{21})$	1.5	2	3
HCl-LiCl	25	0.005	0.007	0.006	0.007	0.009
HCl-NaCl	10	.030	.031	.029	.027	
	20	.026	.028	.027	.031	
	25	.025	.026	.027	.027	.027
	30	.023	.025	.026	.028	
HCl-KCl	25	.012	.018	.024	.025	
HCl-CsCl	25	-.035	-.040	-.046	-.047	-.047
HBr-LiBr	25	.029	.025	.025	.026	
HBr-NaBr	25	.032	.032	.031	.026	
HBr-KBr	25	-.012	-.011	-.015	-.015	

hydrochloric acid-cesium chloride and hydrochloric acid-potassium chloride systems exhibit the same characteristic at concentrations above 1.5 *M*. At concentrations lower than this, ($\alpha_{12} + \alpha_{21}$) appears to be a function of the total ionic strength. Recent isopiestic vapor pressure measurements by Robinson⁷ on the system sodium chloride-cesium chloride substantiate the conclusion that in these 1-1 strong electrolyte systems the rule of linear variation of the logarithm of the activity coefficient is valid for both electrolytes when the solutions are concentrated.

Recently interest in the thermodynamic characteristics of these mixtures has been stimulated by their use in combination with ion exchangers for the separation of the elements. The earlier application of the hydrogen-silver chloride cell was restricted largely to systems containing 1-1 electrolytes. Since its use was not fully exploited for the examination of mixtures containing unsymmetrical electrolytes, electromotive force studies of the systems, HCl-BaCl₂, HCl-SrCl₂, HCl-AlCl₃ and HCl-ThCl₄, are being carried out in this Laboratory. For systems containing two electrolytes of different valence types, equations 1, 2 and 3 and the Gibbs-Duhem relation yields

(5) For details of the deduction of equation (4), see H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 462.

(6) E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *J. Chem. Soc.*, S 299 (1949).

(7) R. A. Robinson, *J. Am. Chem. Soc.*, **74**, 6035 (1952).

(3) (a) H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926); (b) J. E. Hawkins, *ibid.*, **54**, 4480 (1932).

(4) H. S. Harned, *ibid.*, **51**, 1865 (1935).

$$\frac{\alpha_{21}}{z_{2+}z_{2-}} = \frac{\alpha_{12}}{z_{1+}z_{1-}} - \frac{2}{2.303\mu} \left\{ \left[\frac{\phi_{1(0)}}{z_{1+}z_{1-}} - \frac{\phi_{2(0)}}{z_{2+}z_{2-}} \right] - \left[\frac{1}{z_{1+}z_{1-}} - \frac{1}{z_{2+}z_{2-}} \right] \right\} \quad (5A)$$

at each total ionic strength, $\mu = \mu_1 + \mu_2$. In this equation z_{1+} , z_{1-} are the valences of the cation and anion of one electrolyte and z_{2+} , z_{2-} those of the second electrolyte. For mixtures of hydrochloric acid and higher valence type chlorides where $z_{1+} = z_{1-} = z_2 = 1$, this equation reduces to

$$\frac{\alpha_{21}}{z_{2+}} = \alpha_{12} - \frac{2}{2.303\mu} \left\{ \left[\frac{\phi_{1(0)}}{z_{2+}} - \frac{\phi_{2(0)}}{z_{2+}} \right] - \left[1 - \frac{1}{z_{2+}} \right] \right\} \quad (6)$$

Equation 5 requires that

$$z_{2+}\alpha_{12} + \alpha_{21} = \text{constant} \neq f(\mu) \quad (7)$$

As an illustration of the range of validity of equations 1, 2 and 7, we have compiled in Table II preliminary calculations of some recent electromotive force measurements of cells containing hydrochloric acid and strontium chloride at 3 and 5 total ionic strengths obtained by Dr. Robert Gary in this Laboratory. The values calculated by the linear equations given at the foot of the table show remarkable agreement with the observed results. From the determined values of α_{12} , the slopes, α_{21} , were computed by equations (6) from the osmotic coefficients recorded by Stokes.⁸ We note that the parameters, α_{12} and α_{21} , are essentially the same at both 3 and 5 μ as well as $(2\alpha_{12} + \alpha_{21})$, facts which support the assumption represented by equation 2. Detailed presentation of these and similar results with other systems will be published elsewhere.

TABLE II

APPLICATIONS OF EQUATIONS 1, 2 AND 7 TO THE SYSTEM HCl-SrCl₂ AT 25° AND AT 3 AND 5 CONSTANT TOTAL IONIC STRENGTHS

m_1	HCl-SrCl ₂ ($\mu = 3$)		m_1	HCl-SrCl ₂ ($\mu = 5$)	
	γ_1 (obsd.)	γ_1 (calcd.)		γ_1 (obsd.)	γ_1 (calcd.)
3.0	(1.316)	(1.316)	5.0	(2.368)	(2.368)
2.7	1.264	1.263	4.5	2.214	2.215
2.4	1.216	1.215	4.0	2.071	2.072
2.1	...	1.167	3.5	1.941	1.938
1.8	1.121	1.122	3.0	1.813	1.813
1.5	1.078	1.077	2.5	1.694	1.696
1.2	1.035	1.035	2.0	1.586	1.586
0.9	0.994	0.995	1.5	1.483	1.484
.6	.954	.956	1.0	1.385	1.388
.3	.916	.918			

$$\log \gamma_1 = 0.1193 - 0.0579 \mu_2 \quad \log \gamma_1 = 0.3744 - 0.0580 \mu_2$$

$$\alpha_{12} = 0.0579 \quad \alpha_{12} = 0.0580$$

$$\alpha_{21} = -0.083 \quad \alpha_{21} = -0.087$$

$$2\alpha_{12} + \alpha_{21} = 0.033 \quad 2\alpha_{12} + \alpha_{21} = 0.029$$

Differential Diffusion Coefficients of Electrolytes in Dilute Aqueous Solution and the Gradient of the Chemical Potential.—Recently, the diffusion coefficients of a number of electrolytes at concentration less than 0.01 M have been determined with a high degree of accuracy by a conductance method devised in this Laboratory. These measurements are the first of high enough precision

to test the theory developed by Onsager and Fuoss.⁹ Since these results and the details of the theoretical calculations are described elsewhere,¹⁰ only the general features of these investigations will be mentioned.

According to the theory, the diffusion coefficient, \mathcal{D} , may be expressed by the equation

$$\mathcal{D} = 16.629 \times 10^{10} T (\mathfrak{M}/c) \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right) \quad (8)$$

The quantity (\mathfrak{M}/c) is a mobility term and $\left(1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right)$ is the term which is derived from the gradient of the relative chemical potential of the electrolyte. As the concentration of electrolyte approaches zero the thermodynamic term approaches unity and the whole expression reduces to the Nernst limiting equation

$$\mathcal{D} = 17.872 T \left(\frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right) \times 10^{-10} \quad (9)$$

where λ_1^0 and λ_2^0 are the limiting equivalent conductances. (\mathfrak{M}/c) is a complicated expression and according to theory its variation with concentration is caused by the influence of the ionic atmospheres on electrophoresis. Its variation with concentration is not great. Indeed at most, this variation at 0.01 M amounts to about 0.5% of the diffusion coefficient, a fact which makes the experimental proof of its validity a difficult one.

The positive conclusions which have been confirmed for strong electrolytes which have little tendency to form ion-pairs can be summarized briefly. (1) The Nernst limiting expression is valid for salt diffusion. (2) As one can safely assume from the theory of irreversible processes, the thermodynamic term in equation 8 is verified and can be relied upon quantitatively in dilute solutions. (3) So far the evidence supports the estimate of Onsager and Fuoss of the magnitude and sign of the effect of the electrophoretic term when applied to solutions less than 0.008 M . (4) For most strong electrolytes, deviations from theory begin at concentrations between 0.005 and 0.01 M and become large at the higher concentrations.

Salt Diffusion of Calcium Chloride and the Self-diffusion of its Ions in Dilute and Concentrated Solutions.—In Fig. 1, the self-diffusion coefficients of the calcium and chloride ions as determined by Wang¹¹ and the salt diffusion of calcium chloride recently derived from optical measurements by Dr. Philip A. Lyons and Mr. J. F. Riley in this Laboratory are plotted against the square root of the molar concentration. The optical measurements were made throughout the concentration range 0.03 to 7 M and join those obtained by the conductance method at the lower concentrations.

(9) L. Onsager and R. M. Fuoss, *THIS JOURNAL*, **36**, 2689 (1932).

(10) H. S. Harned and D. M. French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945); H. S. Harned and R. L. Nuttall, *J. Am. Chem. Soc.*, **69**, 736 (1947); **71**, 1460 (1949); H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949); H. S. Harned and C. A. Blake, Jr., *ibid.*, **72**, 2265 (1950); **73**, 2448 (1951); **73**, 4255 (1951); **73**, 5882 (1951); H. S. Harned and C. L. Hildreth, Jr., *ibid.*, **73**, 650 (1951); **73**, 3292 (1951); H. S. Harned and R. M. Hudson, *ibid.*, **73**, 652 (1951); **73**, 3781 (1951); **73**, 5083 (1951); **73**, 5880 (1951); H. S. Harned and M. C. Blander, *ibid.*, **75**, 2853 (1953); H. S. Harned and F. M. Polestra, *ibid.*, **75**, 4168 (1953).

(11) J. H. Wang, *ibid.*, **75**, 1769 (1953).

(8) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

The straight lines represent the limiting expressions for the self-diffusion¹² and salt-diffusion. The curve designated O-F represents the Onsager and Fuoss theory.

It is apparent from these plots that only in very dilute solutions do the values of self-diffusion coefficients approach the limiting law of the theory, although they do converge toward the limiting values. As stated by Wang it is interesting to note that the ratios of the self-diffusion coefficients at infinite dilution to those at 5.36 *M* are 13 and 8 for the chloride ion and calcium ion, respectively, while the ratio of the viscosity of a 5.36 *M* calcium chloride solution to that of pure water is 11.

Our observations on numerous electrolytes show that, at concentrations below 0.01 *M*, the gradient of the chemical potential is the major factor in computing the concentration dependence of diffusion coefficients. Above this concentration other factors which influence the mobility become important if not predominant as illustrated by comparison of the curve of the experimental values for the diffusion coefficient of calcium chloride with the computed curve, O-F. In addition to the effect of relative viscosity, there are large effects of forces which tend to counteract the influence of the gradient of the chemical potential in the concentrated solutions and thus decrease the mobility.

This investigation was supported in part by the Atomic Energy Commission under Contract AT-(30-1)-1375.

(12) L. J. Gosting and H. S. Harned, *J. Am. Chem. Soc.*, **73**, 151 (1951)

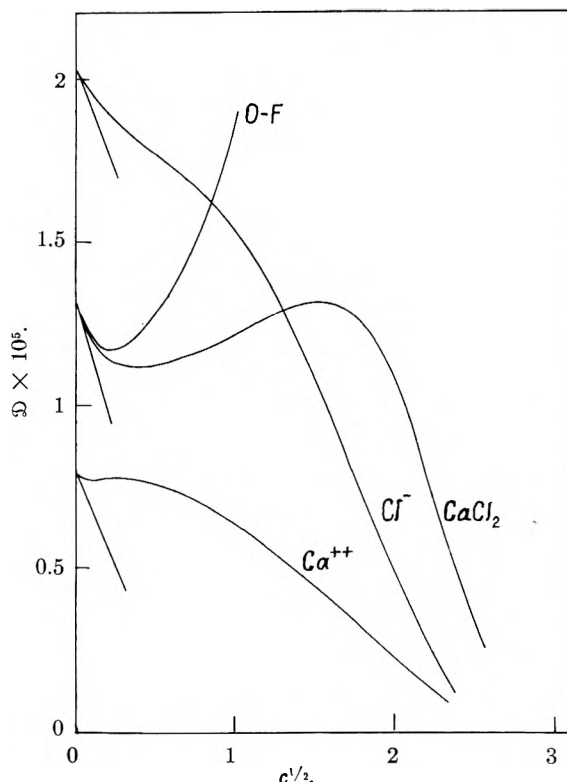


Fig. 1.—Diffusion coefficient of calcium chloride and the self-diffusion coefficients of the calcium and chloride ions in calcium chloride solutions at 25°. Straight lines represent limiting laws. The curve designated O-F was obtained from the Onsager-Fuoss theory.

EFFECT OF IONS ON THE SELF-DIFFUSION AND STRUCTURE OF WATER IN AQUEOUS ELECTROLYTIC SOLUTIONS¹

By JUI H. WANG

Contribution No. 1226 from the Department of Chemistry of Yale University, New Haven, Conn.

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Liquid water has a semi-crystalline structure. Dissolved ions cause distortion or partial destruction of the structure of water. Such a distortion effect can be used to interpret (1) the temperature coefficients of the limiting equivalent conductances of spherical ions in water, and (2) the observed concentration dependence of the tracer-diffusion coefficient of ions with salt concentration in moderately concentrated salt solutions. Direct evidence of such a distortion effect has been obtained in the present work where the self-diffusion coefficient of water in a series of electrolytic solutions has been measured as a function of the concentration of the electrolyte. In some cases the measured self-diffusion coefficient of water in salt solution is much higher than that in pure water, indicating that in these solutions the structure of water is distorted or partially destroyed to a considerable extent. The effect of such a distorted water structure on the equilibrium properties of the ions is discussed. The relationship between the measured viscosity of the solution and the self-diffusion coefficients of the constituent molecular species is also examined.

It is now generally agreed that at temperatures not much higher than 0° liquid water has a "semi-ice" structure, *i.e.*, each water molecule is "hydrogen-bonded" to four immediate neighbors in four approximately tetrahedral directions. Inasmuch as the directions are only approximately tetrahedral long range order (ice-structure) disappears rapidly in liquid water although local order may exist at fairly high temperatures.² According to this picture, the unusually large heat capacity of water

is due to the heats of dissociation of the semi-crystalline lattice. The abnormal temperature dependence of the density of water can also be explained by the assumption that on heating water near 0° the extensive "semi-ice" structure becomes more distorted and broken down, makes closer packing possible, and hence the density increases with temperature until about 4° when the effect of thermal expansion just compensates the shrinkage in volume due to the breaking down of the "semi-ice" structure.

Since in general the spherical ions with inert gas type of electronic structure do not fit into the water

(1) Presented at the Symposium on the Solutions of Electrolytes sponsored by the Division of Physical and Inorganic Chemistry of the A. C. S. on June 16, 1954, at New Haven, Conn.

(2) J. A. Pople, *Proc. Roy. Soc. (London)*, **A205**, 163 (1951).

lattice, they cause local distortion in the structure of the surrounding water. This kind of distortion will undoubtedly affect many physicochemical properties of the solution. We shall first examine the simplest case, *i.e.*, an electrolytic solution at infinite dilution.

Temperature Dependence of the Limiting Mobilities of Ions.—The limiting mobility, ω_i° , of ionic or molecular species *i* in its aqueous solution is defined as

$$\omega_i^\circ = D_i^\circ/kT \quad (1)$$

where D_i° is the tracer-diffusion coefficient of ion or molecule *i* in pure water at temperature *T*, and *k* is Boltzmann's constant. In the absence of any excessive distortion in the structure of the surrounding water, we may write

$$\omega_i^\circ = A_i/\eta_0 \quad (2)$$

where η_0 is the viscosity of pure water and A_i is a constant characteristic of the diffusing species. For example, if the diffusing molecules are spherical and have equal radius *r* much larger than the dimensions of a water molecule, A_i is equal to $1/(6\pi r)$ according to Stokes-Einstein's relationship.

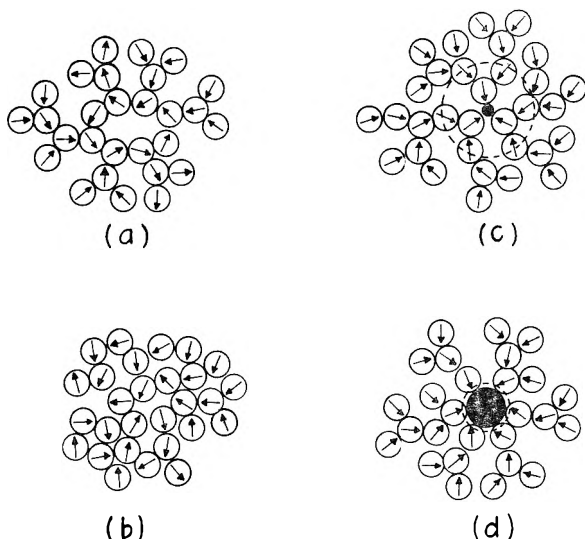


Fig. 1.—Schematic representation of the structure of water: (a) water near its m.p. and under atmospheric pressure; (b) water under high external pressure; (c) water near a Li^+ ion; (d) water near a Cs^+ ion.

But since the constant A_i is in general unknown, it is not possible to compute the value of ω_i° by means of equation 2 except for very large spherical or ellipsoidal molecules. However if the shape and size of the diffusing species change only little with temperature, A_i should be practically independent of temperature, and by combining equations 1 and 2 we obtain

$$D_i^\circ\eta_0/T = \text{constant} \quad (3)$$

which is valid for all diffusing species provided that there is no excessive distortion in the structure of the surrounding water.

The effect of the distortion in the structure of water on its viscosity has been clearly demonstrated by Bridgman's observation³ that at tem-

peratures not much higher than 0° the viscosity of water decreases continually when the external pressure is increased from 1 to about 1000 kg./cm.² This is because the increased external pressure destroys some of the "semi-ice" structure in water and consequently makes it less viscous in spite of the decrease in volume as depicted in Fig. 1. Figure 1 is a schematic illustration of the 3-dimensional "semi-ice" structure of water under different conditions. The unshaded circles represent water molecules with their net dipole moments oriented in the directions of the respective arrows. We may thus infer from Bridgman's observation that if there is excessive distortion in the structure of water surrounding the diffusing ion or molecule, the "local viscosity" of the surrounding water should be less than η_0 , and that the ion or molecule should have a mobility higher than that predicted by equation 2. Furthermore, since the temperature coefficient of the "local viscosity" will in general be different from that of the viscosity of pure water, one may expect the experimental data in such cases to contradict equation 3.

Values of $D^\circ\eta_0/T$ computed from the self-diffusion data for water obtained in the present work with H_2O^{18} as tracer, from the conductance data of the alkali metal ions⁴⁻⁶ and the tetraethylammonium ion,⁴ $(\text{C}_2\text{H}_5)_4\text{N}^+$, are plotted *vs.* temperature in Fig. 2. It may be seen in Fig. 2 that $D^\circ\eta_0/T$ remains practically constant for the large $(\text{C}_2\text{H}_5)_4\text{N}^+$ and the strongly hydrated Li^+ between 5 and 55° ,

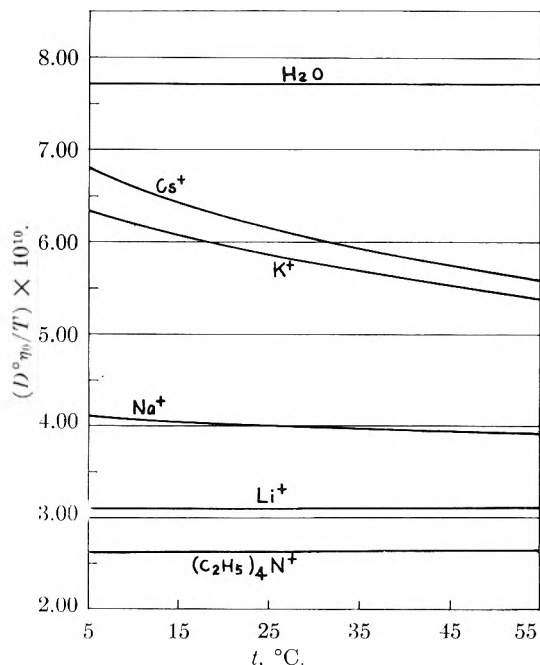


Fig. 2.—Variation of the limiting diffusion coefficients of ions and the viscosity of water with temperature.

but decreases with increasing temperature for the less hydrated ions. This observation can be readily explained by the picture of liquid water discussed

(4) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, Appendix B.

(5) W. E. Voisinet, Jr., Dissertation, Yale University, 1951.

(6) B. B. Owen, private communication.

(3) P. W. Bridgman, "The Physics of High Pressure," The Macmillan Co., New York, N. Y., 1931, p. 347.

above. For simplicity let us consider the two extreme cases Li^+ and Cs^+ as illustrated by (c) and (d), respectively, in Fig. 1. Let each shaded circle in Fig. 1 represent the anhydrous ion, and each broken circle, together with the anhydrous ion and the water molecules in it, represent the hydrated ion. That the number of water molecules "bound" to each ion in our diagram may not be integer should not cause ambiguity in meaning for we may define the "hydration number" or simply "hydration" as the statistically average number of water molecules carried by the ion when the latter diffuses through solution. The total frictional force suffered by each diffusing ion is due to the viscous drag of all its surrounding "free" water molecules, *i.e.*, water molecules outside the broken circle in (c) or (d) of Fig. 1. Because of the more intense electrostatic field in its vicinity, the Li^+ is more highly hydrated than Cs^+ as shown in Fig. 1. Consequently, the amount of distortion in the structure of the "free" water surrounding the hydrated Li^+ should be much less than that surrounding the weakly hydrated Cs^+ as depicted in Fig. 1, although neither of the anhydrous ions fit the structure of water as well as water molecule themselves. This excessive distortion in the structure of water surrounding Cs^+ makes the "local viscosity" in its neighborhood less than η_0 , and hence increases the mobility of Cs^+ . As the temperature increases, η_0 decreases mainly because of the breaking down of the structure of water. But since the structure of water surrounding the weakly hydrated Cs^+ is already distorted more than in the bulk of pure water, the viscosity of water in its immediate neighborhood must decrease less rapidly with increasing temperature than η_0 . Therefore the limiting diffusion coefficient, D^0 , of Cs^+ will increase less rapidly than that predicted by equation 3, and consequently $D^0\eta_0/T$ for Cs^+ will decrease with temperature as shown in Fig. 2. Similarly we may take the constancy of $D^0\eta_0/T$ for Li^+ with temperature as indicating that the amount of excessive distortion in the structure of water surrounding the hydrated Li^+ is negligible. The curve for $(\text{C}_2\text{H}_5)_4\text{N}^+$ in Fig. 2 is similar to that for Li^+ . Those for Na^+ and K^+ fall between Li^+ and Cs^+ . These facts are all consistent with the present picture. Values of $D^0\eta_0/T$ for Cl^- , Br^- , I^- , respectively, show the same trend in their temperature dependence, although these may not be directly comparable with those for the cations because the water molecule is not symmetrical with respect to polarity.

We have assumed in the above discussion that the hydration of ions is not appreciably affected by changes in temperature. If this is not so, decrease of hydration at high temperatures would make $D^0\eta_0/T$ increase with temperature in the absence of excessive distortion effect. Indeed, careful examination shows that the value of $D^0\eta_0/T$ for Li^+ does increase slightly when the temperature is increased from 5 to 55°, although this change is not much larger than the experimental uncertainties in the conductance data quoted above.

It may also be noticed from Fig. 2 that as the temperature increases, the value of $D^0\eta_0/T$ for

water remains practically constant. The explanation is that although the labeled water molecule is smaller than all the other hydrated ions considered above, it fits the structure of water almost as perfectly as all the other unlabeled water molecules. Consequently there should be no excessive distortion in the structure of water surrounding the labeled water molecule, and the value of $D^0\eta_0/T$ should therefore remain constant. This observation can be used as evidence in favor of the present interpretations.

Concentration Dependence of the Tracer-diffusion Coefficients of Ions.—For electrolytic solutions of finite concentration, the effect of interaction between different ions should be taken into consideration. The decrease in mobility of the diffusing ions due to the finite time of relaxation of the ion-atmospheres in very dilute electrolytic solutions has been calculated by Onsager and Fuoss⁷ and by Onsager.⁸

The result of their treatment of the relaxation effect shows that the tracer-diffusion coefficient, D_j , of ionic species j in a salt solution is given by

$$D_j = \frac{RT\lambda_j^0}{|Z_j|F^2} - \frac{\lambda_j^0|Z_j|F}{3N\mathfrak{D}} \times 2.694 \times 10^{16} \times \sqrt{\frac{4\pi}{\mathfrak{D}RT}} [1 - \sqrt{\phi_j}] \sqrt{\sum_i c_i Z_i^2} \quad (4)$$

where Z_i is the charge in electronic units and c_i the concentration in moles per liter of ion i , λ_j^0 the limiting equivalent conductance of ion j , \mathfrak{D} the dielectric constant of the solvent, R the gas constant, F the Faraday constant, and ϕ_j a function given by

$$\phi_j = \frac{1}{\sum_i c_i Z_i^2} \sum_i \frac{c_i |Z_i| \lambda_i^0}{(\lambda_i^0/|Z_i|) + (\lambda_j^0/|Z_j|)} \quad (5)$$

For the diffusion of tracer amount of ions of species 1 in salt solution containing ions of species 2 and 3, we have

$$c_1 \cong 0, \quad c_2|Z_2| = c_3|Z_3|$$

hence equation 5 becomes

$$\phi_1 = \frac{|Z_1|}{|Z_2| + |Z_3|} \left[\frac{|Z_2|\lambda_2^0}{|Z_2|\lambda_1^0 + |Z_1|\lambda_2^0} + \frac{|Z_3|\lambda_3^0}{|Z_3|\lambda_1^0 + |Z_1|\lambda_3^0} \right] \quad (6)$$

The values of the tracer-diffusion coefficients of Na^+ and Cl^- in aqueous potassium chloride and sodium chloride solutions at 25° computed from conductance data by means of equations 4 and 6 are

$$\left. \begin{aligned} D_{\text{Na}^+} \times 10^5 &= 1.334 - 0.236\sqrt{c} \\ D_{\text{Cl}^-} \times 10^5 &= 2.033 - 0.471\sqrt{c} \end{aligned} \right\} \text{in KCl solutions}$$

and

$$\left. \begin{aligned} D_{\text{Na}^+} \times 10^5 &= 1.334 - 0.286\sqrt{c} \\ D_{\text{Cl}^-} \times 10^5 &= 2.033 - 0.526\sqrt{c} \end{aligned} \right\} \text{in NaCl solutions}$$

These theoretical values are plotted *vs.* \sqrt{c} as straight lines in Fig. 3 together with the experimental curves.⁷⁻⁹ It may be noticed from Fig. 3

(7) L. Onsager and R. M. Fuoss, *This Journal*, **36**, 2639 (1932).

(8) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(8a) J. H. Wang, *J. Am. Chem. Soc.*, **74**, 1182, 6317 (1952); *ibid.*, **1612** (1952).

(8b) J. H. Wang and S. Miller, *ibid.*, **74**, 1611 (1952).

(9) F. M. Polestra, Dissertation, Yale University, 1954.

that as the concentration of the salt solution decreases, the tracer-diffusion coefficients of Na^+ in KCl and NaCl solutions, respectively, approach the same Nernst's limiting value. The same is true for the tracer-diffusion coefficients of the chloride ion. This agreement is an independent check on the reliability of the experimental results. While the shape of the experimental curves in Fig. 3 indicate that a detailed explanation of the concentration dependence of these diffusion coefficients in concentrated solutions is probably very involved, they are at least in qualitative agreement with the present picture. Thus in moderately concentrated electrolytic solutions the "local viscosity" of water in the neighborhood of a diffusing ion may be decreased appreciably by the distortion in the structure of water caused by the presence of other ions. If this effect becomes larger than the relaxation and other retarding effects in moderately concentrated solutions, it could cause the tracer-diffusion coefficient of the ion to increase with salt concentration.

According to the discussion in the previous section, there should be more distortion in the structure of water in a moderately concentrated KCl solution than in a NaCl solution of equal concentration. If this is true, we would expect the "hump" in the D vs. \sqrt{c} curve for a given ion to be more pronounced in KCl than in NaCl solution. Figure 3 shows that this is true for both Na^+ and Cl^- . Furthermore since at infinite dilution the amount of distortion in the structure of water surrounding a weakly hydrated chloride ion is already more than that surrounding a strongly hydrated sodium ion, the additional distortion in the neighborhood of the diffusing ion caused by

other ions must be less for the chloride than for the sodium ion. Consequently we would expect that for a given salt solution the "hump" of the D vs. \sqrt{c} curve to be more pronounced for the sodium than for the chloride ion. Figure 3 shows that this is true for both potassium chloride and sodium chloride solutions.

The Self-diffusion Coefficients of Water in Aqueous Electrolytic Solutions.—Since the above interpretations are based entirely on the effect of ions on the structure of water in solution, a more direct approach to the present problem will be to study the self-diffusion of water in electrolytic solutions. Although the distortion in the structure of water caused by dissolved ions tends to make the water molecules diffuse faster in solution than in pure water, there are two other complicating factors. First, most ions have a smaller tracer-diffusion coefficient than water molecules. These slowly moving dissolved ions obstruct the paths of the faster water molecules; *i.e.*, the water molecules near an ion have to diffuse along a longer path to get to the other side of the ion. But since in experimental measurements we compute the self-diffusion coefficient of water by taking a macroscopic dimension of the diffusing apparatus irrespective of whether or not the diffusion path is partially blocked microscopically, the net result of this "obstruction effect" will be to make the measured self-diffusion coefficient of water in solution somewhat lower than that in pure water. Second, some water molecules may be firmly attached to the dissolved ions (hydration), and hence diffuse together with the ion at a smaller velocity. Since in self-diffusion measurements we make no distinction between "free" and "bound" water molecules, this direct hydration effect also tends to make the measured self-diffusion coefficient of total water in solution lower than that in pure water. In spite of these complicating factors there is the possibility that in some aqueous solutions of slightly hydrated ions the distortion effect may more than compensate the other two factors and make the self-diffusion coefficient of water in these solutions even higher than that in pure water.

The self-diffusion coefficients of water in aqueous KI, KCl, NaCl solutions at 10° and in aqueous KI, NaCl solutions at 25° have been determined in the present work with H_2O^{18} as tracer. The results are listed in Tables I and II, but the experimental details will be reported elsewhere.

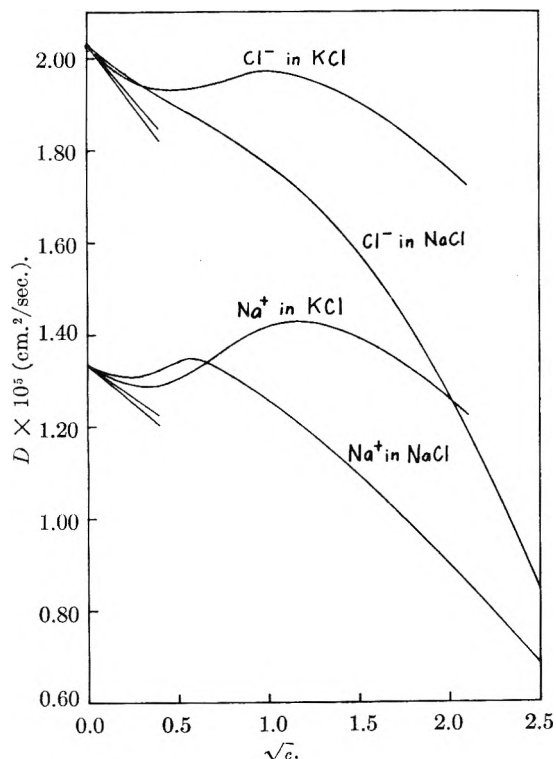


Fig. 3.—Variation of the tracer-diffusion coefficients of Na^+ and Cl^- with the concentration of the electrolyte.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF WATER IN AQUEOUS ELECTROLYTIC SOLUTIONS AT 10°

Concn. of salt soln. (formula-wt./l.)	$D \times 10^5 \text{ (cm.}^2\text{/sec.)}$		
	NaCl soln.	KCl soln.	KI soln.
0.0	1.675 ± 0.016	1.675 ± 0.016	1.675 ± 0.016
0.5		$1.74 \pm .01$	$1.77 \pm .017$
1.0	1.62 ± 0.014	$1.77 \pm .02$	$1.90 \pm .015$
2.0	$1.48 \pm .016$	$1.81 \pm .02$	$2.02 \pm .01$
3.0	$1.337 \pm .003$	$1.76 \pm .02$	$2.12 \pm .02$
4.0	$1.19 \pm .016$		$2.15 \pm .01$
5.0			$2.10 \pm .016$

TABLE II
SELF-DIFFUSION COEFFICIENTS OF WATER IN AQUEOUS
ELECTROLYTIC SOLUTIONS AT 25°

Concn. of salt soln. (formula- wt./l.)	$D \times 10^5$ (cm. ² /sec.)	
	NaCl soln.	KI soln.
0.0	2.57 ± 0.022	2.57 ± 0.022
1.0	2.45 ± .025	2.76 ± .02
2.0	2.20 ± .01	2.86 ± .02
3.0	2.00 ± .017	2.96 ± .02
4.0	1.85 ± .01	2.92 ± .014
5.0		2.85 ± .02

Each value listed in Table I or II is the average result of three to six measurements. These values are plotted vs. c in Fig. 4. The dimensions of the experimental points in Fig. 4 correspond approximately to the standard deviations listed in Tables I and II.

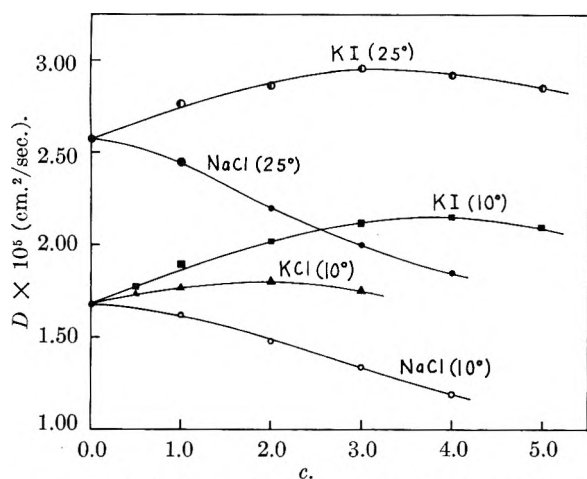


Fig. 4.—Variation of the self-diffusion coefficient of water in solutions of electrolytes with concentration and temperature.

According to the above discussions the distortion effect in these salt solutions should increase in the order $\text{NaCl} < \text{KCl} < \text{KI}$, and the obstruction and direct hydration effect should decrease in the order $\text{NaCl} > \text{KCl} > \text{KI}$. Consequently we may expect the increase in the self-diffusion coefficient of water caused by the distortion in water structure to be most pronounced in KI solution, less in KCl solution, and least in NaCl solution. These predictions are all consistent with the experimental results shown in Fig. 4. Indeed the fact that the self-diffusion coefficient of water in 3 or 4 f KI solution at room temperature is much higher than that in pure water can be taken as strong evidence to show the existence of the excessive distortion in the structure of water in these solutions, for there appears to be no other factor that we can think of to cause water molecules in these solutions to diffuse faster than in pure water. Furthermore since the molecules are more orderly arranged in pure water at 10 than at 25°, we would expect the distortion effect due to dissolved potassium and iodide ions to be more pronounced at 10 than at 25°. This is indeed true, for Fig. 4 shows that while the maximum value of the self-diffusion coefficient of water in KI solutions is 28% higher than D^0 at 10°, it is only 15% higher than D^0 at 25°.

Other Properties of Electrolytic Solutions.—It seems generally agreed that the unusually high dielectric constant of liquid water is due at least in part to molecular association. Consequently if dissolved ions distort the structure of water, they would change the dielectric constant of water. Since the dielectric constant of water is involved in both the theoretical treatment of ion-ion interaction and that of ion-solvent interaction, it is necessary to include these distortion effects in formulating a complete theory of the equilibrium properties of aqueous electrolytic solutions. Hitherto, very little work has been done in this direction except by empirical methods. A complete theoretical treatment of all the important factors, such as ion-ion interactions, covolume effect, distortion in the structure of water, etc., is yet to be developed.

Another problem which interests many solution chemists is the relationship between the mobility of the diffusing ions or molecules and the measured viscosity of the solution. Since in ordinary diffusion measurements the chemical composition of the solution often varies along the diffusion path, the activity coefficient of the diffusing species may also vary. Consequently for a two-component system we have

$$D = kT\omega\left(1 + c \frac{\partial \ln \gamma}{\partial c}\right) \quad (7)$$

where γ is the activity coefficient, ω the mobility and c the concentration of the diffusing solute species. For highly dilute electrolytic solutions, only the interactions due to long range electrostatic forces are sensitive to changes in salt concentration and the concentration dependence of ω has been calculated by Onsager and Fuoss.⁷ For more concentrated solutions, it is the practice of many workers to relate the mobility, ω , to the limiting diffusion coefficient, D^0 , at infinite dilution by

$$\omega = \frac{D^0}{kT} \left(\frac{\eta_0}{\eta}\right) \quad (8)$$

an expression first suggested by Gordon.¹⁰ Equation 8 has been found to agree with the diffusion data for dilute sucrose solutions, but disagree with those for urea, glycine and potassium chloride solutions.¹¹ In view of the present discussion, the structure of water in the neighborhoods of different ions or solute molecules may be distorted to different degrees depending on the nature of the ions or molecules, it is obvious that equation 8 which includes the ratio of the macroscopic viscosities as a correction factor cannot be expected to hold for all cases. As an illustration, the relative self-diffusion coefficients, D/D^0 , of Na^+ , Cl^- and H_2O in aqueous sodium chloride solutions at 25° have been computed from the experimental results of the present and earlier work,^{7,8} and plotted vs. \sqrt{c} in Fig. 5 together with the viscosity data.

It can be seen in Fig. 5 that each diffusing species in the NaCl solution exhibits a D/D^0 vs. \sqrt{c} curve which is different than those for the other species or that for η_0/η . Since all these diffusing species

(10) A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

(11) See, for example, L. J. Gosting and D. F. Akeley, *J. Am. Chem. Soc.*, **74**, 2058 (1952).

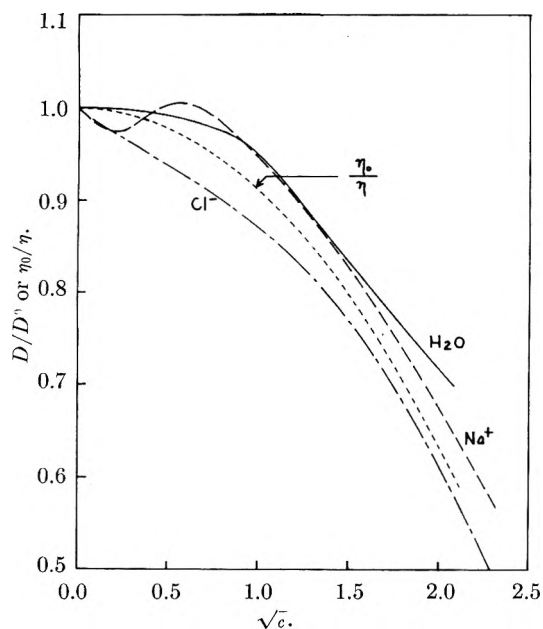


Fig. 5.—Comparison of the self-diffusion coefficients with the viscosities of NaCl solutions.

are in the same solution, and since there is only one macroscopic viscosity at a given concentration, it would obviously be futile in trying to use any single monotonic function of the measured viscosity to correct for the change in self-diffusion coefficient with concentration for all three constituent species. It may be more helpful, however, to approach this problem from the opposite direction, *i.e.*, to interpret the macroscopic viscosity of the solution in terms of the measured self-diffusion coefficients, molecular volumes and concentrations of the constituent species. Since the viscosity of a liquid is a measure of its internal friction (neglecting the contribution due to momentum transfer on the viscosity of liquids), and inasmuch as the experimentally determined values of kT/D can often be used as direct measures of the so-called "friction coefficients" of the constituent species in a liquid mixture, it may be possible to derive a general relationship expressing the viscosity as a function of the self-diffusion coefficients, molecular volumes and concentrations without assuming any particular type of molecular interaction in liquids. But such a relationship is yet to be discovered. The system in Fig. 5 is unfortunately complicated by the hydration of ions. In this system the measured values of D for water represent the self-diffusion coefficients of total water instead of those of "free" water. Since the amount of hydration of the ions is not known, these values can not be used directly to compute the friction coefficients of "free" water molecules. It is the hope of the present writer that enough data on the self-diffusion in solutions of non-electrolytes and molten salts may become available in the near future to be used as a guide for studying this problem. Once the relationship between viscosity and self-diffusion coefficients, etc., is clearly understood, the type of data illustrated in Fig. 5 may be useful in providing some information regarding the hydration of ions.

Acknowledgment.—This work has been supported in part by Contract (30-1)-1375 between the U. S. Atomic Energy Commission and Yale University.

DISCUSSION

M. EIGEN (University of Göttingen).—An effect, similar to that pointed out by Dr. Wang, may be observed in the heat conductivity of aqueous electrolytic solutions. This quantity shows a linear decrease with increasing concentration, in contrast to the sound velocity which shows a linear increase with concentration. This behavior is anomalous, as in general the heat conductivity of liquids is proportional to the sound velocity. We have tried to explain this anomalous behavior in the following way.

The heat conductivity of pure water contains two parts; one of these corresponds to the normal transfer of translational and rotational energy, the other describes a special transfer of dissociation heat of the water aggregates (water structure) similar to the anomalous heat conductivity in dissociating gases. This heat transfer is characterized by the corresponding association part of the specific heat, known from the measurements, and a coefficient of the "structure diffusion", which gives information on the breaking or formation of a hydrogen bond.* In the presence of ions, the structural part of the heat conductivity decreases with increase of concentration, as the water structure is distorted by the ions. Our theoretical treatment of this effect (*cf.* M. Eigen, *Z. Elektrochem.*, 56', 176, 836 (1952)) led to a quantitative agreement with the experimental results. I think the nature of this effect is the same as that reported by Dr. Wang.

J. H. WANG.—I think that Dr. Eigen's computed short lifetime of the water aggregates mentioned in the above footnote further shows that the molecular aggregates $(H_2O)_2$, $(H_2O)_4$ and $(H_2O)_8$ as postulated by Eucken (*cf.* A. Eucken, *Z. Elektrochem.* 52', 255 (1948)) are merely fictitious terms invented to facilitate computation rather than real molecular species. For example, we cannot say that a dimer such as $(H_2O)_2$ exists unless the average lifetime of this dimer is appreciably longer than the duration of contact of two adjacent single water molecules.

H. S. FRANK (University of Pittsburgh).—Dr. Wang has spoken as if the "distortion" of water structure were caused principally by the space requirement of the large bulk, say, of the cesium ion. What Professor Debye said this morning about orders of magnitude suggests a more general way in which ions should be expected to destroy water structure. This will be through the torque exerted on the water dipoles by the spherically symmetrical (on the average) field of the ion. This will compete with the torque exerted on a water molecule by its neighbors which are trying to bring it into structural alignment. It seems likely that for every ion there will be a certain range of distances from the charge center where the water molecules will be subjected to competing torques of such balanced strengths that the structure will be effectively broken down, and it is very interesting that two such unlike experimental techniques as those described by Drs. Wang and Eigen should give such strong evidence that this destruction does in fact take place. The same conclusion can be drawn from entropy data, as the numerical values for the entropy of hydration of many ions show that the solutions contain "too much" entropy in comparison with certain standards. This is presumably a reflection of the effect here under discussion, namely, the existence about the ion of a region in which the water structure has been destroyed. What is always observed, of course, is a net effect produced by whatever "freezing" of water takes place immediately in contact with the ion (Dr. Eigen's school considers that for all ions this is considerable) plus the "melting" farther out. These two effects will be of

* A result of these calculations is the very short lifetime of a hydrogen-bonded water associate. As this is the same order of magnitude as the duration of normal position exchanges of fluid particles, the associates do not move through the liquid as rigid particles and their diffusion can not be described by the Stokes' law. A consideration of this effect may remove the discrepancies in the description of experimental results (especially in kinetic measurements) by different theories of water structure.

different relative magnitude for different ions, and sometimes one may predominate, sometimes the other. In this case, the opposite signs of the influences of NaI and KI on self-diffusion of water would mean that in NaI the freezing effect (plus possible other hindering effects) predominated, while in KI the melting predominated. It need not mean that structure-breaking was absent in NaI.

J. H. WANG.—The distortion of water structure caused by the strong electric field near an ion has not been neglected in the above discussion. For example, the hydration of Li^+ is illustrated in Fig. 1 to be much greater than that of Cs^+ mainly because of the difference in the strengths of the local fields. But since all alkali ions have the same net charge, the strength of the local field is essentially determined by the ionic radius or volume. Consequently we have considered ionic volume alone as the primary factor which causes different alkali ions to have different distorting effects (both through attractive forces and through the special requirement of the ion, *i.e.*, short-ranged repulsive forces) on the structure of the surrounding water. However in discussing the temperature coefficient of the limiting mobilities of the alkali ions, only the special requirement of the bare ions has been emphasized. This is because the variation of limiting ionic mobility with temperature is determined by the temperature coefficient of the viscosity of "free" water immediately surrounding the hydrated ion instead of that of total water. It is my opinion that the effect of electric distortion on the structure of "free" water due to ion-dipole attraction must be small, for otherwise the surrounding water under consideration should be included in the statistical hydration sheath instead of being considered "free." On the other hand, although the distortion in the structure of the "free" water due to spatial requirement of the ion is probably also small for Li^+ because of both the small volume of the bare ion and the large hydration, this kind of distortion can be quite large for weakly hydrated ions with large ionic volume such as Cs^+ . Thus the picture presented above includes both the effect of attractive forces and the effect of spatial requirement (*i.e.*, short-ranged repulsive forces) of the ions, and is

actually more general than the interpretations based on attractive forces alone such as the one just suggested by Dr. Frank.

F. E. HARRIS (Harvard University).—Another phenomenon influenced by ion hydration is the dielectric constant. In aqueous solutions at molar concentrations, the dielectric constant, extrapolated to low frequency from microwave measurements, is significantly less than its value for pure water.* In addition to the decrease occurring because the water of hydration cannot readily orient in an applied field, the decrease is also contributed to because the insertion of a hydrated ion breaks up the water structure around it, reducing the coordination responsible for the high dielectric constant.** The breakdown of the water structure also leads to shorter relaxation times for water in ionic solutions. The dependence of the dielectric constant on ionic size and charge, together with the experimental results for neutral molecules, suggest that the major part of the decrease in low frequency dielectric constant is produced by the charges, rather than by the insertion of foreign bodies.

J. H. WANG.—Haggis, Hasted and Buchanan hold that the effect of distortion of water lattice on the depression of the low frequency dielectric constant is negligible as compared to that due to hydration. With this assumption they computed the number of "irrotationally bound" water molecules, and showed that this number is zero for uncharged solutes but finite for ions or highly polar molecules. If Dr. Harris' observation on the importance of the distortion effect is correct, the situation would be more complex. But since the amount of hydration for different ions is not known, it would be difficult to estimate the extent of distortion caused by different solutes from the measured low frequency dielectric constants of solutions. Dielectric relaxation time data may be more useful in this respect.

* G. H. Haggis, J. B. Hasted and T. J. Buchanan, *J. Chem. Phys.*, **20**, 1452 (1952).

** F. E. Harris, Ph.D. Thesis, University of California, Berkeley February, 1954.

THE TRUE IONIZATION CONSTANT OF CARBONIC ACID IN AQUEOUS SOLUTION FROM 5 TO 45^o1

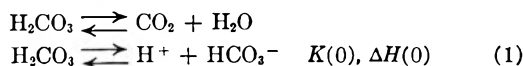
By KURT F. WISSBRUN, DOUGLAS M. FRENCH AND ANDREW PATTERSON, JR.

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The true ionization constant of carbonic acid in aqueous solution has been determined at 5, 15, 25, 35, 38 and 45° through calculations utilizing the results of high field conductance measurements at the same temperatures. The true ionization constants, in contrast with the apparent ionization constants, change but little with change in temperature.

The true ionization constant of carbonic acid at 25° has been computed from high field conductance data in a previous paper.² The only other data available for comparison with this result at 25° were those of Roughton.³ In order to obtain a check on the consistency of the data derived from high field conductance measurements and to afford a comparison with the variation of the apparent ionization constant with temperature, the high field conductance measurements have been extended to include the temperatures 5, 15, 25, 35, 38 and 45°, and the true ionization constant of carbonic acid (eq. 3, ref. 2) has been calculated at these temperatures. As Roughton³ has pointed out, in view of the important role of the reactions



in controlling the speed of elimination of carbon dioxide in expired air during mammalian metabolic processes, it is desirable to have measurements of the value of $K(0)$ (true) at body temperature. These new results permit interesting speculation on the heat effects of the successive reactions mentioned in ref. 2.

Experimental

The experimental procedure for the high field conductance measurements was essentially that of Gledhill and Patterson⁴; further details also have been given.² In the present measurements the analytical determination of the concentration of total carbon dioxide present has been greatly improved, and the precision and accuracy of measurement of field strength have been enhanced.

At temperatures lower than that of the room, the amount of dissolved carbon dioxide required to obtain the desired cell resistance increased markedly, as might be expected. The difficulty of keeping the gas in the conductance cell and later of analyzing such solutions at room temperature without significant loss of carbon dioxide increased in proportion. It was found that the act of pipetting a sample from the cell caused such a loss of carbon dioxide that checks between successive titrations of the same solution were impossible. Evidently opening the cell to introduce the pipet and application of suction to the pipet to draw solution into it permitted appreciable loss of carbon dioxide. To avoid such loss, a standard taper solution removal cap was prepared with a glass tube ring-sealed through it, long enough to reach almost to the bottom of the cell, and with a glass side arm tube. Short lengths of rubber tubing were placed on each of these tubes, that on the side arm equipped with a rubber bulb. The cell was removed from the thermostat for analysis and immediately surrounded with flaked ice, the standard taper solution removal cap put in place of the

closed cap used during the runs, and the entire arrangement, with ice, clamped on a ring stand. A drained pipet was inserted in the rubber tube extending from ring seal and air pressure applied gradually with the rubber bulb to fill the pipet. Both rubber tubes were closed with pinch clamps while titration of the sample was completed. Loss of carbon dioxide through the rubber tubing was not significant during the short time required for analysis, but the loss is large enough to give intolerable conductance changes over a period of several hours. For this reason, the conductance cells were always closed with a sealed standard taper cap after the carbon dioxide solution was prepared as described in ref. 2.

It was noticed with the more concentrated solutions that the turbulent flow produced by the sudden change of cross-sectional area where the narrow lower tube of the pipet joins the bulb would cause formation of bubbles with consequent loss of carbon dioxide. A slow, uniform, deliberate application of pressure to the solution was necessary. By proceeding in the way just described it was possible to remove highly reproducible samples of cell solution for analysis. The analysis was made by adding a slight, measured excess of standard barium hydroxide, 0.05 *f*, and back titrating with standard hydrochloric acid, 0.1 *f*, using phenolphthalein as indicator. Contamination of the barium hydroxide solution in the titration flask by carbon dioxide from the air was avoided by filling the flask with a gas heavier than air. The only heavy gas available in the laboratory at the time was cyclopropane suitable for anesthesia, but this served admirably. As a result of these several improvements in detail, it was found possible to make analyses reproducible to one part in 2000 for the solutions used above 25°, and to better than one part in 1000 for the solutions used below 25°. With the more concentrated, cold solutions the principal remaining difficulty was that of loss of carbon dioxide as bubbles on the pipet walls, a loss greatly minimized by scrupulous attention to cleanliness of the pipet.

During the course of the measurements a DuMont-Polaroid oscilloscope camera became available to us; it was used to photograph the output pulse of the pulse modulator. Examination of the pulse shape as disclosed by these photographs showed a much greater decrease in pulse voltage during the duration of the pulse than that for which the equipment was designed. Investigation of this effect, which had not previously been noticed because of the null matching procedure commonly employed in bridge balancing, showed that it was due to deterioration of the pulse power tubes in the output stage of the modulator. When these were replaced and the pulse output voltages recalibrated, it was found not only that the pulse shape was restored to normal, but also that the pulse voltages were markedly greater than before replacement. This discovery, and the almost simultaneous improvements made in analytical techniques caused us to repeat a number of measurements, including those at 25°. The results given for 25° in this paper are, therefore, entirely new and supersede those reported in ref. 2, since it is not known to what degree the high field conductances there reported were in error.

The field strength measurements become especially important in this determination because it is the slope of the high field conductance *vs.* field strength curve which is employed in calculating the true ionization constant. For this series of results the amplitude of the high voltage pulses applied to the cells was determined through the use of a calibrated capacitive voltage divider the output of which was applied directly to one of the vertical deflection plates

(1) Presented at the Symposium on Solutions of Electrolytes of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Sterling Chemistry Laboratory, Yale University, 16-18 June, 1954.

(2) D. Berg and A. Patterson, *J. Am. Chem. Soc.*, **75**, 5197 (1953).

(3) F. J. W. Roughton, *ibid.*, **63**, 2930 (1941).

(4) J. A. Gledhill and A. Patterson, *THIS JOURNAL*, **56**, 999 (1952).

of the oscilloscope. The deflection of the pulse from the undeflected base line of the oscilloscope trace was then compensated or bucked out by application of a measured variable d.c. potential. The oscilloscope trace was first carefully centered on one of the graticle marks on the face, and the flat top of the deflected pulse return to this same mark on the oscilloscope face through the application of the variable d.c. potential. The d.c. potential was measured with a Weston type 622 thermocouple voltmeter. This pulse voltage measurement and the calibration of the capacitive voltage divider have been described at length by Gledhill.⁵ The division ratio for the particular divider and its associated electrical connections was found by Gledhill to be 281.1 ± 0.6 . The precision with which the oscilloscope trace could be centered on a given graticle mark was estimated as 0.4%; the precision with which the d.c. voltmeter could be read was of the same order. Each of these measurements was thus made with a precision somewhat poorer than the precision with which the divider ratio was known, about 0.2%.

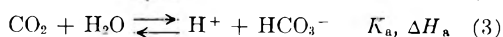
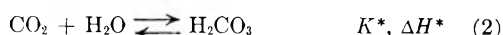
Results

The results of the high field conductance measurements are similar to those shown in Fig. 1, ref. 2. There is an apparent trend toward smaller high field conductance quotient with increasing temperature, but since the quotient is also concentration dependent this trend is not by itself meaningful. Instead of presenting the experimental results in the form of graphs, we have tabulated the reduced slopes, Q (eq. 17, ref. 2), and the corresponding values of ρ_0 . Table I gives in addition to these data at the several temperatures studied, the total concentration of carbon dioxide, the average value of $K(0)$, $K(\text{apparent})$, and the ratio $K(\text{apparent})/K(0)$ which is in effect the fraction of total carbon dioxide present which is hydrated. The high field measurements were repeated at least four times on each given cell solution for which a concentration is given; in some cases more than one solution was studied at a given temperature, as noted. To obtain the quantities Q and ρ_0 the data have been treated as described in ref. 2.⁶

Discussion

The true ionization constants found in this investigation change but little with change in temperature, in contrast with the apparent ionization constants which are also listed in Table I. The precision of our measurement is at best some ± 0.05 unit; with this in mind, it appears that the true ionization constants go through a maximum at a temperature of about 17°.

Of the data available with which these new results may be compared, let us first consider those of Roughton, ref. 3, which yielded the result $2.5 \pm 0.3 \times 10^{-4}$ for $K(0)$; this result was obtained from measurements in what were essentially sodium chloride solutions. In addition to reaction 1, above, these additional reactions are needed



(5) J. A. Gledhill, Dissertation, Yale University, 1949.

(6) We have noted three omissions in the theoretical section of ref. 2, as follows: In eq. 20, the first Q to appear in the denominator should be squared, making the first term within brackets read $F^2(b)(1 - 2Q)^2/(Q)^2$. In eq. 21, in the expression for A_2 the first fraction should read $7/18Q$ rather than $7/8Q$. Equation 22 was omitted altogether; eq. 22 for ref. 2 is given herewith: $(1 - 2Q)^2/(Q - Q^2) = \rho_0 = K(0)/C$.

TABLE I

THE TRUE IONIZATION CONSTANTS OF CARBONIC ACID IN AQUEOUS SOLUTION AS A FUNCTION OF TEMPERATURE

Temp., °C.	Q	ρ_0	$C_{\text{total } M} \times 10^2$	$K(0)_{\text{av.}} \times 10^4$	$K(\text{app.}) \times 10^4$	$K(\text{app.})/K(0) \times 10^2$
5	0.2265	1.708	4.703	1.56	3.040	0.195
15	.1838	2.666	3.280	1.76	3.802	.216
	.2097	2.034	3.754			
25	.1728	2.997	2.208	1.72	4.452	.259
35	.1780	2.835	1.997	1.67	4.914	.294
38	.1646	3.273	1.64	1.59	5.007	.315
	.1691	3.117	1.51			
45	.1492	3.879	1.417	1.60	5.139	.323
	.1525	3.738	1.192			

^a Values of $K(\text{apparent})$ from Harned and Davis, ref. 7.

Equation 1 is the reaction of ionization for which the constants of the present paper have been derived. Equation 2 is the reaction of hydration, upon the slowness of which the success of this method is dependent. Equation 3 is the over-all reaction involved in the more common apparent ionization constant determinations. Harned and Davis⁷ have determined K_a in aqueous solution, while Harned and Bonner⁸ have made a similar determination in solutions of sodium chloride. By plotting Harned and Bonner's data for K_a in sodium chloride solutions as a function of the molarity of sodium chloride it was possible to determine that at 0.06 M the concentration of sodium chloride used by Roughton, that the ratio of K_a (in salt solution) to K_a (in water) was 1.51 at 15°. Assuming that K^* is but little affected by the presence of sodium chloride, then Roughton's value of $K(0)$ may be corrected for comparison with the result of this paper; since $K_a = K(0) K^*$, then $(2.5 \times 10^{-4})/(1.51) = 1.66 \times 10^{-4}$. In view of the precisions claimed by each investigator, this constant is in surprisingly good agreement with the value obtained in the present investigation, $1.76 \pm 0.05 \times 10^{-4}$.

By plotting the logarithms of the ratios of K_a (ref. 7) over $K(0)$ (this paper) vs. $1/T$ and taking the slopes, we have computed ΔH^* at 17, 27 and 37°, approximately the temperatures at which Roughton has performed measurements. Table II compares these results with those of Roughton, ref. 3. The assumption has been made that Roughton's results as given in ref. 3 refer to reaction 2, above, although his paper appears to refer to the reverse of eq. 2.

TABLE II

VALUES OF THE HEAT OF HYDRATION OF CARBON DIOXIDE

Temp., °C.	ΔH , cal.	
	This paper	Roughton
17	3560	1420
27	2650	1040
37	1950	450

Harned and Embree⁹ have given the equation

$$\log K(0) = \log K(0)_{\text{max}} - 5 \times 10^{-5}(t - \theta)^2 \quad (4)$$

(7) H. S. Harned and R. Davis, *J. Am. Chem. Soc.*, **65**, 2030 (1943).

(8) H. S. Harned and F. T. Bonner, *ibid.*, **67**, 1026 (1945).

(9) H. S. Harned and N. D. Embree, *ibid.*, **66**, 1050 (1934).

(using the symbols of the present paper) to express the dependence of $\log K(0)$ upon temperature and the commonly found maximum value of $K(0)$. Our data may be made to fit this simple equation within the limits of our precision of measurement. $K(0)_{\max}$ falls at 17° . From this equation one may obtain the relation that

$$\Delta H(0) = -4.576 \times 10^{-4} T^2(t - \theta) \quad (5)$$

From this equation Roughton has computed θ , while from it we are able to compute $\Delta H(0)$. Roughton obtained 55° for the temperature, θ , at which $K(0)$ has its maximum value. Harned and Bonner found for K_a a θ of 50° . Inspection of our results shows $K(0)$ to have $\theta = 17^\circ$. It has been found by Harned and Embree⁹ that in many cases the higher the value of the ionization constant, the lower the maximum value of K_a found. The same value of $K_{a \max}$ would not be expected for the over-all reaction, eq. 3, and for the reaction of ionization only, eq. 1. Since the variation of $\log K_a$ with temperature is effectively the combination of the variations of $\log K(0)$ and $\log K^*$, and since K^* is an increasing quantity in the temperature range considered here (see Table I), the maximum value of $\log K(0)$ would be expected to fall at a lower temperature.

In Table III is given $\Delta H(0)$ computed from eq. 5 for our data, and as obtained by Roughton. The values are not comparable except that they decrease with increasing temperature.

TABLE III

Temp., ° C.	VALUES OF THE HEAT OF IONIZATION OF CARBONIC ACID	
	This paper	Roughton
0	580	1710
17	0	1240
27	-412	960
37	-880	685

By adding ΔH^* , the heat of hydration to $\Delta H(0)$ the heat of ionization, one obtains ΔH_a for the over-all reaction. Values of ΔH_a were obtained by MacInnes and Shedlovsky from conductance measurements.¹⁰ Table IV gives values of ΔH_a for our results, and for those of Harned and Bonner,⁸ MacInnes and Shedlovsky,¹⁰ and Roughton.³ It will be noted that the data of the present paper, obtained from K 's of limited precision, are, with the exception of the value at 17° , not in serious disagreement with the values obtained by other investigators. It is also apparent that the presence of sodium chloride does not greatly change the heat effects.

(10) D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, **57**, 1705 (1935).

TABLE IV

VALUES OF THE COMBINED HEAT OF HYDRATION AND IONIZATION OF CARBONIC ACID, ΔH_a

Temp., ° C.	This paper	Harned ⁸	MacInnes ¹⁰	Roughton ³	Harned ⁸ in 0.1 <i>m</i> sodium chloride
17	3560	2960	2660	..	3050
27	2240	2080	1930	2000	2250
37	1070	1160	1210	1140	1350

Roughton's value for $\Delta H(0)$ was obtained by direct measurement of the total heat of reaction for the reverse of eq. 3 above, and, by an interpretation of the rate of reaction, subtraction from this of the heat of reaction of eq. 1, reversed, to give the heat of reaction 2, again reversed. Inspection of Tables II and III suggests that a possible explanation for the difference in Roughton's data and our data for $\Delta H(0)$ is that Roughton overestimated the heat of ionization, and thus underestimated the heat of hydration.

Acknowledgment.—This work was supported by the Office of Naval Research.

DISCUSSION

M. EIGEN (University of Göttingen).—I should like to ask whether in the explanation of these results, the possibility of a dispersion of the dissociation field effect is taken into consideration. This effect must be expected if the impulse duration becomes of the same order as the relaxation time of the system under investigation (given by the rate constants of the dissociation and recombination processes). If this effect is not observed in the measurements, then we may conclude that the relaxation time is shorter than 10^{-7} sec., this means—if we consider the very small concentrations of the protons and HCO_3^- ions—that the rate constant of the ionic recombinations has the same high order of magnitude (10^{10} to 10^{11} liter/mole/sec.) as we have found with corresponding investigations in other systems, involving proton reactions (*cf.* M. Eigen, *Disc. Faraday Soc.*, 1954).

A. PATTERSON, JR.—Since the reaction $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ is presumably a fast ionic reaction with a relaxation time shorter than 10^{-7} sec., we have not attempted to explain the results in terms of dispersion of the dissociation field effect. In our experiments, the concentrations of ions and the results of the measurements are quite similar to those in other acids which we have studied, where the dispersion effect was known to be absent.

L. G. LONGSWORTH (Rockefeller Institute).—How would you expect the addition of carbonic anhydrase to the solution to affect its high field conductance?

A. PATTERSON, JR.—It is our intention to try the matter experimentally, but, as Prof. Onsager has pointed out, it would take a marvellous catalyst to affect the conductivity in 4 microseconds. I should imagine the question of reaction rate in catalytically controlled systems would hold much physiological interest. Our type of measurement is not easily adapted to reaction rate studies if the rates are too slow.

A NEW CELL DESIGN FOR PRECISION CONDUCTIMETRY

BY JAMES C. NICHOL¹ AND RAYMOND M. FUOSS*Sterling Chemistry Laboratory, Contribution No. 1220, Yale University, New Haven, Conn.**Received March 15, 1954*

The design of a conductance cell intended for use with dilute non-aqueous solutions is described. The electrodes (bright platinum) are concentric cylinders with the lead to the outer electrode being a platinum tube which acts as an electrical shield for the lead to the inner electrode. Stray electrical paths are thus eliminated. The electrode assembly is mounted on a Teflon plug which is turned to a standard taper, so that the electrodes are interchangeable. Tests covering the resistance range $1000 \leq R \leq 50,000$ ohms over the frequency range $500 \leq f \leq 5000$ cycles per second show that the frequency variation is significantly less than that obtained with cells of other designs. Resistances up to 50,000 ohms can be measured with a precision of at least 0.02%. The $R-f^{-1/2}$ plot is nearly linear at low resistances but its curvature steadily increases with cell resistance; the curve can be accurately reproduced by a parabola. Consequently, a simple numerical extrapolation to infinite frequency can be made, using data at three frequencies equally spaced on a $f^{-1/2}$ scale (e.g., 5000, 1250 and 556 cycles).

Introduction

In order to obtain conductance data on non-aqueous systems which are useful for extrapolation, it is necessary to work at quite low concentrations. Two experimental consequences follow: resistances well over 10,000 ohms frequently must be measured, and bright platinum electrodes must be used to minimize difficulties due to adsorption² of solute on the electrodes. These are precisely the conditions under which errors due to polarization and to parasitic currents are most likely. It has been standard practice since 1935 to extrapolate observed resistance linearly to infinite frequency on a reciprocal root frequency scale, following the recommendation of Jones and Christian³ although these authors mention that their data show a small systematic deviation from linearity. Their resistances were in the range of 50–2000 ohms; when the resistance is of the order of 10^4 ohms in organic solvents, the curvature becomes extremely pronounced and linear extrapolation on an $R-f^{-1/2}$ scale becomes impossible. To eliminate the difficulties arising from the Parker effect⁴ it has been recommended^{5,6} that cells be constructed in such a way that no shunt circuits which contain capacity in series with the cell contents be present. This goal is readily achieved by spacing the leads relatively far from the cell when the cell impedance is low, but the necessary design becomes awkward when the cell resistance is greater than 5,000–10,000 ohms. The erlenmeyer type cell⁷ offers the convenience of being simultaneously the conductance cell and the mixing vessel, but we have found that it shows a Parker effect at high resistances. Furthermore, each such cell obviously has a fixed cell constant; one could cover a wider range of concentrations in one run if the cell constant could be changed. Dipping electrodes would permit change of cell constant, but they are bad electrically because the leads to the electrodes necessarily go through the solution, and as Shedlovsky⁶ pointed out, there is then a series capacity-resistance shunt across the unknown resistance.

(1) On leave of absence from Willamette University, Salem, Oregon. Grateful acknowledgment is made to the California Research Corporation for a research fellowship for the academic year 1953–1954.

(2) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

(3) G. Jones and S. M. Christian, *J. Am. Chem. Soc.*, **57**, 272 (1935).

(4) H. C. Parker, *ibid.*, **45**, 1336, 2017 (1923).

(5) T. Shedlovsky, *ibid.*, **54**, 1411 (1932).

(6) G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

(7) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933).

The purpose of this paper is to describe a cell design which permits interchange of electrodes in a vessel equipped with a standard taper opening, and which does not involve any stray electrical paths. Briefly described, the electrodes are concentric cylinders, with the lead to the outer electrode being a platinum tube which acts as an electrical shield for the lead to the inner electrode. Only one soft glass-platinum bead seal is necessary; the cell is therefore much easier to construct than the one with platinum tube seals through hard glass.⁸ We have found that the observed resistance with these electrodes is accurately a quadratic in $f^{-1/2}$; we present below a numerical method of extrapolating data to infinite frequency in order to eliminate the effects of polarization. It must be emphasized that the method may only be used when one is certain that no parasitic currents are present. Our shielded dipping electrodes satisfy this criterion. As far as the cell is concerned, we feel that it is now possible to measure resistances up to 50,000 ohms with a precision of at least 0.02%.

Experimental

Cell Construction.—Figure 1 shows a cutaway diagram of the electrode design finally adopted (electrode pair I). The steps in the construction of such a cell are as follows: electrodes A and B and tube C are shaped by rolling sheet platinum around glass tubing of suitable diameters as mandrels and then soldering the seams with pure gold (oxygen-gas flame). For sturdy construction, at least 10 mils of platinum sheet for A and B and 6 mils for C is recommended. To the inside wall at one end of C is gold-soldered a short length of B. and S. No. 25 platinum wire, D'. The other end of C is connected to A by means of four platinum strips, E (10 mils thickness) using gold as solder (two of the strips are indicated in the diagram). The sections of E between A and C are at an angle of 100–105° to the axis of C in order to increase the rigidity of the connection. Additional rigidity, as well as increased electrical shielding of B, is attained by gold-soldering two circular platinum strips, F, across E. The openings which remain are ample to permit free passage of liquid. Inner electrode B is supported by a short section of 1 mm. diameter platinum rod, G, gold-soldered across one end of B, the rod itself being welded at its midpoint to a second section of rod which in turn is welded to the platinum wire lead D". A layer of soft glass, H, built up along part of the second section of rod, starting about 5–6 mm. above B, serves to seal the electrode support into the platinum tube C. Strips of platinum, J, are gold-soldered across the bottom of A to provide further electrical shielding. The platinum tube is fitted snugly into a Teflon stopper K which has been machined to fit a standard taper joint ($\frac{1}{8}$ 29/42 is a convenient size). A piece of glass tubing, L, is inserted into C and around D" to insulate the latter from C. The ends of D' and D" are arc

(8) V. F. Hnizda and C. A. Kraus, *ibid.*, **71**, 1595 (1949).

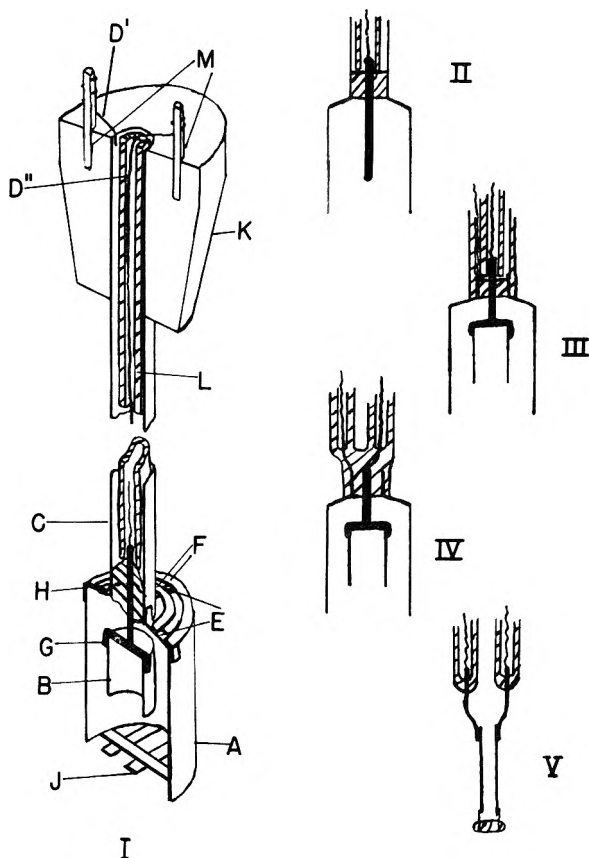


Fig. 1.—Dipping electrode cells (electrode vessels not shown): I, cutaway diagram of shielded electrodes; II—V, schematic diagrams of other electrode assemblies.

wound around and soft-soldered to the copper posts, M, set in the Teflon plug. The cell is completed by constructing an electrode vessel of appropriate size and shape.

The electrode dimensions naturally depend on the cell constant desired. The latter is approximately equal to $(1/2\pi l)\ln(b/a)$ where l is the length of the cylinders and b and a are the radii of the outer and inner electrodes. As a specific example, in a case where the cell constant is 0.03833, the outer and inner electrodes are, respectively, 3 and 2 cm. long and 2 and 1 cm. in diameter. For reasons to be discussed below, the diameter of the inner electrode should not be less than 1 cm. The length of the tube C depends on the dimensions of the electrode vessel. The diameter of C for reasons of sturdiness should be at least 5 mm.

In Fig. 1 are also shown schematic diagrams of other dipping electrodes (II—V) which were constructed for comparison experiments. In II a 1 mm. diameter rod replaces cylinder B of I. In III a wire replaces tube C as the lead to the outer electrode. The two electrode leads are enclosed in a soft glass tube and are separated from each other by a second smaller glass tube. In IV the leads are contained in separate glass tubes which pass through the solution in the cell, and in V the lead arrangement is the same as in IV while the cylindrical electrodes are replaced by flat rectangular ones.

The electrode vessels for the testing experiments are not shown. They consisted simply of large test-tubes fitted with $\frac{3}{8}$ 29/42 joints and provided with a side-arm for filling. Two such vessels joined by short glass tubes were used to compare the resistances of two electrode pairs in the same solution.

We will refer to the complete assemblies of electrodes and vessels as cell I, cell II, etc. A cell of the erlenmeyer type (flat electrodes 4 mm. apart, cell constant 0.04153) also used in comparison runs is designated as cell VI.

Resistance Measurements.—The bridge used has been described by Eisenberg and Fuoss.⁹ Its R - f performance

was checked using pure resistances (10^2 – 10^5 ohms) with capacitances up to 0.01 μ f in parallel as "unknowns." A variation of less than 0.01% was found in the resistance readings over the range $f = 250$ to 5000 cycles per second. The oscillator scale readings were checked using a Type 813 A General Radio 1000 cycle oscillator by observing the appropriate Lissajous figures on the bridge oscilloscope. All resistance readings involving cell resistance ratios were corrected for bridge lead and cell lead resistances. The latter were calculated from resistance data on platinum wire.¹⁰

Solutions.—For the majority of the tests of cell performance, 10^{-3} – 10^{-6} N solutions of tributylammonium picrate in 95% ethyl alcohol were used, mainly because a good supply of the salt was at hand and because past experience had shown that stable resistances were readily obtained with this solution. The above concentration range corresponds to a resistance range of 1,000–50,000 ohms for a cell constant of about 0.04. No attempt was made to determine accurately the solution concentrations since only approximate values were needed in comparing the behavior of different cells. It was noted in a few instances when aqueous solutions were measured that ionic impurities appeared to be dissolving from the soft glass plug, as indicated by a downward drift in the resistance reading. This drift was eliminated by boiling the electrode assembly in distilled water for several hours.

Results and Discussion

The cells were rated according to three criteria, namely, the magnitude and nature of the frequency dependence of resistance of a given cell over a range of resistances, the variation of the resistance ratios of different cells with changing resistance, and the sensitivity of the resistance to changes in the position of the electrodes in the cells. The better the cell the smaller is the frequency dependence of the resistance, and for a pair of good cells the resistance ratio should be independent of concentration. (If the design of a cell is such that resistance-capacitance shunts are present, then the ratio of its resistance to that of a good cell will decrease with increasing resistance of the solution,^{5,6} i.e., the cell will show a Parker effect.) For a dipping electrode to be satisfactory, of course, there should be no sensitivity to electrode position and depth of immersion.

The frequency dependence of resistance for cells I–VI is shown in Fig. 2 where R is plotted as a function of $f^{-1/2}$. The cell constants are about 0.04 except for cell II (constant = 0.15). The curves are displaced vertically for the sake of compact presentation; the absolute resistance for any point is obtained by adding the ordinate from the graph to the number of ohms shown at the left of each curve. Resistance readings observed at frequencies of 5000, 2000, 1000 and 500 cycles per second are shown. The absolute ordinate scale is the same for all the curves of Fig. 2, namely, 10 ohms per vertical unit as drawn. At a cell resistance of 1000 ohms, one unit is therefore 1%, while at 50,000 ohms, one unit corresponds to 0.02%.

It will be observed that the erlenmeyer cell VI is usable up to about 8000 ohms, in the sense that the frequency dependence is small and monotone. Beyond 10^4 ohms, however, a minimum appears in the R - $f^{-1/2}$ curve, which presumably is due to the f^2 terms in the impedance. These terms are the consequence of a high impedance shunt which consists of capacity from the lead wires to the cell

(9) H. Eisenberg and R. M. Fuoss, *J. Am. Chem. Soc.*, **75**, 2914 (1953).

(10) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Company, Cleveland, Ohio, 33rd edition, p. 2806.

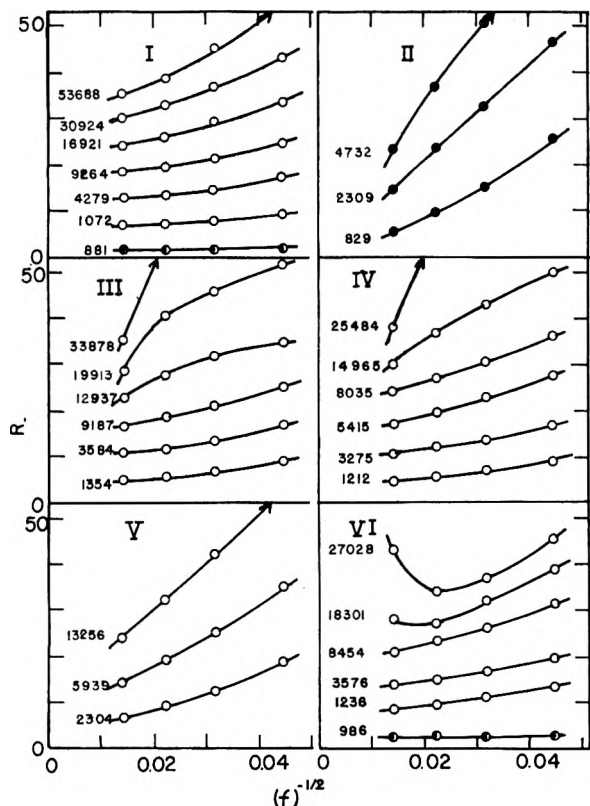


Fig. 2.— $R-f^{-1/2}$ curves for cells I-VI: O, tributylammonium picrate-95% EtOH; ●, HOAc-H₂O; ●, KCl-H₂O.

(through glass and thermostat oil), in series with the resistance of the cell contents. Cell V contains conventional dipping electrodes; as shown in Fig. 2V, the apparent resistance changes very rapidly with frequency. Incidentally, this design is sensitive to vibration, and the hazard of accidental change of cell constant by inadvertently bending the electrodes is always present. The data for cell IV show the remarkable improvement in the behavior of the dipping electrodes when one electrode shields the other. But solution is still present in the electrical field between the lead wires, and the corresponding Parker effect appears as a downward concavity on the $R-f^{-1/2}$ plot, which makes extrapolation hopelessly uncertain at high resistances. Only a slight improvement (III) is obtained by putting both leads in the same tube; while there is no solution between the lead wires themselves, there is solution in the field from the outer cylinder to the lead from the inner cylinder. Cell I, in which the lead to the inner cylinder is completely shielded by the lead to the outer electrode gives the highly satisfactory performance shown in Fig. 2I. One precaution must be mentioned in connection with this design: The diameter of the inner cylinder may not be too small, or the unsatisfactory pattern of Fig. 2II appears.

The per cent. changes in resistance ratio as a function of cell resistance for several cells compared to cell I (cell constant = 0.03833) are shown in Fig. 3. The ratio at a resistance of about 1000 ohms ($10^{-3} N$ solution) is taken as the reference point. For a cell of the type I design and cell constant 0.06097 there is no significant change in the ratio.

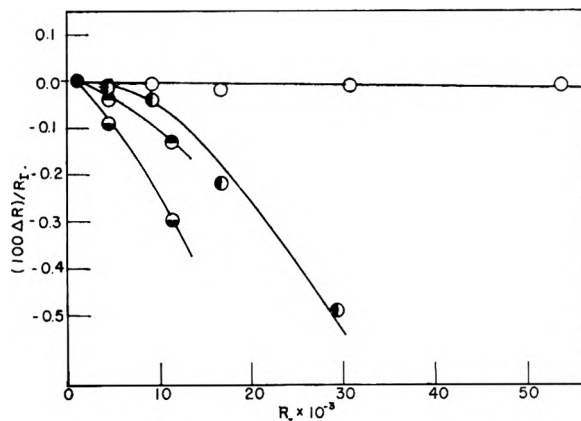


Fig. 3.—Per cent. change in ratio of resistance of various cells to resistance of cell I (constant = 0.03833): ●, reference point ($10^{-3} N$ solution); O, cell of same design as cell I but constant = 0.05997; ●, cell III; ●, cell VI; ●, cell IV.

For cells III, IV and VI there is a downward trend with increasing resistance, which indicates the presence of capacitance-resistance bypaths. These data clearly demonstrate the superior performance of the shielded concentric cells.

Tests of the effect of electrode position on the resistance confirm the above conclusion. No change in resistance is observed for cell I (as long as the bottom of the outer electrode extends a few mm. below that of the inner), either on moving the electrode assembly so that the outer cylinder touches the walls of the electrode vessel, or on changing the depth of immersion of tube C in the solution. This is true whether the bottom shielding strips (J of Fig. 2) are attached or not. If these strips are not used, however, the resistance depends on the vertical position of the electrodes with respect to the bottom of the cell when the distance becomes less than 3-4 mm.

For cells III, IV and V increasing sensitivity of the resistance readings to change of resistance and depth of immersion of the electrode leads is noted; a change of 5 cm. in the depth of immersion, for example, produces a 0.1% change in the resistance reading for cell IV. For cell V, the effect is about 2%.

While the above data show that cell I is definitely superior to the other cells, curvature is nevertheless present in the $R-f^{-1/2}$ plots, and the question of how to extrapolate to infinite frequency to obtain R_∞ arises. The usual procedure of drawing a best-fit straight line through the experimental points³ is unsatisfactory for plots showing such marked curvature. However, we have found that the data can be represented by the quadratic equation

$$R = R_\infty + ax - bx^2$$

where $x = f^{-1/2}$. R_∞ can be calculated simply, without recourse to graphing, by the following procedure: resistance measurements are made at three frequencies chosen so that the corresponding x values increase by equal increments. Three of the points in Fig. 4 satisfy this condition, namely, those for 5000, 1250 and 556 cycles where the values of x are 0.01414, 0.02828 and 0.04242. The coefficient b can now be determined with sufficient accuracy by

calculating the two $\Delta R/\Delta x$ ratios indicated in Fig. 4, dividing these values by the midpoint values of x (0.02121 and 0.03535), averaging the two numbers so obtained, and dividing the average by 2 (since $d^2R/dx^2 = 2b$). The three bx^2 products are calculated and subtracted from the appropriate R values to give three numbers $R' = R_\infty + ax$. From Fig. 4 it can be seen that the R' values lie on a straight line of very gentle slope which extrapolates to R_∞ . Since the x increments are equal, subtraction of the average $\Delta R'$ value from R (5000) immediately gives R_∞ . The value obtained agrees with that determined by drawing a parabola through the original points.

If one fits a straight line to the data by the method of least squares (dotted line, Fig. 4) the value of R_∞ so determined is 0.6 ohm lower, a significant difference in this example where the resistance is of the order of 1000 ohms. For aqueous solutions of not too high a resistance, the $R-f^{-1/2}$ curves are practically linear, and the resistance can be expressed satisfactorily by the equation

$$R = R_\infty + ax$$

the higher terms in x being negligible. Hence the linear extrapolation recommended by Jones and Christian does not introduce a very large error for these solutions. In the case of non-aqueous solutions which in general have a much higher resistance, however, the square term in x becomes the major factor and it is necessary to use a quadratic equation in making the extrapolation.

DISCUSSION

T. SHEDLOVSKY (Rockefeller Institute).—I should like to suggest that you try saturating your solutions with hydrogen. My guess is that this may result in less irreversible electrode polarization and therefore show less frequency dependence of the measurements.

R. M. FOSS.—Even if saturation with hydrogen would reduce polarization, it probably would not eliminate it entirely, and we therefore prefer elimination by extrapolation to a complication of the experimental technique.

H. I. SCHIFF (McGill University).—The direct current method of measuring electrolytic conductances developed

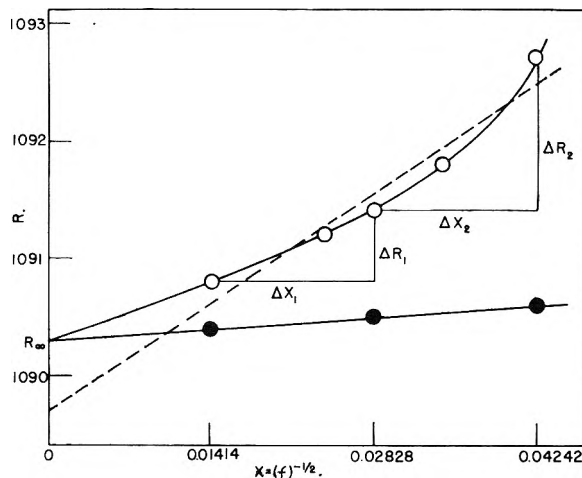


Fig. 4.—Extrapolation curves for a typical set of data: O, observed resistances; ●, $R' = R_\infty + ax$; dotted line, linear extrapolation plot calculated using the method of least squares.

by Dr. A. R. Gordon and his associates is free of the impedance difficulties discussed in the paper of Nichol and Fuoss. Moreover, it is capable of yielding high precision data with very simple apparatus. However, the method as described is restricted to solutions for which suitable reversible electrodes can be found. This is a serious limitation in the case of very dilute and non-aqueous solutions. For example, we found AgCl to be soluble in nitromethane solutions of quaternary ammonium chlorides.

It has been found possible to circumvent this difficulty by immersing the Ag, AgCl probe electrodes in aqueous KCl and forming a liquid junction between this solution and the non-aqueous solution whose conductance is to be measured. Since the d.c. method involves the measurement of the potential difference between two such probe electrodes the junction potentials cancel. The observed probe bias potentials were not substantially larger than those reported by Gordon. Moreover, when precautions are taken to keep the liquid junctions sufficiently distant from the main body of the cell the conductance measurements remain constant to 0.01% for more than 4 hours. The conductance is also independent of the current passed through the main body of the cell over the same range as is claimed for aqueous solutions.

It therefore appears that this modification may render the d.c. method applicable to the measurement of conductances of any electrolyte.

THERMOPOTENTIALS IN THERMOCELLS

BY P. MAZUR¹*University of Maryland, College Park, Md.**Received July 22, 1954*

The thermodynamics of irreversible processes is applied to thermocells. The results of the theory are discussed in connection with the experimental data. Some general relations between thermopotentials of thermocells and the temperature coefficient for isothermal cells are given.

1. Introduction.—Eastman^{2a} and Wagner^{2b} have discussed the thermopotential of thermocells in a way analogous to Thompson's treatment of the metallic thermocouple, that is, by a so-called "quasi" thermostatic method.

Recently Holtan, de Groot and the author^{3,4} have given a treatment for the thermopotentials of thermocells along the lines of the thermodynamics of irreversible processes.^{5,6} It is our purpose to summarize this treatment here and discuss the equations obtained in connection with experimental results. A detailed account of the comparison between theory and experiment has been published by Holtan elsewhere.⁷

We will consider systems consisting of two electrodes, connected to a precision compensator, and in contact with an electrically conducting medium. For simplicity's sake we will consider only pure thermocells, *i.e.*, thermocells with identical electrodes. During the experiment the electrodes are kept at different temperature. The thermopotentials are measured at zero current passing through the cell, and before any appreciable concentration gradients have been set up due to the Soret effect.

2. The Homogeneous Thermopotential.—The general expression for the entropy source strength σ in a system of n components, in mechanical equilibrium, ($k = 1, \dots, n$), excluding viscous phenomena and chemical reactions can be shown to be⁵

$$T\sigma = -J_q(\nabla T)/T + \sum_{k=1}^n J_k \{F_k - (\nabla \mu_k)_T\} \quad (1)$$

Here T is the absolute temperature, J_q the so-called reduced heat flow⁶, and J_k the flow density of component k with respect to an arbitrary reference frame. The external force per unit mass acting on component k is denoted by F_k , whereas μ_k is the chemical potential of k taken per unit mass. The subscript T in (1) indicates that the gradient of μ_k must be taken at uniform temperature.

The phenomenological equations describing the irreversible phenomena occurring in the system may then be written as

(1) On leave of absence from the University of Utrecht, Netherlands.

(2) (a) E. D. Eastman, *J. Am. Chem. Soc.*, **48**, 1482 (1926); **49**, 794 (1927); (b) C. Wagner, *Ann. phys.*, [5] **3**, 629 (1930); [5] **6**, 370 (1930).

(3) H. Holtan Jr., P. Mazur and S. R. de Groot, *Physica* **19**, 1109 (1953).

(4) H. Holtan Jr., Thesis, Utrecht, 1953.

(5) S. R. de Groot, "Thermodynamics of Irreversible Processes," North Holland Publ. Comp., Amsterdam, 1951.

(6) I. Prigogine, "Etude Thermodynamique des Phénomènes Irreversibles," Desoer, Liège, 1947.

(7) H. Holtan, Jr., *Proc. Kon. Ned. Akad. v. Wet. Amsterdam*, **B56**, 498 (1953); **B56**, 510 (1953).

$$J_q = -M_{qq}(\nabla T)/T + \sum_{k=1}^n M_{qk}J_k, \quad (2)$$

$$F_k - (\nabla \mu_k)_T = -M_{kq}(\nabla T)/T + \sum_{i=1}^n M_{ki}J_i \quad (3)$$

with the following Onsager reciprocal relations amongst the coefficients

$$M_{ki} = M_{ik} \quad (4)$$

$$M_{qk} = -M_{kq} \quad (5)$$

As can be shown, these coefficients also satisfy the relations

$$\sum_{k=1}^n \rho_k M_{kq} = 0 \quad (6)$$

$$\sum_{k=1}^n \rho_k M_{ki} = 0 \quad (7)$$

where ρ_k is the density of component k . It is clear from (2) that M_{qk} represents the heat transferred at uniform temperature with the unit of mass of component k . Therefore the M_{qk} are identical with the so-called heats of transfer Q_k^* and must, according to (5) and (6), satisfy the relation

$$\sum_{k=1}^n \rho_k Q_k^* = 0 \quad (8)$$

For the system under consideration F_k is given by

$$F_k = -e_k \nabla \varphi \quad (9)$$

where e_k is the charge per unit mass of k , and φ the electrical potential. With (5) and (9), equation (3) can be rewritten as

$$\nabla \varphi = e_k^{-1}(\nabla \mu_k)_T - e_k^{-1} \sum_{i=1}^n M_{ki}J_i - e_k^{-1} Q_k^*(\nabla T)/T \quad (10)$$

Let us now introduce the partial electric current density due to the k th charged component

$$I_k = e_k J_k \quad (11)$$

and the total electric current density

$$I = \sum_{k=1}^n I_k \quad (12)$$

Let us also introduce the transference numbers t_k defined as the ratios of the partial currents I_k and the total current I , at uniform temperature and chemical potentials

$$t_k = (I_k/I)_{\nabla T=0; \nabla \mu_k=0}; \sum_{k=1}^n t_k = 1 \quad (13)$$

From (10) one finds, for uniform temperature and uniform chemical potentials

$$\sum_{i=1}^n e_i^{-1} e_i^{-1} M_{ki} t_i = -\nabla \varphi / I \equiv R \quad (14)$$

where R is the coefficient of electrical conductance.

We can now multiply both members of (10) by t_k and sum over k . We then obtain with (4), (11), (12) and (14)

$$\nabla \varphi = - \sum_{k=1}^n t_k e_k^{-1} (\nabla \mu_k)_T - \sum_{k=1}^n t_k e_k^{-1} Q_k^*(\nabla T)/T - RI \quad (15)$$

With the conditions of vanishing total electric current ($I = 0$) and vanishing concentration gradients ($\nabla\mu_k = 0$), we finally obtain the following expression for the homogeneous thermopotential.

$$F\nabla\varphi = - \sum_{k=1}^n t_k z_k^{-1} Q_k'^* (\nabla T)/T \quad (16)$$

where $Q_k'^*$ is the molar heat of transfer, z_k the molar charge in faraday's and F the faraday number. Formula (16) has been derived with transport quantities t_k and $Q_k'^*$ with respect to an arbitrary reference frame. In the following, they will be defined with respect to a frame in which the electrodes of the thermocell are at rest.

The homogeneous thermopotential in the metallic wire connecting the electrodes through the compensator is a special case of (16) and is given by

$$F\nabla\varphi = Q_d^{1*} (\nabla T)/T \quad (17)$$

where Q_d^{1*} is the heat of transfer of the electrons in the wire.

3. The Heterogeneous Electrode Potential Difference.—The electrical potential difference at the interface between the electrodes (phase 1) and the electrolytic medium (phase 2) in the state of vanishing electric current is given, as in ordinary thermostatics, by the condition that the electrochemical affinity of the electrode reaction equals zero. We can therefore write for the potential difference at a junction between electrode and medium

$$F(\varphi_1 - \varphi_2) = \Delta G \quad (18)$$

where ΔG is the change in Gibbs free energy, due to the electrode reaction, when one faraday of electricity passes from the electrode to the medium. For thermocells with identical electrodes, one at temperature T , and the other at $T + \Delta T$, the resulting heterogeneous thermopotential is given by

$$F\Delta\varphi_{het} = \Delta G_{T+\Delta T} - \Delta G_T = -\Delta S\Delta T \quad (19)$$

Here ΔS is the change of entropy due to the electrode reaction, when one faraday of electricity has passed through the cell. As in § 2, it has been assumed in (19) that concentration gradients do not occur in the medium between the electrodes.

4. The Total Thermopotential of a Thermocell.—The resulting potential of a pure thermocell can be obtained by adding up the homogeneous and heterogeneous potential differences around the circuit

$$\Delta\varphi_{tot} = \Delta\varphi_{med} + \Delta\varphi_{met} + \Delta\varphi_{het} \quad (20)$$

$\Delta\varphi_{tot}$ is the total potential measured in the experiment, "med" refers to the medium, "met" to the metallic wire. From (16), (17), (19) and (20) one finds for the total thermopotential of the cell

$$F\Delta\varphi_{tot}/\Delta T = - \sum_{k=1}^n t_k z_k^{-1} Q_k'^*/T - Q_{el}^{1*}/T - \Delta S \quad (21)$$

Again, of course, this formula is valid only when no concentration gradients occur in the medium.

Introducing the so-called entropies of transfer S^* defined by

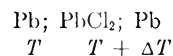
$$S_k^* = (Q_k'^* + TS_k)/T \quad (22)$$

where S_k is the partial molar entropy of component k , equation 21 can be rewritten in the form

$$F\Delta\varphi/\Delta T = - \sum_{k=1}^n t_k z_k^{-1} S_k^* - \Delta S_{el}^* + \sum_{k=1}^n t_k z_k^{-1} S_k - S_{el} \quad (23)$$

It can easily be verified that, when ΔS is evaluated for each special case, the last three terms on the right-hand side of (23) will not contain ion entropies, which are not known, but only known salt entropies.

As an example consider the cell with solid electrolyte



In this case $-\Delta S$ equals

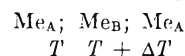
$$-\Delta S = \frac{1}{2} S_{Pb} - \frac{1}{2} S_{Pb^{++}} - S_{el} \quad (24)$$

Since lead chloride is a pure anion conductor, the transference number of the anion is equal to unity. Equation (23) then reads

$$F\Delta\varphi/\Delta T = S_{d-}^* - S_d^* + \frac{1}{2} S_{Pb} - \frac{1}{2} S_{PbCl_2} \quad (25)$$

The right-hand side of this expression contains, apart from the entropies of transfer, only the partial molar entropies of lead and lead chloride.

As another example and special case of (23) consider the metallic thermocouple



We have here simply

$$-\Delta S = {}_A S_d - {}_B S_d \quad (26)$$

and therefore from (23)

$$F\Delta\varphi/\Delta T = {}_A S_{el}^* - {}_B S_{el}^* \quad (27)$$

that is, the usual expression for the thermopotential of a metallic thermocouple.⁵

Turning back to formula (23), we thus see that the sum of the last three terms on the right-hand side contains only known quantities (transference number and partial molar entropies). Let us for convenience denote this sum, which can be calculated, by $F(\Delta\varphi/\Delta T)_c$, so that

$$F(\Delta\varphi/\Delta T) = F(\Delta\varphi/\Delta T)_c - \sum_{k=1}^n t_k z_k^{-1} S_k^* - S_{el}^* \quad (28)$$

Comparison of $(\Delta\varphi/\Delta T)_c$ with the experimental results $\Delta\varphi/\Delta T$ therefore yields information concerning the entropies of transfer S_k^* and S_d^* .

Holtan performed such a comparison for a number of cells. It turned out that for most thermocells with solid electrolyte, which were considered, the calculated values coincide with the experimental ones within the limits of experimental error.^{4,7} This seems to indicate that the last two terms of (28) are of negligible magnitude in these cases. For thermocells containing electrolytic solutions such a result has not been found. It should be noted however that the *hydrated* ions in the electrolytic solutions must be considered as *components*, as defined in the derivation of expression (23). For the calculation of $(\Delta\varphi/\Delta T)_c$ in this case, one therefore needs data concerning the transport of solvent during electrolysis. Since the available data are not accurate enough, no definite conclusions concerning the magnitude of

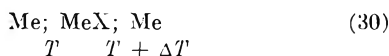
the terms containing entropies of transfer can be drawn.

5. Relations between Thermocells and Isothermal Cells.—The formalism developed in the previous paragraphs enables us to derive some general relations between thermopotentials of thermocells, and the temperature coefficient for the electromotive force of isothermal cells.

Consider the isothermal cell



and the two thermocells



The temperature coefficient of the isothermal cell (29) is given by

$$F(d\Delta\varphi/dT)_{is} = S_{mc} + \frac{1}{2} S_{X_2} - S_{MeX} \quad (32)$$

The thermopotential of thermocell (30) is given by (cf. equation 23)

$$F(\Delta\varphi/\Delta T)_1 = S_{X^-} - S_{e_1} - S_{MeX} + S_{Me} \quad (33)$$

and the thermopotential of (31) by

$$F(\Delta\varphi/\Delta T)_2 = S_{X^-} - S_{e_1} - \frac{1}{2} S_{X_2} \quad (34)$$

In these equations, S_{e_1} is the entropy of transfer for the electrons in the metal of cell (30), while S_{e_1} represents the entropy of transfer of the electrons in the solid substance in which the gas of cell (31) is absorbed.

Subtracting (34) from (33) and using (32) we find $F(\Delta\varphi/\Delta T)_1 - F(\Delta\varphi/\Delta T)_2 = F(d\Delta\varphi/dT)_{is} + S_{e_1} - S_{e_1}$ (35)

In general S_{e_1} is not the same in the two cells. The difference is equal to the thermoelectric force of a thermocouple consisting of the metal Me of

cell (30) and of the metal in which the gas of cell (31) is absorbed. As the thermopotential of metallic thermocouples is usually of the order of magnitude of 10^{-5} volt/degree, while the thermopotential in thermocells is about 10^{-3} volt/degree, the last two terms on the right hand side of (35) may be neglected. The relation thus obtained (that is, neglecting $S_{e_1} - S_{e_1}$) has been found experimentally by Reinhold⁸ and finds its justification in the above considerations.

Similar relations may be also derived for more complicated cells.⁴

DISCUSSION

GEORGE SCATCHARD (Massachusetts Institute of Technology).—Dr. Mazur has shown that the deviations from Reinhold's conclusions are very small. It seems to me that they will be identically zero for the normal method of measuring these potentials. The necessary conditions for identity are that the potentiometer remain at constant temperature and that the two metallic thermal gradients be made in the same metals as in the isothermal cells if the comparison is made directly, or the two metallic thermal gradients both be made in the same metal if the comparison is made with thermal coefficients from calorimetric measurements.

PETER MAZUR.—Reinhold's rule holds exactly in some cases. The equations which have been derived show that this will be the case, for instance, if the gas of the second thermocell is absorbed in the same metal, as the electrodes of the first thermocell are made of. Professor Scatchard indicates another possibility for this rule to be satisfied exactly. The measurements of thermopotentials are, however, quite frequently performed on systems in which the metallic thermal gradient is completely confined to the metal, of which the electrodes are made. Furthermore, in the case described by Professor Scatchard, the thermopotential of a thermocell would not be determined uniquely by specifying only the electrodes and the electrolytic medium.

(8) H. Reinhold, *Z. anorg. Chem.*, **171**, 181 (1928).

THE THERMODYNAMICS OF ELECTROLYTES AT HIGHER CONCENTRATION

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The thermodynamic behavior of electrolytes in aqueous solutions up to high concentrations is described on a uniform theoretical basis. In addition to the electrostatic interaction of the ions two properties of the electrolyte prove to be especially characteristic of the thermodynamic behavior: 1st, the space requirement of hydrated ions in the ionic atmosphere; 2nd, an incomplete dissociation appearing for a large number of electrolytes at higher concentrations. The quantity characteristic for the space requirement of the hydrated ions and for the formation of undissociated molecules is the hydration radius "a," which is approximately known from values of the apparent molar functions at infinite dilution. By introduction of new distribution formulas for the ionic atmosphere in the theory of Debye and Hückel, which follow from statistical and thermodynamical considerations analogous to adsorption statistics or to Fücken's treatment of hydration shells, the properties of some completely dissociated electrolytes such as Li halides, MgCl₂, and others are calculated and found to be in good agreement with experimental data. Other applications of the distribution formula—especially with respect to colloid ions—are indicated. In the general case one has to consider the additional effect of incomplete dissociation. Then the calculations of mean activity coefficients, heats of dilution, and apparent molar heat capacities from the expression for the free energy are in fair agreement with experimental data for 1-1, 2-2, 1-2, and 1-3 electrolytes up to concentrations of about 1 to 4 molar. The effect of incomplete dissociation appears most obviously, separated from other effects, in sound absorption results of some electrolytic solutions. In addition, the relaxation effects of the hydration shells of the ionic atmosphere, and of the dissociation equilibrium are discussed with respect to heat conductivity, electrical conductivity, and sound absorption data of electrolytic solutions. The last mentioned quantity gives information about the kinetics of extremely fast ionic reactions in aqueous solutions.

1. Introduction

The fundamental work of Debye, Hückel, On-

sager and others³ on the theory of strong electro-

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(3) For detailed expositions see, e.g., H. S. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," John Wiley and Sons, Inc., New York, N. Y., 1950; H. Falkenhagen, "Elektrolyte," Leipzig, 1953; or G. Kortüm, "Elektrolytösungen," Leipzig, 1941.

lytes, resulting in the explanation of the well-known limiting laws of statistical and irreversible behavior, was one of the most successful applications of statistical thermodynamics to properties of matter. This theory, applied in the region of high dilution, represents a really exact and satisfactory solution of the problem. At higher concentrations however, the applications of the theory are restricted because the suppositions involved become insufficient. An exact treatment of the problem at higher concentrations without simplifications does not yet exist up to now.

In a series of preceding papers,⁴ we have tried to describe the thermodynamic behavior by introducing a model into the theory of Debye and Hückel⁵ containing some features characteristic of electrolytes at higher concentrations. In the following we will briefly characterize our conceptions and give a survey of our calculations and results obtained.

2. Space Requirement

Hydration, and Incomplete Dissociation of Electrolytes.—The space requirement of ions in aqueous solution is essentially determined by the strength of their hydration. According to Eucken⁶ atoms of strong electrolytes in aqueous solution are surrounded in general by one to two hydration shells containing eight or more oriented water molecules. The inner one of these hydration layers is practically stable up to about 100°, while the second layer is partly decomposed in this range. ("Decomposed" means in this connection that the water dipoles are not oriented in the direction of the ionic field.) This model of hydrated ions was very useful in the interpretation of the temperature dependence of apparent molar functions at infinite dilution (*e.g.*, apparent molar heat capacities or volumes),⁷ which give information about the steric and energetic interactions between the ions and the solvent molecules.

The hydrated ions are not rigid and impenetrable complexes because the time which is required for the orientation and disorientation of the water molecules in hydration shells is comparable with the duration of normal position exchanges of particles in fluids.⁸ Thus the motion of the ions through water is accompanied by a continuous "formation" and "decomposition" of their hydration shells (see Section 5). Due to this fact the hydration shells of oppositely charged ions can partly penetrate into each other, as the orientation of the water molecules in these shells is of opposite direction. This is observed in the investigation of fast ionic reactions,⁹ to which we refer in the last section. In contrast to this, the hydration shells of like-charged ions must repel each other as rigid and impenetrable complexes because of the similar orientation of the water molecules involved. For the radii of these impenetrable complexes values of about 5–6 Å. are to be expected (ionic radius +

distance of 1 to 2 hydrogen bonds). For homologous ions (*e.g.*, Li⁺, Na⁺, K⁺ . . .) these values may vary at the most about 1 Å. corresponding to a variation in volumes of about 100%. The different steric interaction of like-signed and oppositely charged ions is important in the distribution of ions in the ionic atmosphere^{4b} (see Fig. 1).

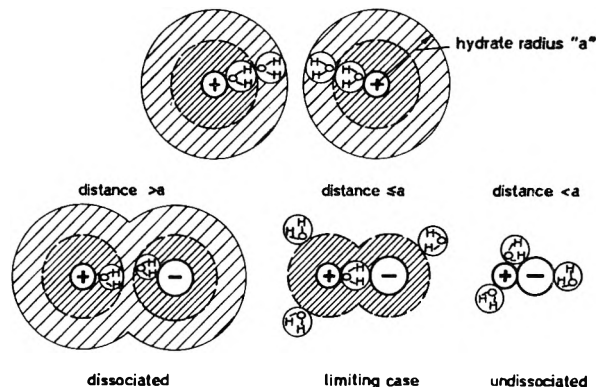


Fig. 1.—Models for steric interactions of equally and unequally charged, hydrated ions.

On the other hand the penetration of hydration shells of oppositely charged ions causes the formation of undissociated molecules. For these, a minimal distance of the free ions "*a*" may be introduced which includes the radii of the ions and the diameter of about one water layer. All distances $< a$ of free ions are assumed unstable, the coulombic and chemical forces then exceeding the hydration forces, and the residual water molecules between the ions will be displaced more or less completely. A possible hydration, remaining partially upon the formation of the ion pairs, depends presumably on special properties of the electrolyte in question, and thereby may cause characteristic differences in the behavior of homologous electrolytes. Even apart from the action of chemical forces, which then may become effective, the electrostatic interaction of two neighboring dehydrated ions still cannot be described by use of the macroscopic dielectric constant of water, in the way that is approximately valid for free ions at greater distances. Therefore it corresponds to a physical reality, to treat the ion-ion interactions in two separated steps: 1st, the electrostatic interaction of free ions with distances $\geq a$, due to the ionic atmosphere; 2nd, the electrostatic and chemical interactions of ion pairs with distances $< a$ (undissociated molecules). We will first deal with interactions of the first type.

3. Ionic Atmosphere and Distribution Formulas

In the theory of Debye and Hückel⁵ the calculation of the charge distribution in the ionic atmosphere is based on the well known Boltzmann formula

$$N_r/n^\pm = \exp \mp (z_0 e \psi(r)/kT) \quad (3-1)$$

with n_r = number of ions/cm.³ in the distance r from a positive central ion, n^\pm = average number of ions/cm.³ in the solution (in the distance ∞ from the central ion), z_0 = ionic charge (z taken as absolute value) $\psi(r)$ = electrostatic potential, (at the distance r from the central ion), k = Boltz-

(4) E. Wicke and M. Eigen, *Naturwissenschaften*, **38**, 456 (1951); (b) *Z. Elektrochem.*, **56**, 551 (1952); (c) *Z. Naturforsch.*, **8a**, 161 (1953); (d) *Z. Elektrochem.*, **57**, 219 (1953).

(5) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(6) A. Eucken, *Z. Elektrochem.*, **51**, 6 (1948).

(7) M. Eigen and E. Wicke, *ibid.*, **55**, 354 (1951).

(8) See ref. 42.

(9) M. Eigen, *Z. physik. Chem.*, "Neue Folge," **1**, 176 (1954).

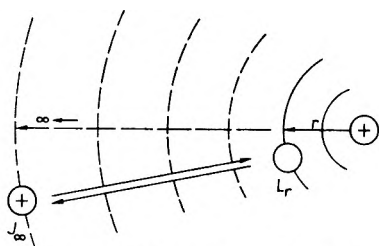


Fig. 2.—Illustration of the exchange equilibrium eq. 3-2.

mann constant, and T = absolute temperature. The assumption made in this formula, *i.e.*, treating the ions as mathematical points, limits the application to low concentrations only. At higher concentrations, however, the influence of finite ionic volumes becomes more effective. Calculations, in which a finite ionic radius of the central ions is introduced by the boundary conditions of the Poisson-Boltzmann equation, can only describe the experimental results in a limited concentration range.¹⁰ Starting from such considerations we have shown in the above mentioned papers that it is possible to extend the Debye-Hückel theory up to higher concentrations by replacing the supposition of the theory, the Boltzmann expression (3-1), by another distribution formula in which the hydration and volume effects are more rigorously taken into consideration.¹¹ Our idea may briefly be characterized as follows.

While in the Boltzmann distribution each ion has practically unlimited possibilities for arranging, this is not possible for particles of finite size. For these only a limited number of "places" is available, being either occupied or not. The calculation of the distribution of hydrated ions and ion places may be carried out in a manner analogous to that used in adsorption statistics (Langmuir formula),¹² or to Eucken's treatment of hydration shells.⁶ The problem is also similar to that of separation of a two-component fluid in the ultracentrifuge, which was treated by Pedersen.¹³ With respect to the model referred to in the preceding section, two cases of ion distribution are of special interest: 1st, all ions require a rigid exclusion volume of equal extension; 2nd, the hydration shells are penetrable for oppositely charged ions, only ions with charges of like sign being displaced. The real behavior of the ions in solution will be between these two limiting cases; for strongly hydrated ions the second case seems to be better approximated according to our experiences. For this case the distribution formula reads

$$\frac{n_r}{n_{\pm}} \times \frac{N^{\pm} - n_{\pm}}{N - n_r} = \exp \mp (ze_0\psi(r)/kT) \quad (3-2)$$

(10) For details see ref. 3.

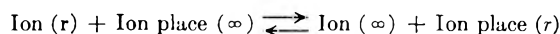
(11) Another formula, derived by a "Fermi-Dirac method" was proposed by Dutta and Bagchi (*Indian J. Phys.*, **24**, 61 (1950)), who were the first, substituting the Boltzmann formula by another one. Bagchi (*J. Indian Chem. Soc.*, **27**, 170 (1950)) applied the model to calculations of activity coefficients. The physical basis of this model and its results do not agree with ours. However, new interpretations of the suppositions involved in the theory, and modifications in the ion-distribution formula, as pointed out in later papers by Dutta (*Naturwiss.*, **39**, 108 (1952)) and Bagchi (*ibid.*, **39**, 299 (1952); *Z. Elektrochem.*, **57**, 138 (1953)), are tending to our developments. (*Z. Elektrochem.*, **57**, 140 (1953); *Naturwiss.*, **39**, 108 (1952)).

(12) See also G. Damköhler, *Z. physik. Chem.*, **B23**, 58 (1933).

(13) K. O. Pedersen; *ibid.*, **A170**, 41 (1943).

where N^{\pm} is the number of possible "sites" (ion-places) per cm.³, corresponding to the reciprocal volume of the hydrated ion ($N^+ = 1/v^+$; $N^- = 1/v^-$).

Equation (3-2), written in this form, already shows the physical content involved. In contrast to equation (3-1), the quantity n_r/n_{\pm} in expression (3-2) is multiplied by a quotient containing the number of vacant "sites" per cm.³ at the distances r and ∞ from the central ion. This factor means that we have an equilibrium between the ions and vacant "sites" of the form (see Fig. 2)



to which the law of mass action may be applied, with $ze_0\psi(r)$ representing the free energy of the exchange reaction. A more detailed and rigorous statistical and thermodynamical treatment of this problem, only indicated here, is given in the above mentioned paper.^{4b}

In the other case, *i.e.*, when particles of equal size without mutual penetration are supposed, the factor representing the concentrations of vacant "sites" contains the concentrations of the counter ions too. Then the distribution is given by

$$\frac{n_r}{n_{\pm}} \times \frac{(N - n^+ - n^-)}{(N - n_r^+ - n_r^-)} = \exp \mp (ze_0\psi(r)/kT)$$

The application of this formula yields for the charge density in the ionic atmosphere around the central ion (with $z^+ = z^-$; $n^+ = n^- = n$)

$$\bar{\rho}_e(r) = -2nze_0 \frac{\sinh(ze_0\psi(r)/kT)}{1 + 2n/N [\cosh(ze_0\psi(r)/kT) - 1]} \quad (3-4)$$

while use of formula (3-2) leads to

$$\bar{\rho}_e(r) = -2nze_0 \frac{(1 - n/N) \sinh(ze_0\psi(r)/kT)}{1 + 2n/N(1 - n/N) [\cosh(ze_0\psi(r)/kT) - 1]} \quad (3-5)$$

At higher concentrations and potentials these expressions differ evidently from that used by Debye and Hückel

$$\bar{\rho}_e(r) = -2nze_0 \sinh(ze_0\psi(r)/kT) \quad (3-6)$$

This is illustrated by Fig. 3. The charge density

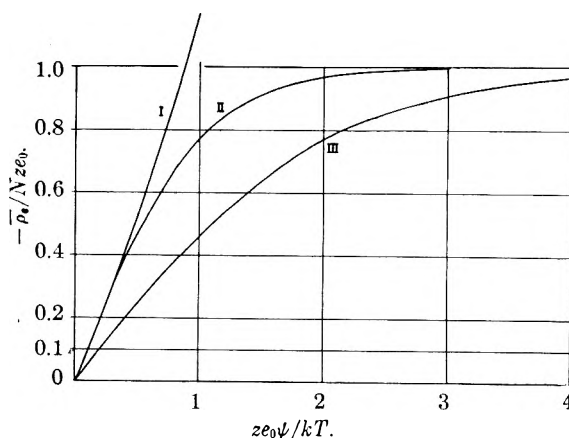


Fig. 3.—I, exponential course according to eq. 3-6; II, according to eq. 3-4; and III, according to eq. 3-5, both with $n/N = 1/2$ (satn.); where eq. 3-4 is $\bar{\rho}_e(r) = -Nze_0 \tanh(ze_0\psi(r)/kT)$ and eq. 3-5 is $\bar{\rho}_e(r) = -Nze_0 \tanh(ze_0\psi(r)/2kT)$.

according to equations (3-4) and (3-5) does not become infinite for $ze_0\psi(r) \gg kT$ as that given by (3-6), but reaches a saturation value, in which the ions are arranged compactly, containing nearly all water molecules in their hydration shells.

For $ze_0\psi(r) \ll kT$, deviations from the expansion of the Boltzmann exponential (3-6) occur for equation (3-5) already in the first-order term. One obtains

$$\bar{\rho}_e(r) = -\frac{e_0^2\psi(r)}{kT} \sum_{+-} z_i^2 n_i \left(1 - \frac{n_i}{N_i}\right) \quad (3-7)$$

This expression will be used in our calculations, for, with respect to hydrate radii of about 4, 5 Å. and more, the condition $ze_0\psi(r) \ll kT$ is realized in general. For rigid complexes of equal size, deviations from the expansion of equation (3-6) appear only in higher terms. However, the supposition of equal space requirement of positive and negative ions, which is not necessary in the case of mutual penetration, is very limiting. In general one has to take into consideration differing space requirements of anions and cations, particularly for applications to colloid problems, for which these formulas may become useful. Calculations of this type have been carried out by Freise¹⁴ and, parallel to him, by Schlögl.¹⁵ Freise treated the problem of the electrical double layer and calculated by a thermodynamical method a generalized distribution formula, in which a different space requirement of anions and cations is considered and, in addition, the ion places or "sites" are interpreted as solvent particles or associates. This formula has also been derived for the general case of several different particle sorts, using a statistical method, by Schlögl, who discussed some very interesting applications. The influence of the unequal size of ions and solvent molecules in the charge distribution of the diffuse double layer is shown by Fig. 4. If the ionic volumes are unequal, deviations from the Boltzmann distribution, used by Gouy and Chapman¹⁶ for the diffuse double layer, occur already in the first order term. Here also the most striking difference with respect to the Boltzmann distribution consists of the saturation value analogous to a "Stern double layer."¹⁷ For ions of equal space requirement, as supposed in our respective calculations, the formulas of Freise and Schlögl agree with eq. (3-3).

Another generalization of the distribution formula (3-3) was proposed by Falkenhagen and Kelbg.¹⁸ These authors, too, treated the problem of several particle sorts, but their calculation agrees with that of Schlögl, Freise and ourselves only for the case of equal space requirement of all particle sorts. As stated above the problem of ionic interactions in strong electrolytic solutions may be treated most successfully on the basis of the model represented by distribution formula (3-2). This model seems to be suited to render the essential features of the hydration influence on the ionic

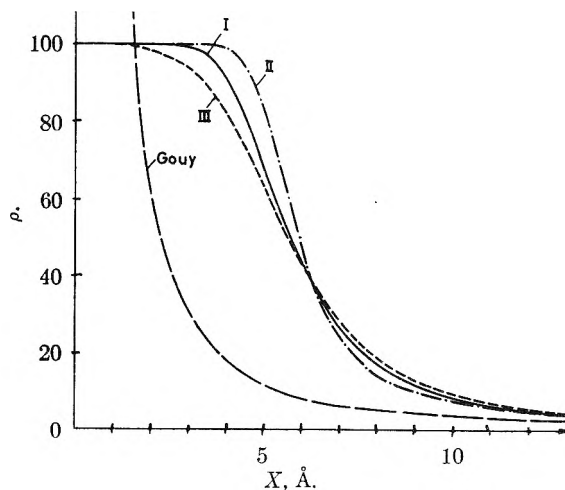


Fig. 4.—Charge density in the diffuse double layer, comparison of Freise's¹² calculations: I, $v_+ = v_- = v_{soliv}$; II, $v_{ions} = 0.5v_{soliv}$; III, $v_{ions} = 2v_{soliv}$, with the exponential course of Gouy and Chapman¹⁴ (Boltzmann distribution).

interactions and, therefore, to approximate the real situation, especially in cases of strongly hydrated ions.

4. Thermodynamic Functions

(a) **Complete Dissociation.**—The calculation of the electrostatic part of the free energy $\Delta_e f$ has been carried out according to Debye and Hückel by solving the Poisson-Boltzmann equation with suitable boundary conditions and applying the Debye charging process, leading to

$$\Delta_e f = -n \frac{\kappa' Q}{\epsilon} \times \sum_{+-} z_i^2 \nu_i \epsilon_0^2 \quad (4-1)$$

with

n = number of electrolyte molecules per cm.³, dissociated into ν^+ cations and ν^- anions ($n = N_{LC}/1000$, N_L = Avogadro's number) and c = electrolyte concn. in moles/l.

ϵ = dielectric constant of the solvent

z_i = valency of the ion sort i

$Q = |\ln(1 + a\kappa') - a\kappa' + (a\kappa')^2/2| / (a\kappa')^3$

a = mean hydration radius (see section 2)

$$\kappa' = \left[\frac{4\pi e_0^2}{\epsilon kT} n \left(1 - \frac{n}{N}\right) \sum_{+-} z_i^2 \nu_i \right]^{1/2} = \kappa (1 - n/\bar{N})^{1/2}$$

where

$1/\kappa$ = radius of the ionic atmosphere after Debye and Hückel

$$1/\bar{N} = \frac{\sum z_i \nu_i}{\sum z_i} \bar{v} \quad \text{where } \bar{v} = \frac{1}{2} \left[\frac{1}{N^+} + \frac{1}{N^-} \right]$$

= the mean hydration volume of positive and negative ions

Corrections for the higher terms in the expansion of exponential—according to Gronwall, La Mer and Sandved¹⁹—do not essentially influence this expression of the free energy, if hydration radii of 4 Å. and more are supposed.

Equation (4-1) differs from the corresponding expression, used by Debye and Hückel, in the presence of the additional factor $(1 - n/\bar{N})$ in κ' , which produces a minimum in the concentration dependence. According to our model of mutual penetration of the hydration spheres of oppositely charged ions (Fig. 1) the "distance of closest approach"

(19) T. H. Gronwall, V. K. La Mer and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

(14) V. Freise, *Z. Elektrochem.*, **56**, 822 (1952).

(15) R. Schlögl, *Z. physik. Chem.*, **202**, 379 (1954).

(16) G. Gouy, *Ann. Phys.*, **7**, 129 (1917); D. L. Chapman, *Phil. Mag.*, 475 (1913).

(17) O. Stern, *Z. Elektrochem.*, **30**, 22 (1924); see also Bikermann, *Phil. Mag.*, **33**, 383 (1942).

(18) H. Falkenhagen and G. Kelbg, *Ann. Phys.*, **11**, 60 (1952).

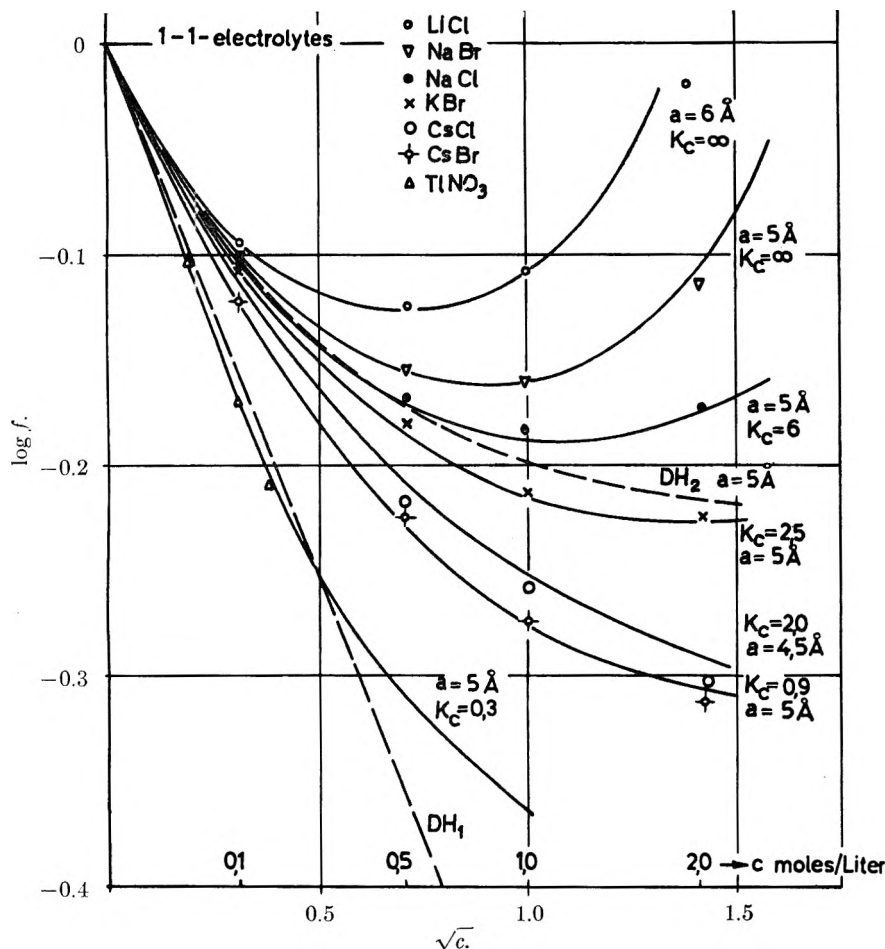


Fig. 5.—Mean activity coefficients of 1-1 electrolytes at 25°: full lines calcd. by eq. 4-3 or 4-12; dashed lines, DH_1 = limiting law (Debye-Hückel), DH_2 = Debye-Hückel second approx. with $a = 5 \text{ \AA}$.

between the central and counter ions, "a," may be connected with the hydration radius, determining the steric interactions in the ionic atmosphere, by the "approximate relationship"

$$\bar{v} = 4/3 \pi a^3 \quad (4-2)$$

"a" is then the only disposable constant in equation (4-1). From expression (4-1) some well-known thermodynamic functions—suitable for comparison with experiment—may be obtained by simple differentiation processes as follows.

1st, the differentiation with respect to the stoichiometric concentrations of the ions n_i yields the chemical potential and the activity coefficient \bar{f} of the completely dissociated electrolyte. We obtain

$$n\bar{f}/n\bar{f}_1 = \kappa/\kappa' \left(1 - \frac{2n}{\bar{N}}\right) \cdot [1/(1 + a\kappa') - 2Q] + 2Q \kappa'/\kappa \quad (4-3)$$

where

$$\ln \bar{f}_1 = -z_+ z_- e_0^2 \kappa / 2ekT \quad (4-4)$$

is the limiting law value of the Debye-Hückel theory.

Equation (4-3) shows—if "a"-values of about 4.5-6 Å. are chosen—the characteristic feature of the concentration dependence of completely dissociated electrolytes at higher concentrations: the minimum and the subsequent rise above unity.

This is represented for some 1-1, 1-2, 1-3 and 2-2 electrolytes in Figs. 5-8 (see below). Examples for nearly complete dissociation are hydrochloric acid, Li halides, MgCl₂ and others. The experimental values for activity coefficients of these electrolytes are well reproduced by expression (4-3).

2nd: The differentiation of $\Delta_e f/T$ with $1/T$ leads to the "integral heat of dilution" W^e . For a completely dissociated electrolyte the calculation yields

$$\begin{aligned} W^e &= -T^2 \left(\frac{\partial \Delta_e f/T}{\partial T} \right) \frac{N_+}{n} \\ &= \frac{W_{e1} \kappa'}{\varphi \kappa} \left\{ \frac{\varphi}{1 + a\kappa'} - \left(\frac{2}{1 + a\kappa'} - 6Q \right) \frac{\partial \ln a}{\partial \ln T} - \frac{n/\bar{N}}{1 - n/\bar{N}} \left(\frac{1}{1 + a\kappa'} - 2Q \right) \frac{\partial \ln \bar{N}}{\partial \ln T} \right\} \quad (4-5) \end{aligned}$$

with

$$\varphi = 1 + \frac{\partial \ln \epsilon}{\partial \ln T} \approx -0.37$$

for water at 25°, following Wyman²⁰

and the limiting law value $W_{e1,21}$

$$W_{e1} = -N_L / \sum_{+-} z_i^2 e_0^2 \frac{\kappa \varphi}{2\epsilon} \quad (4-6)$$

In addition to "a," expression (4-5) contains as disposable parameters the differential quotients $\partial \ln a / \partial \ln T$ and $\partial \ln \bar{N} / \partial \ln T \equiv N'$; these may be estimated with sufficient accuracy from the above mentioned experimental determinations of the temperature dependence of apparent molar functions at infinite dilution.²² The concentration dependence of the heat of dilution of a completely dissociated electrolyte according to equation (4-5), shown in Fig. 9, is found to agree better with experimental data (e.g., LiBr) of Lange and Robinson²³ at higher concentrations than that calculated by Lange and Meixner²⁴ on the basis of the Debye-Hückel theory.

(20) J. Wyman, *Phys. Rev.*, **35**, 623 (1930).

(21) E. Lange, *Fortschr. Chem., Phys. physikal. Chem.*, **19**, 6 (1928). For a calculation of eq. (4-5) see also E. Lange and K. Möhring, *Z. Elektrochem.*, **56**, 927 (1952).

(22) The connection between a and \bar{N} according to equation (4-2) is not suitable for the temperature dependence of these values; the variation of the distance "a" with temperature is only very small according to the small temperature dependence of the interior hydration layers (see Fig. 1), while the variation of \bar{N} , which is essentially determined by the temperature dependence of the exterior hydration layers is in general quite considerable (5). The values for $\partial \ln \bar{N} / \partial \ln T \equiv N'$, estimated from experiments, are quoted in Fig. 9.

(23) E. Lange and A. L. Robinson, *Chem. Revs.*, **9**, 89 (1931).

(24) E. Lange and J. Meixner, *Physik Z.*, **30**, 670 (1929).

3rd: The third possibility for testing the theory is given by the second differential quotient ($\partial^2 \Delta_e f / \partial T^2$), leading to the concentration dependent part of the apparent molar heat capacity,²⁶ for which we obtain

$$\Delta^e \bar{C}_p = -T \left(\frac{\partial^2 \Delta_e f}{\partial T^2} \right)_p \frac{N_i}{n} = \Delta_i \bar{C}_p \times \frac{W^e}{W^{e_1}} + W^{e_1} \left(\frac{\partial W^e / W^{e_1}}{\partial T} \right)_p \quad (4-7)$$

with the "limiting law heat capacity"

$$\Delta_i \bar{C}_p \approx 3.13 \left(\sum_{+,-} z_i^2 \nu_i \right)^{1/2} \sqrt{c}, \text{ cal./deg. mole} \quad (4-8)$$

which was first derived by La Mer and Cowperthwaite²⁶ (neglecting the difference between free energy and free enthalpy) and also discussed in detail by Gucker.²⁷ The second term on the right hand side of equation (4-7) is in general negligible with respect to the other term, as shown by a numerical estimation^{4d} (even by use of extreme values of the less exactly known differential quotient $\partial^2 \bar{N} / \partial T^2$). The influence of this term lies in any case within the limits of error of the experimental values of the apparent molar heat capacities, which amount to about ± 1 cal./deg. mole. Therefore we have approximately

$$\Delta^e \bar{C}_p \approx \Delta_i \bar{C}_p (W^e / W^{e_1}) \quad (4-9)$$

and the concentration dependence of $\Delta^e \bar{C}_p$ becomes similar to that of W^e , represented by equation (4-5). This means for concentrations above 0.5 *m*, within the error limits of about ± 1 cal./deg. mole, a course nearly proportional to \sqrt{c} . The declination of this curve, however, is smaller than that of the limiting law. This is represented in Fig. 10; the calculations with eq. (4-9) fit the experimental data^{7,27,28} for LiCl and LiBr.

Analogous treatment with respect to the pressure derivatives, resulting in the apparent molar volumes²⁹ and compressibilities,³⁰ leads to expressions which are very similar to those above considered ($\partial / \partial T$ to be substituted by $\partial / \partial p$).

The calculations of the three thermodynamic functions, starting from the uniform basis of eq. (4-1), have shown that there exists a group of electrolytes for which, in all three cases, agreement with the experimental data up to relatively high concentrations is obtained, and for which therefore the supposition of complete dissociation may be justified. An essential feature of the model, used in these calculations (for instance in the case of LiCl), consists in the different steric interaction of the ions of like and unlike sign. The anions and cations approach each other only to a distance "a," in which they still keep their interior

(25) We note that the apparent molar heat capacity consists of two parts of which one is independent of concentration. This part ($\Delta_0 \bar{C}_p$) describes the ion-solvent interactions at infinite dilution as mentioned in the second section (cf. ref. 7). We will here engage the second (concentration dependent), in the ionic interaction part only.

(26) V. K. La Mer and I. A. Cowperthwaite, *J. Am. Chem. Soc.*, **55**, 1004 (1933).

(27) F. T. Gucker, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 680 (1949).

(28) M. Randall and F. D. Rossini, *J. Am. Chem. Soc.*, **51**, 1004 (1933).

(29) O. Redlich and P. Rosenfeld, *Z. physik. Chem.*, **A155**, 65 (1931).

(30) Ch. Bachem and H. Falkenhagen, *Z. Elektrochem.*, **41**, 570 (1935).

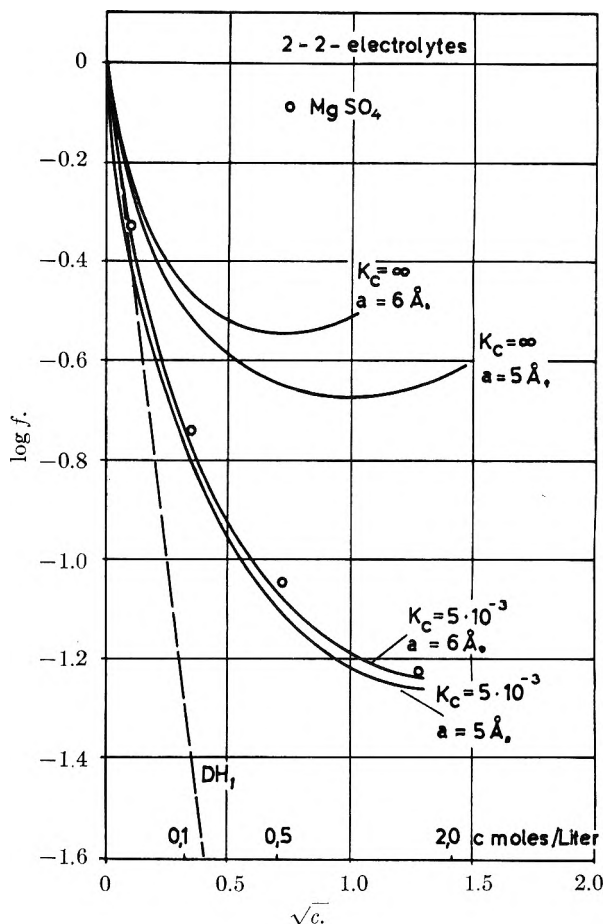


Fig. 6.—Mean activity coefficients of 2-2 electrolytes at 25° (see Fig. 5).

hydration layers (distance 6 Å.). The electrolyte can therefore be termed as "completely dissociated" (see Fig. 1). This steric interaction, however, influences the "vacant site factor" in the distribution formula only unimportantly with respect to the "exclusion" of the hydrate spheres of equally charged ions, for which the whole hydration sphere, being especially rigid through the electrical repulsions, has to be taken into account (radius 6 Å.).

(b) **Incomplete Dissociation.**—In the numerical calculation of activity coefficients, the individual behavior of the different electrolytes may be described by variation of the parameter "a." This, however, is only successful, if we permit the "a" values to vary from 1 Å. or less up to about 6 Å. The resulting ionic or hydration volumes would then vary over several orders of magnitude—rather in contrast to all conventional hydration models. This contrast becomes still more striking in the treatment of the heats of dilution, of which none of the negative values which are observed for some electrolytes at higher concentrations can be described by changing the "a"—parameter, or by other corrections in the electrostatic term. For these and other reasons, we have introduced the additional assumption of incomplete dissociation, as already suggested by Nernst,³¹ Onsager,³² Fuoss

(31) W. Nernst and W. Orthmann, *Z. physik. Chem.*, **135**, 199 (1928).

(32) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

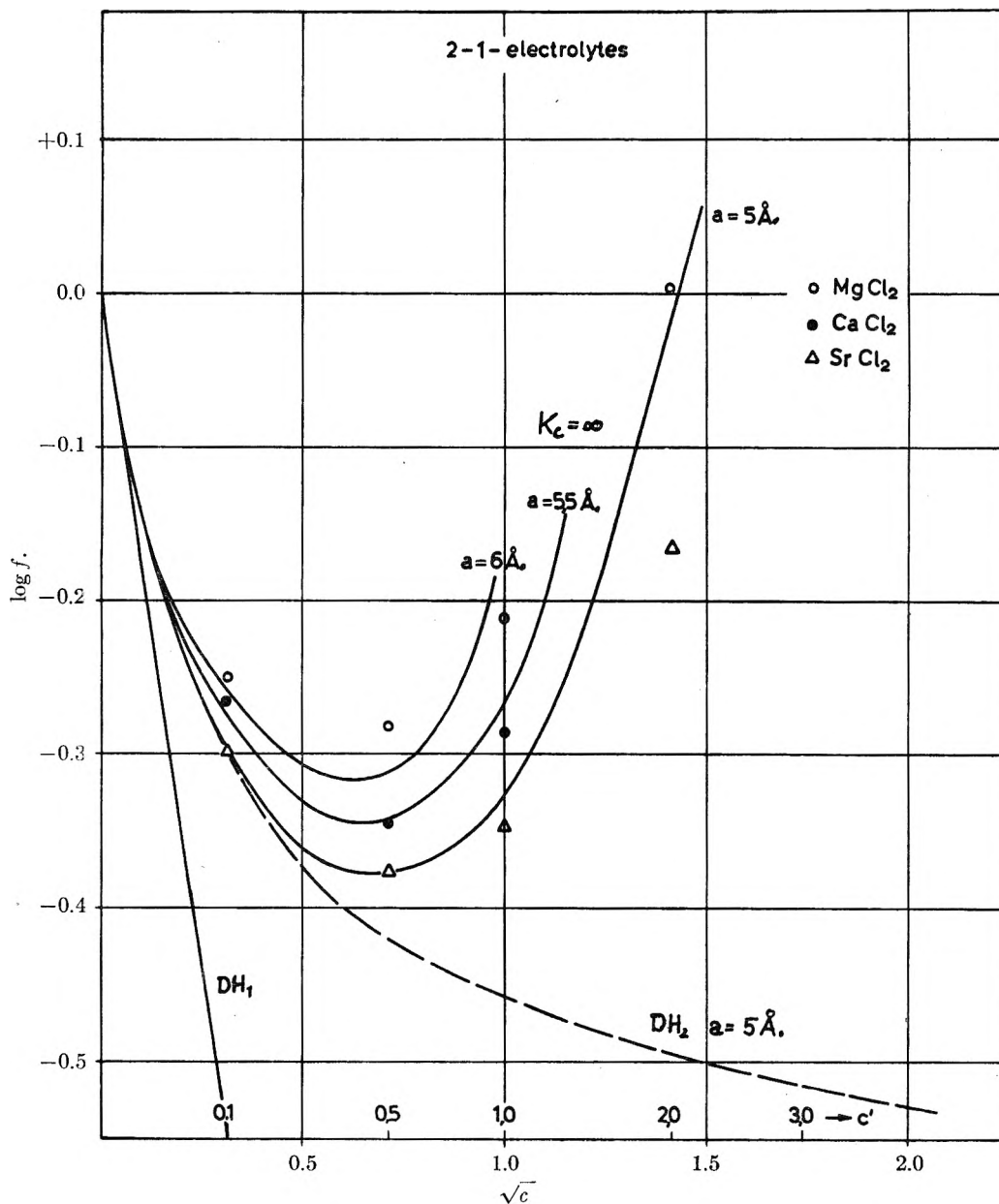


Fig. 7.—Mean activity coefficients of 2-1 electrolytes at 25° (see Fig. 5).

and Kraus³³ and others. The quantity characteristic of this second kind of ionic interactions is the degree of dissociation, α , defined by the law of mass action

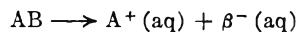
$$\frac{\alpha^2 \bar{f}^2}{(1-\alpha)} = K_e \quad (4-10)$$

Where \bar{f} is the mean activity coefficient according to eq. (4-3), which is to be modified by using the "true" ionic concentrations αc instead of c . K_e stands for the dissociation constant, which is connected with the heat of dissociation D_∞ by the well known Van't Hoff relation

$$\frac{\partial \ln K_e}{\partial T} = \frac{D_\infty}{RT^2} \quad (4-11)$$

(D_∞ is the enthalpy for $c \rightarrow 0$ of the reaction

(33) R. M. Fuoss and Ch. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476, 2387, 3614 (1933) (cf. ref. 1.).



producing two ions of the same valency (these considerations are restricted to this case). K_e and D_∞ are two new empirical constants, for which we have to choose suitable values. The arbitrariness of these choices is rather restricted by the condition that we must fit three different experimental curves with one set of constants.

The more detailed calculations are already communicated in a previous paper.^{4d} Here we will briefly deal with the results only, and give an account of the additional terms occurring in the thermodynamic functions considered above.

1st: In case of an incompletely dissociated electrolyte the expression (4-3) for the mean activity coefficient \bar{f} is to be completed by the term $\ln \alpha$. Thus we have

$$\ln \bar{f}_\alpha = \ln (\alpha \bar{f}) \quad (4-12)$$

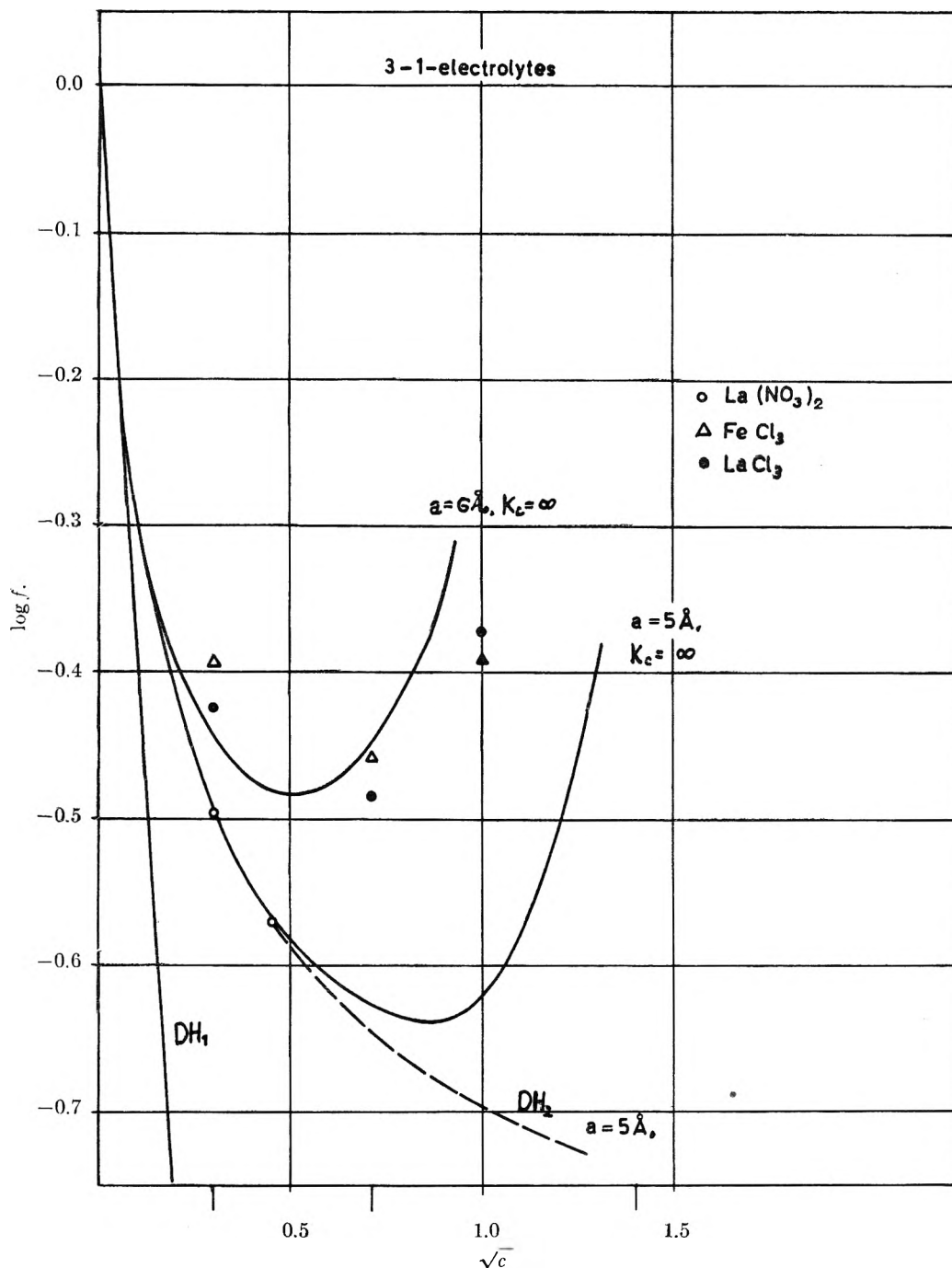


Fig. 8.—Mean activity coefficients of 3-1 electrolytes at 25° (see Fig. 5).

with α according to eq. (4-10) and \bar{f} being a function of (αc) instead of c . Measurements with the various methods lead directly to the quantity f_α .

2nd: For the heat of dilution we find the extra term $\Delta_\alpha W = -(1 - \alpha)D_\infty$ in addition to the electrostatic part W^e according to eq. (4-5) which is now also a function of (αc)

$$W_\alpha^e = \alpha W^e - (1 - \alpha)D_\infty \quad (4-13)$$

3rd: For the apparent molar heat capacity, two additional terms have to be taken into account

$$\Delta_\alpha \bar{C}_p = D_\infty (\partial \alpha / \partial T)_p - (1 - \alpha) (\partial D_\infty / \partial T)_p \quad (4-14)$$

but the numerical calculation shows that the second term is negligible within the above-mentioned limits

of error. The first term reads explicitly

$$\Delta_\alpha \bar{C}_p \approx G(\alpha) \times \frac{D_\infty^2}{RT^2} \quad (4-15)$$

with

$$D_c = D_\infty - 2RT^2 (\partial \ln \bar{f} / \partial T)_p$$

the heat of dissociation at the concentration c (in general $\approx D_\infty$) and $G(\alpha) = \alpha(1 - \alpha) / 1 + (1 - \alpha)$. The complete concentration-dependent part of the apparent molar heat capacity then becomes

$$\Delta_\alpha \bar{C}_p = \alpha \Delta^\circ \bar{C}_p + \Delta_\alpha \bar{C}_p \quad (4-16)$$

An analogous expression is obtained for the influence of dissociation on the isothermal compressibility of the solution

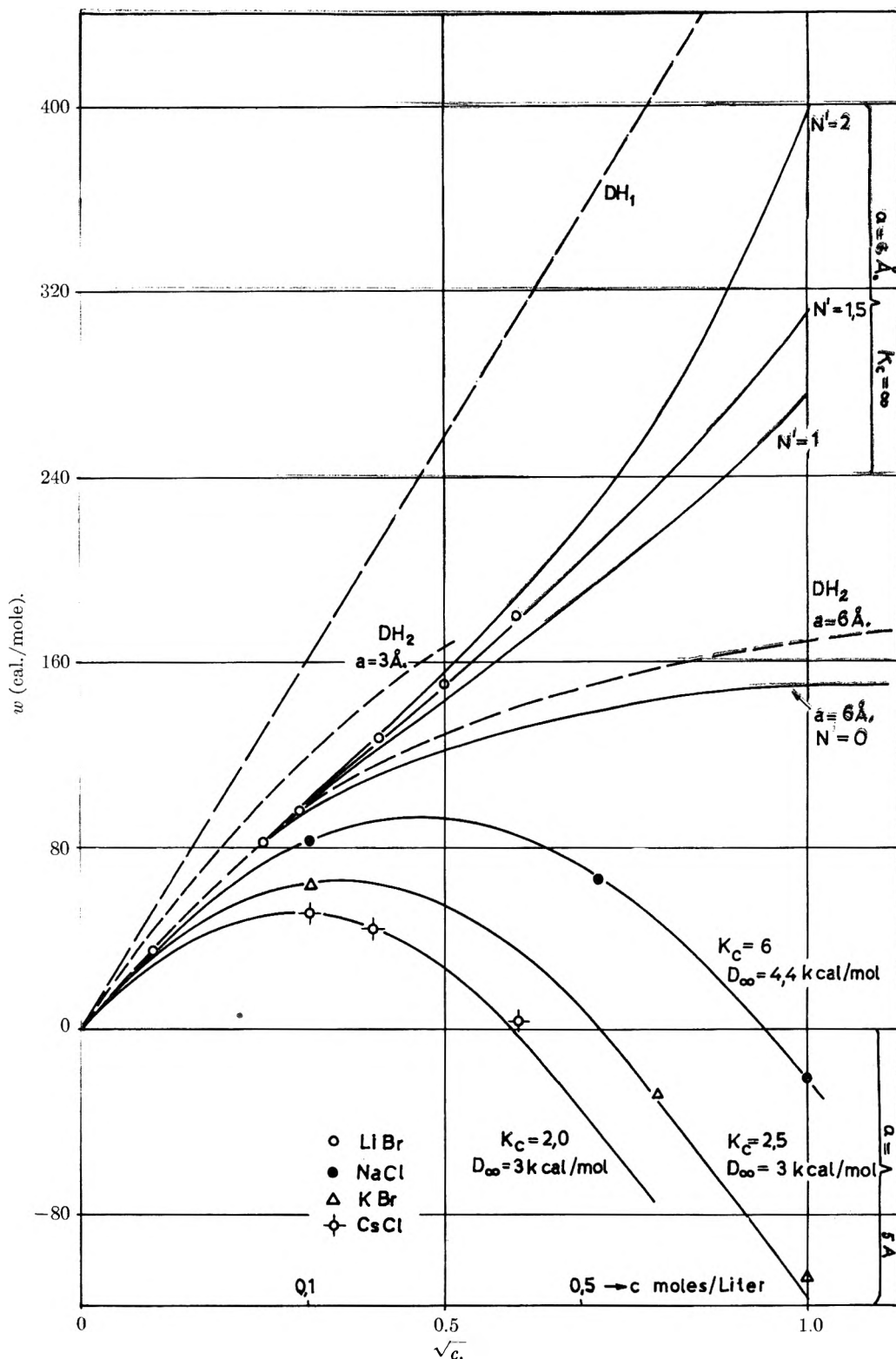


Fig. 9.—Integral heat to dilution of 1-1 electrolytes at 25°: full lines are course according to eq. 4-5 or 4-13; dashed lines according to Debye-Hückel theory,²³ exptl. values in ref. 21.

$$\Delta_{\alpha\beta T} = \frac{n}{N_L} \times G(\alpha) \times \frac{(\Delta V_c)^2}{RT} \quad (4-17)$$

where ΔV_c represents the difference of partial molar volumes analogous to the above-mentioned enthalpy difference D_c . We come back to this

expression in the following section because this quantity, occurring in the expression for the sound absorption of an incompletely dissociated electrolyte, gives the possibility of determining the dissociation part independently from the other ionic and solvent interaction terms.

(c) **Discussion of the Results.**—The numerical evaluation of the above quoted formulas for the activity coefficients, heats of dilution and apparent molar heat capacities of incompletely dissociated electrolytes is represented by Figs. 5–10. The limiting case of complete dissociation with $K_c \rightarrow \infty$ has already been discussed in Section 4a. For the other cases the respective empirical constants are noted beside the curves.

Of particular interest with respect to the incomplete dissociation seems to be the activity coefficient of $MgSO_4$ (Fig. 6). The Debye-Hückel theory can also reproduce the experimental values by using essentially smaller “ a ”-parameters. On the other hand, our calculations lead to a term of incomplete dissociation, which agrees with results of Davies, and of Jones and Monk³⁴ and which we also have been able to confirm independently with the above-mentioned sound absorption method (see Section 5).

The experimental values of all three functions are well reproduced by one set of constants over a relatively wide concentration range. The “ a ” values differ only between 4.5 and 6 Å. and are not in contrast to the usual conceptions of the hydration of atom ions. The values of K_c (see in Table I) and D_∞ may be taken only as orders of magnitude with respect to the very crude model, used in the calculations. But they enable us to explain especially the negative heats of dilution which are a characteristic phenomenon of incomplete dissociation, which cannot be explained by the “electrostatic” or “exclusion” effects.

TABLE I

DEGREES OF DISSOCIATION OF SOME z - z ELECTROLYTES IN AQUEOUS SOLUTION AT 20°

Concn. moles/l.	0.01	0.1	1	K_c , moles/l.
NaCl	1.0	0.99	0.93	6
KBr	1.0	0.98	0.86	2.5
CsBr	0.99	0.94	0.69	0.9
TiNO ₃	0.97	0.85	0.47	0.3
MgSO ₄	0.63	0.36	0.20	0.005

Furthermore the calculations with reference to the incomplete dissociation reproduce the $\Delta_e \bar{C}_p$ curves of the apparent molar heat capacities at higher concentrations^{7,27,28} which were hitherto hardly to be understood theoretically. For degrees of dissociation nearly equal to unity, which are realized in the case of the above-mentioned 1-1

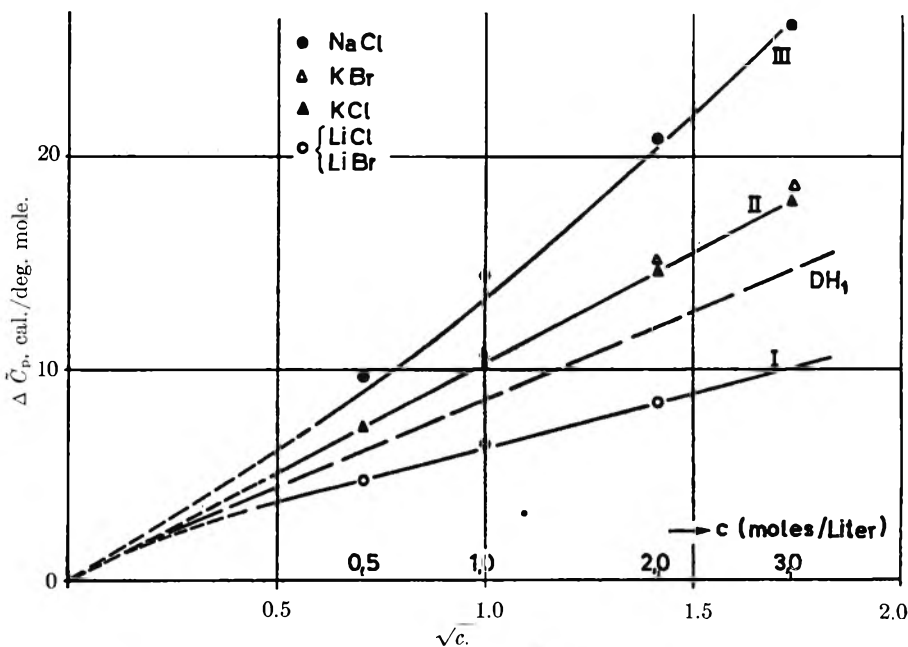


Fig. 10.—Concentration dependence of apparent molar heat capacity of 1-1 electrolytes at 25°: full lines are I, calcd. for complete dissoen. (eq. 4-9) with $a = 6 \text{ \AA.}$, $N' = 1.5$, $K_c = \infty$; II and III calcd. for incomplete dissoen. (eq. 4-16) with $a = 5 \text{ \AA.}$ and $N' = 1.5$ (II, $K_c = 2.5$, $D_\infty = 3.0 \text{ kcal./mole}$, III, $K_c = 6$, $D_\infty = 4.4 \text{ kcal./mole}$). Dashed line shows the limiting law. For exptl. values see refs. 7, 26, 27. The respective $\Delta_0 \bar{C}_p$ values are: LiBr, -20; NaCl, -23; KCl, -28; KBr, -29 cal./deg. mole.

salts (see Table 1), the additional term is nearly proportional to \sqrt{c} (see Fig. 11) and is responsible for the individual \sqrt{c} dependence of the apparent molar heat capacity of these salts. For smaller dissociation constants, as in the case of metal sulfates, the dissociation term goes through a maximum at $\alpha \approx 50\%$ according to the quantity $G(\alpha)$ in equation (4-15). This theoretically predictable fact seems to be realized for these types of electrolytes as shown by Fig. 12, in which experimental values for $ZnSO_4$, obtained by La Mer and Cowperthwaite²⁶ are plotted against \sqrt{c} . This really is the course to be expected from equation (4-16).

The foregoing treatment of ion-ion interactions, based on the two additional hypotheses, *i.e.*, the hydrate volume “exclusion” and incomplete dissociation, seems to be suited to render the essential features of the thermodynamic functions of electrolytes at higher concentrations. Apart from some simplifications, made in the theory and justified partly by respective numerical estimations, the results are obtained by use of three constants, which are sufficient to fit at least three different experimental curves of any electrolyte. This seems to indicate that our assumptions and models, in spite of their rather crude nature, correspond to real phenomena, at least qualitatively. But it does not mean that our considerations comprehend all influences occurring at higher concentrations, or that our method of treating the different effects is the only possible one. In this connection we remark developments by Bjerrum³⁵ and by Stokes and Robinson,³⁶ who considered a direct influence

(35) N. Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

(36) R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, **70**, 1871 (1948).

(34) C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927); H. W. Jones and C. B. Monk, *ibid.*, **48**, 929 (1952).

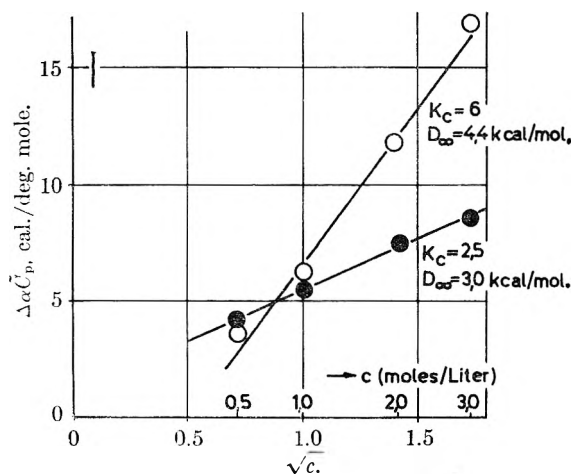


Fig. 11.—Calcd. values of disson. term $\Delta\alpha\bar{C}_p$, eq. 4-1, in this case \sqrt{c} dependence.

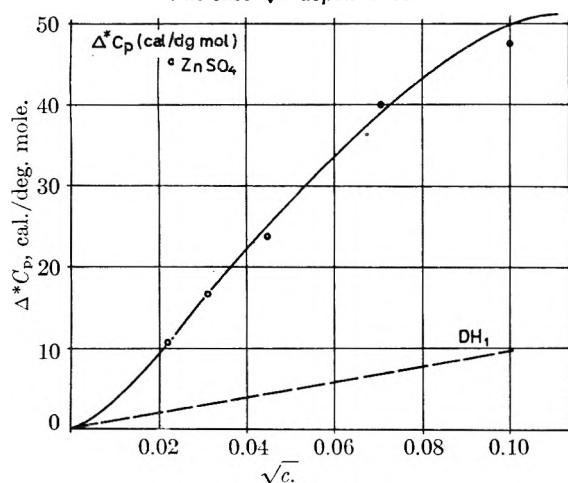


Fig. 12.—Concn. dependence of partial molar heat capacity Δ^*C_p of $ZnSO_4$: full line exptl. curve²⁴ corresponding to eq. 4-16; dash line, Debye-Hückel limiting law.

of hydration, and especially of Van Rysselberghe and Eisenberg,³⁷ Mayer,³⁸ Poirier,³⁹ and of Falkenhagen and Schmutzer,⁴⁰ who discuss a "co-volume" or "virial" influence of the hydrated ions in the solution like that of real gases. The reflections of these authors aim almost at the same effects as ours. Thus, in our model, additional influences of this kind are—though surely present—only of subordinate importance. The nature of our "co-volume" effect is for the prevailing part an electrostatic one, for this effect is determined essentially by the electrostatic and hydration interactions and not to be treated independently from the other electrostatic effects. Apart from this for the residual effect of a non-electrostatic "co-volume" of ions the situation is another and more compli-

(37) P. Van Rysselberghe and E. Eisenberg, *J. Am. Chem. Soc.*, **61**, 3030 (1939); **62**, 451 (1940).

(38) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

(39) J. C. Poirier, *ibid.*, **21**, 965-972 (1953).

(40) H. Falkenhagen and Schmutzer, *Naturwiss.*, **40**, 314, 602 (1953), who start from the distribution formula (3-3) (2b), modified for several particle sorts¹⁹ and calculate "co-volume" effect of an analogous gas from the pressure gradient on the wall of the vessel, or as another way—they start directly from the entropy term in the statistical calculation of the distribution formula (cf. ref. 4b: page 556, eq. 21 and 22.) The calculation of the activity coefficients by this method requires two empirical constants. The formula differs somewhat from ours, but describes the same physical effect in another way.

cated one than that of real gases. With respect to the more empirical calculations of Bjerrum, Robinson and Stokes it may be noted that the essential influence of water structure restricts itself to the molar thermodynamic properties at infinite dilution like that of $\Delta_0\bar{C}_p$ (see page 12 ref.²⁵). An essential influence beyond this occurs only at relatively high concentrations, for instance if competition of the ions for the H_2O molecules in the hydration shells comes into play. Another effect of this type may be the disturbance of the water structure (association equilibria), in this sense, reflections of Frank and Robinson⁴¹ may become interesting. They consider corresponding effects with respect to the entropy of dilution. Such refinements are not yet taken into account in our model, and it would be of some interest, what modifications would be necessary in the considerations of such effects.

5. Relaxation Effects

Our calculations in the preceding sections were restricted to reversible thermodynamic behavior and therefore to equilibrium effects only. On the other hand, for an extension of our considerations to irreversible phenomena the problem of the rate of attainment of equilibrium and of relaxation effects may become important. Therefore, it seems to be justified to make in closing some remarks on this problem, which leads us—in addition—to some interesting applications.

In our calculations three equilibria have been considered in detail: 1st, the equilibrium between ions and water molecules, *i.e.*, hydration equilibrium; 2nd, the equilibrium of distribution in the ionic atmosphere; 3rd, the dissociation equilibrium of the electrolyte. Information about the rate of attainment of the first equilibrium may be obtained from a study of the heat conductivity of water and aqueous solutions, as pointed out previously.⁴² Pure water shows an anomalous heat conductivity, arising from an additional structural part (transport of heat), analogous to that in dissociating gases. The theoretical treatment of these effects enables us to estimate the time required for formation or breaking of single hydrogen bonds in the liquid water, which is found to be 10^{-12} to $5 \cdot 10^{-13}$ sec. The time required for the orientation and disorientation of the exterior hydrate water molecules is of the same order of magnitude, while that required for the formation or dissociation of higher associates or of interior hydration bonds is essentially longer. No difficulties exist thereby for the water molecules in the exterior hydration layers to arrange themselves within times of the order of that required for normal position exchanges. Analogous conclusions result from models of the anomalous mobility of protons in water, for which the diffusion rate of a structure sphere (hydration shell) determines the mobility.⁴³

The rate of attainment of the second equilibrium mentioned above, the relaxation of the ionic atmosphere, is important in the electrical con-

(41) H. S. Frank and A. L. Robinson, *J. Chem. Phys.*, **8**, 933 (1940).

(42) M. Eigen, *Z. Elektrochem.*, **56**, 176, 836 (1952).

(43) E. Wicke, M. Eigen and Th. Ackermann, *Z. physik. Chem.* "Neue Folge," **1**, 340 (1954).

ductivity of electrolytes and appears most obviously in the "Debye Falkenhagen effect,"⁴⁴ the well known dispersion effect of electrical conductivity at high frequencies. According to Debye and Falkenhagen the relaxation time of this effect is given by

$$\theta = \frac{1}{2} \frac{\bar{\rho}}{kT\kappa^2} \quad (5-1)$$

with $\bar{\rho}$ being the mean frictional coefficient of the ions. Equation (5-1) becomes, *e.g.*, for KCl at 25°

$$\theta = \frac{0.273}{c} \times 10^{-10} \text{ sec.}$$

The introduction of the new distribution formulas (3-2) and (3-3) into the theory of Onsager,⁴⁵ Debye and Falkenhagen⁴⁴ does not influence this time lag, as shown by Falkenhagen, Kelbg and Leist.⁴⁶ But an influence exists for the expression of the electrical conductivity, and the consideration of this and of the radius effect of the central ions leads to a good agreement with experimental data up to concentrations of about 0.5-1 molar.⁴⁶

The time required for the attainment of the dissociation equilibrium $AB \xrightleftharpoons[k_2]{k_1} A^+ + B^-$, may be written

$$\tau = \frac{1}{k_1 + 2\alpha\kappa k_2} \quad (5-2)$$

the k 's being the conventional rate constants. If τ is essentially different from the relaxation time θ of the ionic atmosphere, then it may be possible to separate the two relaxation effects by suitable dispersion measurements. Suited for such measurements are, for instance, the 1st and 2nd Wien-effect,⁴⁷⁻⁵⁰ *i.e.*, the conductivity shift for strong and weak electrolytes at high electrical field densities. The "dispersion" of the dissociation field effect (2nd Wien-effect) was recently theoretically treated. Experiments of this type are under way and are described elsewhere.⁵¹

Another method—still more suitable—is the measurement of the above-mentioned sound absorption, which was discussed recently together with Tamm and Kurtze.⁵² The dissociation effect gives rise to a sound absorption term⁵³

$$\mu\alpha = 2\pi \frac{\omega\tau}{1 + \omega^2\tau^2} \frac{\Delta\alpha\beta_s}{\beta_0} \quad (5-3)$$

with $\omega = 2\pi\nu$, ν = frequency, τ = relaxation time $\Delta\alpha\beta_s$ = dissociation term of adiabatic compressibility

(44) P. Debye and K. Falkenhagen, *Physik. Z.*, **29**, 121, 401 (1928).

(45) L. Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

(46) H. Falkenhagen, M. Leist and G. Kelbg, *Ann. Phys.*, [6] **11**, 51 (1952).

(47) M. Wien, *ibid.*, **83** 327 (1927); **85**, 795 (1928); **1**, 408 (1929).

(48) M. Wien and J. Schiele, *Physik. Z.*, **32**, 545 (1931).

(49) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1933).

(50) D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.*, **62**, 2047 (1940).

(51) M. Eigen, *Disc. Faraday Soc.*, (1954).

(52) M. Eigen, G. Kurtze and K. Tamm, *Z. Elektrochem.*, **57**, 103 (1953). For the measurements see, G. Kurtze and K. Tamm, *Acustica Zurich*, **3**, 33 (1953); G. Kurtze, *Nachr. Ges. Wiss. Göttingen*, 57 (1952); K. Tamm, *ibid.*, 81 (1952).

(53) μ is defined by the exponential decrease of the energy density E , in a progressive plane sound wave: $E' = E'_0 \exp -(\mu d/\lambda)$, where d = distance in direction of propagation; λ = wavelength.

sibility and β_0 = adiabatic compressibility of the solution.⁵⁴

This term increases to a maximum at $\omega = 1/\tau$ which in many cases lies several orders of magnitude above that for the sound absorption of water or of solutions of completely dissociated electrolytes. The effect is well reproduced by eq. (5-3), especially too in cases of typically weak electrolytes (NH₃).⁹

In a different direction, the relaxation measurements, *i.e.*, the sound absorption, the dispersion of the dissociation field effect, and a corresponding temperature relaxation effect⁵⁰ give the possibility for a study of extremely fast ionic reactions in aqueous solutions (*e.g.*, of reactions with half times of 10⁻³ to 10⁻⁹ sec. such as neutralization, hydrolysis, and other ionic reactions),^{9,50} which cannot be followed with the conventional methods. Thus the consideration of the relaxation effects opens some further interesting aspects, in addition to the possibility for an independent proof of some of our above treated theoretical developments.

DISCUSSION

GEORGE SCATCHARD (Massachusetts Institute of Technology).—It is difficult to discuss this very interesting paper in a few words. The Eucken model of aqueous solutions, which pictures liquid water as composed of H₂O, (H₂O)₂, and (H₂O)₃, and (H₂O)_n, may be considered the antithesis of that by Debye, which pictures liquid water as a structureless medium characterized by its dielectric constant. The conclusions from either, except for the Debye-Hückel limiting law, may be expressed at least approximately in terms of the law of mass action. There are three types of interaction which I have described as ion-ion, ion-molecule and molecule-molecule.*

Eigen and Wicke are successful in representing approximately the behavior of salt solutions with only a few parameters, but it would take a more quantitative comparison to show that their approximation is closer for the halogen chlorides than one I made from the Debye picture† using the crystal radii of Pauling and only two other parameters for fifteen salts.

The treatment of Eigen and Wicke seems to me to have three difficulties which make the interpretation of the parameters uncertain. (1) At least in the rigid sphere approximation, the activity coefficients calculated are those of the ions as they exist in dilute solutions, that is, the hydrated ions, but they are compared with those of the anhydrous ion components. (2) Although the work of displacing the charged medium should be included in the electrostatic work, the statistics used for the case of unequal volumes seem seriously at fault in that the electrostatic interaction of two ions of the atmosphere is calculated as depending only on their distance from the central ion and not on their distance from each other. (3) Two ions held at a fixed distance will attract water between them much more strongly if their charges have the opposite sign than if they have the same sign. Any penetration of the hydration shells must be due to the competition of the stronger attraction between the two ions of opposite signs. This competition does not stop with one layer of water left between the ions.

I can sum up my position by quoting from an earlier review. "We may say that any truly satisfactory solution must wait a development that can express chemical action in precise physical terms and one that can treat a liquid taking into account the existence as molecules of every species present. . . . In the meantime progress will be made by developing different phases of the theory along different lines. It will be desirable to use every available method,

(54) The difference between adiabatic and isothermal compressibility can practically be neglected for aqueous solutions because of $(\partial T/\partial p)_s \approx 0$ in this case.

* G. Scatchard, *Chem. Rev.*, **13**, 7 (1953).

† G. Scatchard, *ibid.*, **19**, 309 (1936).

and this will lead to some confusion for it will be difficult to avoid counting the same effect twice as expressed in different terms."

M. EIGEN.—We agree with Professor Scatchard's opinion that our theoretical treatment is merely a provisional attempt on the way to a truly satisfactory solution of the problems in question. But, in spite of its rather crude nature, it seems to render the essential characteristic influences occurring at higher concentrations.

With respect to the three difficulties indicated by Prof. Scatchard, our treatment of these effects may be justified as follows:

First: The difference between activity coefficients of anhydrous and hydrated ion components has been considered by N. Bjerrum. But these considerations correspond to a hydration model of rigid, stoichiometric compounds (described by a change of the molar fraction of the water). The treatment according to our model can not use this correction, otherwise we would count the same effect twice.

It corresponds to our model to treat the hydration shells—with respect to the statistical exchange with free water molecules or associates—not as part of rigid, stoichiometric compounds with the ions, but only as a changed water structure in the surroundings of the ion.* The main influence of this structure change upon the free energy is linear in the electrolyte concentration and leads, for the partial molar functions, only to terms which are independent of concentration (cf.

* The same effect causes the different distance of closest approach for like-charged and oppositely charged ions. Our calculations contain this hydration influence only upon the ionic interaction; they do not lead to the thermodynamic functions of the whole hydration complexes (i.e., ions + water molecules involved in the hydration shells). The hydration influence occurs in our model as a repulsion effect of partly electrostatic nature, effecting a weakening of the electrostatic part of the free energy. The activity coefficients, obtained by differentiation with n , then show the characteristic minimum and rise above unity, while the part of free energy, $\Delta^{\circ}f$, is always smaller than zero.

the terms mentioned in ref. 7 in our paper). Our omission of this influence in the calculation of activity coefficients, heats of dilution, and concentration dependent part of apparent molar heat capacities concerns therefore—if we compare with experimental values—only the concentration terms of higher order.

Second: Our model indeed is too crude to describe any individual interactions between ions in the ionic atmosphere around the central ion; but our distribution formula should be a better approximation than the Boltzmann formula used in the Debye-Hückel theory, as it contains the influence which we consider essential at higher concentrations, namely, the limited number of ion sites. In this respect, the situation is comparable with that of adsorbed gases, for which the Langmuir formula is also a better approximation than the simple Boltzmann formula.

Third: With respect to this point, concerning the interpretation of the " a "-values and the incompleteness of dissociation, more information was obtained from the sound absorption measurements, mentioned only shortly in our paper. In fact these results, in which ionic atmosphere effects and dissociation effects occur separately, restrict the arbitrariness of the assumptions made in our calculations of the "dissociation influence" upon the thermodynamic functions (for instance in the case of 2-2 electrolytes). It should be interesting, too, to compare these results on formation and structure of ion complexes with those given by other methods (for instance, spectroscopic or magnetic resonance measurements).

Finally, we may admit that the quantitative interpretation of our parameters may be uncertain because of the omissions and other formal assumptions made in the calculations. But the fact that these parameters have the right order of magnitude, as known from other investigations of ionic hydration, and that the calculations fit the experimental values of three different thermodynamic functions by use of one single set of values for these parameters, seems to indicate that the effects which are treated in our model correspond to real physical phenomena.

THE STATISTICAL MECHANICS OF ELECTRICAL CONDUCTION IN FLUIDS¹

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A method has been developed to discuss irreversible processes in fluids from a statistical mechanical point of view. The flows of macroscopically observable quantities are shown to be linear functions of corresponding thermodynamic forces with coefficients given explicitly in terms of certain random processes. In this presentation the theory will be applied specifically to a model of an electrolyte in which certain molecular species carry electrical charges and in which external fields are possibly present. Expressions for conductivities and other irreversible coefficients in terms of specific random processes will be given. The thermodynamic forces will be discussed.

I want to talk today about the application of a general statistical theory of irreversible phenomena² to the problem of electrical conduction in fluids. To talk about this theory at an electrochemistry symposium at Yale University is, perhaps, to bring it back to its source since its two motivating ideas are (a) Onsager's theory of reciprocal relations,³ (b) Kirkwood's statistical theory of Brownian motions,⁴ both of which are closely associated with the theory of electrolytes and with Yale University.

As in Onsager's theory the macroscopic state of the system is described by certain functions de-

fined in its phase space

$$a_1(\mathcal{X}) \cdots a_r(\mathcal{X})$$

(\mathcal{X} signifies a point in phase space and represents the position and momentum of all particles of the system.) In our case there are enough of these to give an adequate description of the spacial distribution of the several species present as well as of the energy density and velocity. The number required may be quite large, perhaps of the order of a million or a billion, but, of course is still small compared to the number of degrees of freedom of the system.

The primary mathematical object of the theory is a Fokker-Planck type equation which governs the probability of transition from one macroscopic state to another. In many cases, however, and ours is one of them, an adequate description is given by a set of ordinary differential equations

(1) This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

(2) M. S. Green, *J. Chem. Phys.*, **20**, 1281 (1952); **22**, 398 (1954).

(3) L. Onsager, *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931).

(4) J. G. Kirkwood, *J. Chem. Phys.*, **14**, 180 (1946).

for the most probable values $a_1(t) \cdots a_r(t)$ of the macroscopic variables.

$$\frac{da_i}{dt} = \langle v_i \rangle + \sum_{j=1}^r \xi_{ij} \frac{\partial \log W}{\partial a_j} + \frac{\partial \xi_{ij}}{\partial a_j}$$

$v_i(\mathfrak{X})$ is the rate of change of the variable $a_i(\mathfrak{X})$ at the point \mathfrak{X} while the brackets mean average in the ensemble which represents the macroscopic state. W is what one might call the phase volume density of the macroscopic state and therefore $k \log W$ is the entropy of the macroscopic state. The quantities ξ_{ij} are related to the elements of the correlation matrix of the v_i at different times.

$$\xi_{ij} = \int_0^\tau (\langle v_i(0)v_j(\sigma) \rangle - \langle v_i \rangle \langle v_j \rangle) d\sigma$$

Here $v_j(\sigma)$ is the rate of a_j at time σ considered as a function of the phase point \mathfrak{X} through which the system passed at time 0. $v_i(0) = v_i(\mathfrak{X})$. The integrand represents the correlation between v_i and v_j at two different times and may be expected to be small when the interval between the times, σ , is larger than a certain macroscopic time τ . The integral is taken between zero and τ . The quantities $\langle v_i \rangle$, ξ_{ij} and $\log W$ may all be functions of the macroscopic state, *i.e.*, of $a_1 \cdots a_r$.

Many of you will recognize the relation of this equation to Kirkwood's form of the Langevin equation of Brownian motion theory and to Onsager's form of the phenomenological equations of irreversible phenomena. The quantities ξ_{ij} are generalizations of Kirkwood's friction constant while the quantities $\partial \log W / \partial a_j$ are essentially Onsager's thermodynamic forces. The first term in these equations can be shown to represent reversible effects while the second and third terms contain all irreversible effects. In our case the third terms can be shown to be negligible.

As you all know, electrical conduction is a special case of a general conduction-diffusion problem which is appropriately considered as a whole. In this problem we are interested in the rates of change of the most probable local concentrations of the several species $\rho_\lambda(\mathfrak{X})$, $\lambda = 1 \dots \nu$. Some of these species may be ions bearing charges e_λ . I want to consider for a moment, and then leave the question of a possible hydrodynamic mass motion of the fluid. The first reversible terms in the equations for the most probable macroscopic state lead to the statement that the composition is constant along the stream lines of the mass motion. Diffusion-conduction then represents the irreversible deviation from this first reversible approximation.

In order to evaluate the second terms we have to determine the entropy as a function of the macroscopic state. This is the familiar albeit usually very difficult problem of determining the volume of a region of phase space. The analogous problem for a system of uncharged species has been considered elsewhere. The result given there must be modified to allow for two new circumstances. (a) The possible existence of small local deviations from electrical neutrality which give rise to long range interaction between widely separated parts of the system and (b) the possible

existence of sources of electrostatic field external to the system. An "educated guess" at the necessary modification is

$$\log W = \frac{1}{k} \int S(E^*(\mathbf{x}), \rho_1(\mathbf{x}) \cdots \rho_\nu(\mathbf{x})) d\mathbf{x}$$

where S is the entropy density considered as a function of concentrations $\rho_\lambda(\mathbf{x})$ and the intrinsic energy density $E^*(\mathbf{x})$ and the integration is over the whole volume of the system. The intrinsic energy of a volume element is defined to be its total energy less $1/2$ of the energy of interaction of its space charge with all other space charges of the system less the potential energy of its space charge in the external field. The thermodynamic force corresponding to $\rho_\lambda(\mathbf{x})$ is the partial derivative or rather the functional derivative of $\log W$ with respect to $\rho_\lambda(\mathbf{x})$. It contains two terms—one, the negative chemical potential of the λ th species divided by kT , the second, $-e_\lambda \varphi(\mathbf{x})/kT$ where $\varphi(\mathbf{x})$ is the total electrostatic potential at the point \mathbf{x} , *i.e.*, that due to internal and external charges. The result is the negative electrochemical potential divided by kT .

$$-(\mu_\lambda(\mathbf{x}) + e_\lambda \varphi(\mathbf{x})/kT)$$

The equations for the rates of change of the concentrations are

$$\frac{\partial \rho_\kappa}{\partial t} = \sum_\lambda \nabla L_{\kappa\lambda} \nabla (\mu_\lambda + \lambda_\lambda \varphi)$$

and the most significant conclusions of the theory are autocorrelation expressions for the coefficients $L_{\kappa\lambda}$ which appear in them.

$$L_{\kappa\lambda} = 1/3kT \int_0^\infty d\sigma \lim_{V \rightarrow \infty} V^{-1} \langle \mathbf{C}_\kappa(0) \cdot \mathbf{C}_\lambda(\sigma) \rangle$$

Here $\mathbf{C}_\lambda(\sigma)$ is the sum of the velocity vectors of all particles of λ at the time σ and the limit is taken as the volume of the system goes to infinity keeping the concentrations and the intrinsic energy density constant.

There are three things which can be proved in general about these coefficients. The first is a consequence of the principle of conservation of momentum. Because $\sum_{\kappa=1}^\nu m_\kappa \mathbf{C}_\kappa$ the total momentum of the system, is a constant of the motion, where m_λ is the mass of a particle of species λ , can be shown that

$$\sum_{\kappa=1}^\nu m_\kappa L_{\kappa\lambda} = \sum_{\lambda=1}^\nu L_{\kappa\lambda} m_\lambda = 0$$

The second is Onsager's well-known symmetry relation

$$L_{\kappa\lambda} = L_{\lambda\kappa}$$

and the third, which is equivalent to the principle of increase of entropy in an irreversible process, is that the matrix $L_{\kappa\lambda}$ is positive (semi-)definite.

The general formula for the $L_{\kappa\lambda}$ as well as the general statements which can be derived from it have a wide range of validity and in particular are independent of the nature and concentrations of the species subject to two provisos. Possible internal degrees of freedom of the species have not been taken into account so that, for instance, the

role of an electric polarizability has not been determined. (This probably makes no difference in the formal result.) Secondly and more seriously it has been assumed that the relaxation time for a

deviation from electroneutrality while macroscopically short, is long compared to the correlation time of the C_λ . This is probably not true for a very high concentration of ions.

THERMODYNAMIC PROPERTIES OF MIXTURES OF ELECTROLYTES IN AQUEOUS SOLUTIONS

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The mean apparent molal volume of two electrolytes in an aqueous solution may be calculated from known values of the apparent molal volume of each electrolyte in the binary solution whose ionic strength is that of the ternary solution. The relatively small discrepancies between the values so calculated and experimental data can be represented by simple algebraic expressions, *i.e.*, "interaction terms." Combination of the interaction terms with the basic equation leads to equations which may be differentiated to yield explicit expressions for partial molal volumes. The calculations agree well with "experimental" determinations of partial molal volumes. The forms of the curves representing the changes in enthalpy occurring when two solutions of the same ionic strength are mixed are comparable with the corresponding volume curves. Some general relations have been observed between the constants of equations for the enthalpies of binary solutions of electrolytes of the 1-1, 1-2, 2-1 charge types. These relationships when extended by further experiments promise to make it possible to base predictions of enthalpies of solutions upon the constitutions of the electrolytes involved.

According to the ionic strength principle the mean ionic activity coefficient, γ_{\pm} , of any "strong electrolyte is the same in all solutions of the same ionic strength."²⁻⁵ It follows that $\bar{F}(\text{excess})$, defined by equation 1 is also determined by the ionic strength, μ

$$\bar{F}(\text{excess}) = RT \ln \gamma_{\pm} = \bar{F} - \bar{F}^{\circ} - RT \ln m_{\pm}^{\nu} \quad (1)$$

Here \bar{F}° denotes the standard partial molal free energy of the electrolyte, m_{\pm} the geometrical mean molality of the ions, ν the number of ions resulting from the dissociation of one formula unit ("molecule") of the electrolyte, R the gas constant and T the absolute temperature.

If $\bar{F}(\text{excess})$ is to be determined by the total ionic strength at each temperature it follows that $\bar{H}(\text{excess})$ defined by equation 2 is also a function of the ionic strength, μ

$$\bar{H}(\text{excess}) = \bar{H} - \bar{H}^{\circ} = \bar{L} \quad (2)$$

Here \bar{H} denotes the partial molal enthalpy and \bar{H}° is its standard value. Similarly, if $\bar{F}(\text{excess})$ is to be determined by μ at each pressure throughout a range of pressures, $\bar{V}(\text{excess})$ defined in equation 3 is also determined by the total ionic strength

$$\bar{V}(\text{excess}) = \bar{V} - \bar{V}^{\circ} \quad (3)$$

\bar{V}° in equation 3 denotes the standard partial molal volume. For the purposes of this paper both \bar{H}° and \bar{V}° refer to properties of the solute in infinitely dilute solution.^{3,6,7}

The validity of the ionic strength principle is

- (1) The Ethyl Corporation, Baton Rouge, La.
- (2) G. N. Lewis and M. Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).
- (3) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.
- (4) P. Debye, *Physik. Z.*, **25**, 97 (1924).
- (5) "The Collected Papers of Peter J. W. Debye," Interscience Publishers, Inc., New York, N. Y., 1954, p. 326.
- (6) I. M. Klotz, "Chemical Thermodynamics; Basic Theory and Methods," Prentice-Hall, Inc., New York, N. Y., 1950.
- (7) F. D. Rossini, "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1950.

restricted unfortunately to very limited concentration ranges. It is difficult therefore to obtain sufficiently precise data to demonstrate the relationship of \bar{H} and \bar{V} to the ionic strength. Nevertheless H. E. Wirth⁸ attacked the problem for aqueous solutions of potassium chloride with sodium chloride, potassium bromide with sodium chloride, and potassium sulfate with sodium chloride. He found that the (excess) partial molal volumes of the salts in these mixtures were in excellent agreement with the volume collary of the ionic strength principle even for values of μ as large as one molar.

Later, aqueous solutions of sodium chloride with hydrogen chloride⁹ and of sodium perchlorate with perchloric acid¹⁰ were investigated. For solutions of these electrolytes the failure of the ionic strength principle was as spectacular as was its success when applied to the three sets of solutions studied earlier.

Some years ago an attempt was made in this laboratory to explain the properties of dilute solutions of sulfuric acid in terms of the concentrations of the ionic species involved.¹¹ One step in the theoretical analysis of the heat of dilution curve was a hypothetical mixing of two solutions of the same ionic strength to produce a ternary solution of that ionic strength. It was assumed that the heat of mixing under these conditions is zero or negligible. Klotz and Eckert¹² in their study of the apparent molal volumes of dilute sulfuric acid solutions made the similar assumption that the change in volume resulting from the mixing of two solutions of the same ionic strength is zero (or small). The assumptions were at first regarded as approximations, probably rougher

- (8) H. E. Wirth, *J. Am. Chem. Soc.*, **59**, 2549 (1937).
- (9) H. E. Wirth, *ibid.*, **62**, 1128 (1940).
- (10) H. E. Wirth and F. N. Collier, Jr., *ibid.*, **72**, 5292 (1950).
- (11) T. F. Young and L. A. Blatz, *Chem. Revs.*, **44**, 93 (1949).
- (12) I. M. Klotz and C. F. Eckert, *J. Am. Chem. Soc.*, **64**, 1878 (1942).

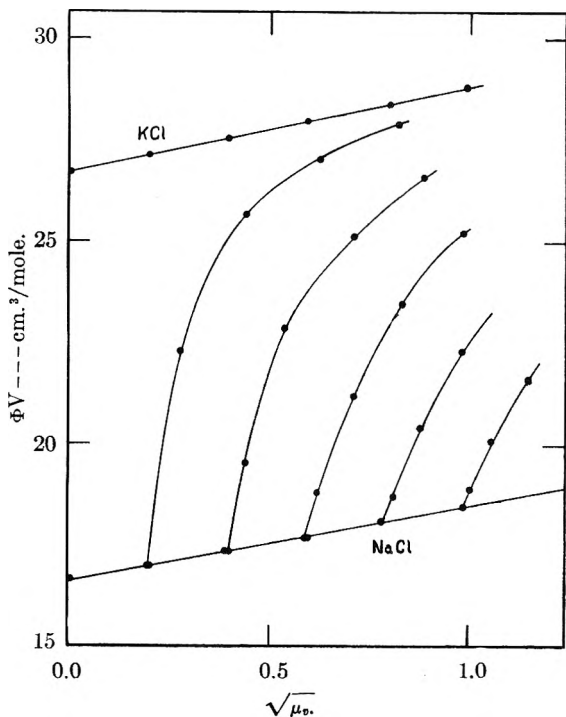


Fig. 1.—The mean apparent molal volume (at 25°) of KCl and NaCl as a function of μ_v . Points are experimental; lines for the ternary solutions were calculated from equation 5. The topmost curve denotes binary solutions of KCl in water; the lowest, binary solutions of NaCl in water.

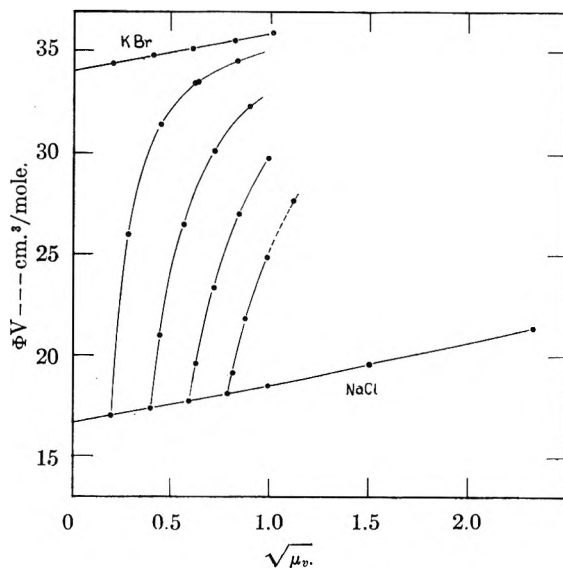


Fig. 2.—The mean apparent molal volume of KBr and NaCl shown as a function of μ_v . Points are experimental; lines for ternary solutions were calculated from equation 5.

than the ionic strength principle, but more convenient for some purposes. This paper contains reports of several studies of a mixture rule embodying these assumptions.

Apparent Molal Volumes.—Extensive tests of the new rule were made possible by the beautifully planned and very precise density measurements of Wirth^{8,9} and Wirth and Collier.¹⁰ This paper deals with tests of the rule for electrolytes of the 1-1 charge type only. Hence μ_v in this paper indicates merely the total molarity, and μ_w the total molality. Let the mean apparent molal volume ΦV be defined by equation 4

$$\Phi V = \frac{V - n_1 \bar{V}_1^\circ}{n_2 + n_3} \quad (4)$$

in which \bar{V}_1° denotes the molal volume of pure water and V the volume of solution containing n_1 moles of water, n_2 moles of one solute and n_3 moles of a second solute. The mixture rule to be tested may be stated thus

$$\Phi V = \frac{n_2 \varphi_2 + n_3 \varphi_3}{n_2 + n_3} \quad (5)$$

In this equation φ_2 denotes the apparent molal volume of substance number two in a binary solution whose ionic strength is that of the ternary mixture. Similarly φ_3 represents the apparent molal volume of the other solute in a solution of the same ionic strength and containing only water and that one solute. Equation 5 is tantamount to the statement that the mixing of the two binary solutions of the same ionic strength produces a ternary solution whose volume is exactly the sum of the volumes of the binary solutions.

As pointed out by B. B. Owen¹³ the only data available for an adequate test of equation 5 are those contributed by Wirth. Figure 1 shows ΦV for solutions of potassium chloride and sodium chloride; Fig. 2 shows ΦV for potassium bromide and sodium chloride. The differences between the calculated and experimental values are probably within the limits of precision of the measurements. These solutions therefore obey both

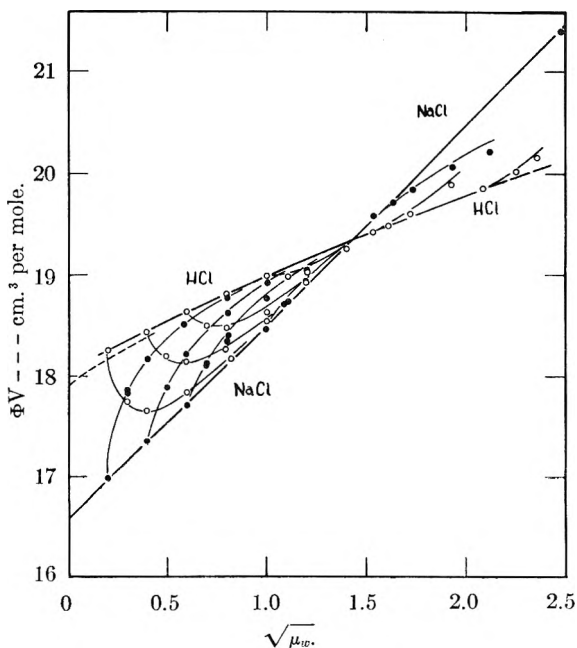


Fig. 3.—The mean apparent molal volume of HCl and NaCl in aqueous solution at 25°. Both series of points are experimental. The short dashed line at the extreme left represents the data of Redlich and Bigeleisen (ref. 14). Two lines denote the binary solutions of HCl and NaCl, respectively. The other lines were calculated from equation 5 and are for ternary solutions. The abscissae are for μ_w .

(13) B. B. Owen, in "Electrochemical Constants," National Bureau of Standards Circular 524, Washington, D. C., 1953, p. 193.

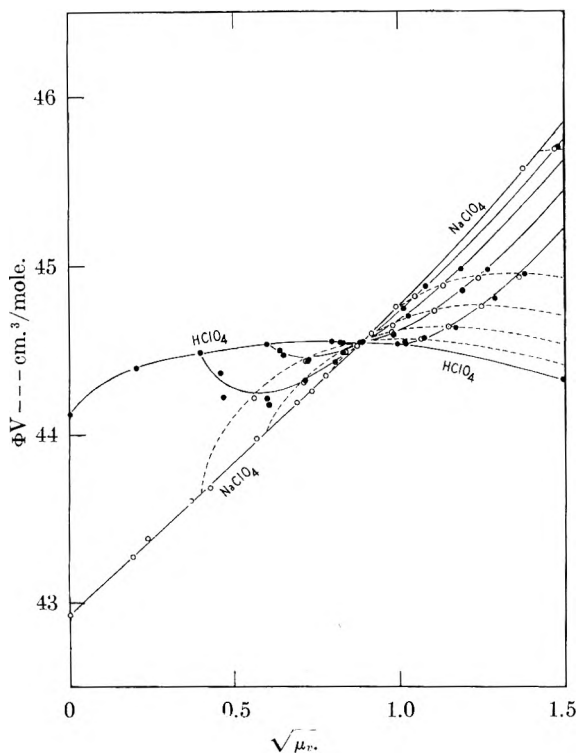


Fig. 4.—The mean apparent molal volume of HClO_4 and NaClO_4 in aqueous solution at 25° . The meanings of the symbols are similar to those in Fig. 3.

the new rule and the older ionic strength principle. ΦV for solutions of sodium chloride and hydrochloric acid¹⁴ is shown in Fig. 3. The independent variable arbitrarily chosen for this figure is the weight ionic strength rather than the volume ionic strength. The deviations are not greatly affected by a change of μ_v to μ_w . It is to be understood that when μ_w is used φ_i denotes the magnitude of the apparent molal property in a binary solution whose μ_w is that of the ternary mixture. When μ_v is used φ_i is the magnitude of the apparent molal property in a binary solution whose μ_v is the same as that of the ternary or more complex mixture. In Fig. 3 there are two sets of points for ternary solutions. Each curve in one set represents a series of additions of sodium chloride to a single solution of hydrogen chloride. Each curve of the other set represents a series of solutions in which the molality of sodium chloride is constant but that of hydrogen chloride is variable. The two sets of theoretical lines were calculated from equation 5. It is obvious that (because of mathematical considerations) all of the curves originating in the region where μ_w is less than 2 molal pass through the same point at $\mu_w = 2$ molal. Some of the discrepancies between theory and experiment are clearly outside of the limits

(14) According to Wirth's data the slope of the $\text{HCl}-\text{H}_2\text{O}$ curve does not approach the limiting slope expected from the Debye-Hückel theory. In later work the left portion of the curve was investigated extensively by Redlich and Bigeleisen [*J. Am. Chem. Soc.*, **64**, 758 (1942)]. Their data are represented by the short dashed line drawn just below the left end of Wirth's curve. According to these later measurements the limiting slope appears to be the same for HCl , NaCl and for other electrolytes of the 1-1 charge type. Compare B. B. Owen and S. R. Brinkley, Jr. [*Ann. N. Y. Acad. Sci.*, **51**, 753 (1949)].

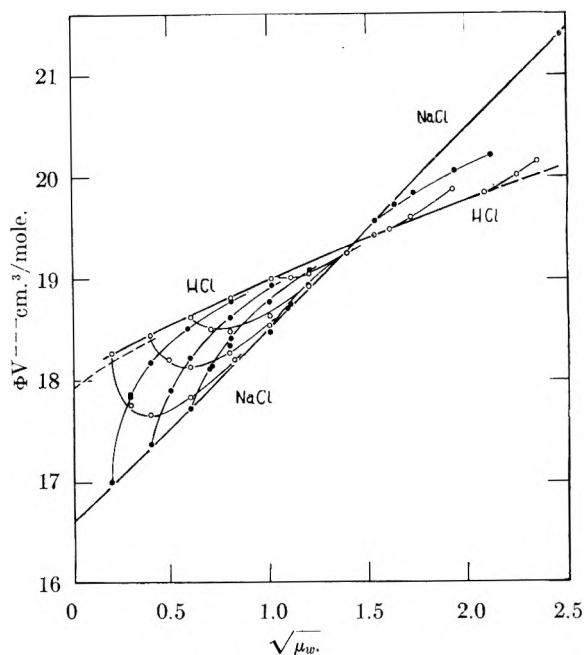


Fig. 5.—The mean apparent molal volume of HCl and NaCl calculated from equation 6 which contains the correction term δ . One empirical constant is adequate for all of the solutions shown, *i.e.*, for μ_w as large as 4 molal.

of experimental error. Nevertheless the success of equation 5 is remarkable.

Figure 4 shows a similar comparison of calculated and experimental values of ΦV for solutions containing sodium perchlorate and perchloric acid. All of the discrepancies are probably within experimental error. Indeed the average deviation is only a little larger than the average deviation found by Wirth and Collier¹⁰ between experiment and the empirical equations derived by them to represent their data. The equation for each of their lines contains two empirical constants (other than the φ of the solute in the binary solution in which the curve starts)—twenty empirical constants for the ten curves. Since in Fig. 4 all of the curves for the ternary solutions were computed without the introduction of a single empirical constant it is obvious that equation 5 is quite satisfactory for these solutions.

The usefulness of a mixture rule such as equation 5 is measured not only by its ability to represent the facts by itself but also by the nature of deviations from it. A rule is most useful if deviations from it can be represented by simple equations amenable to mathematical manipulation. In the systems discussed here the only discrepancies large enough to study are those for the $\text{HCl}-\text{NaCl}$ mixtures. Even they are too small to permit a thoroughly satisfactory examination. Hence it was assumed that the deviations δ at a single ionic strength were proportional to $S(2)S(3)$, the product of the respective solute fractions defined by

$$S(2) = \frac{n_2}{n_2 + n_3}; S(3) = \frac{n_3}{n_2 + n_3} \quad (6)$$

and that $\delta/S(2)S(3)$ is proportional to μ . These two assumptions lead to

$$\delta = K\mu S(2)S(3) \quad (7)$$

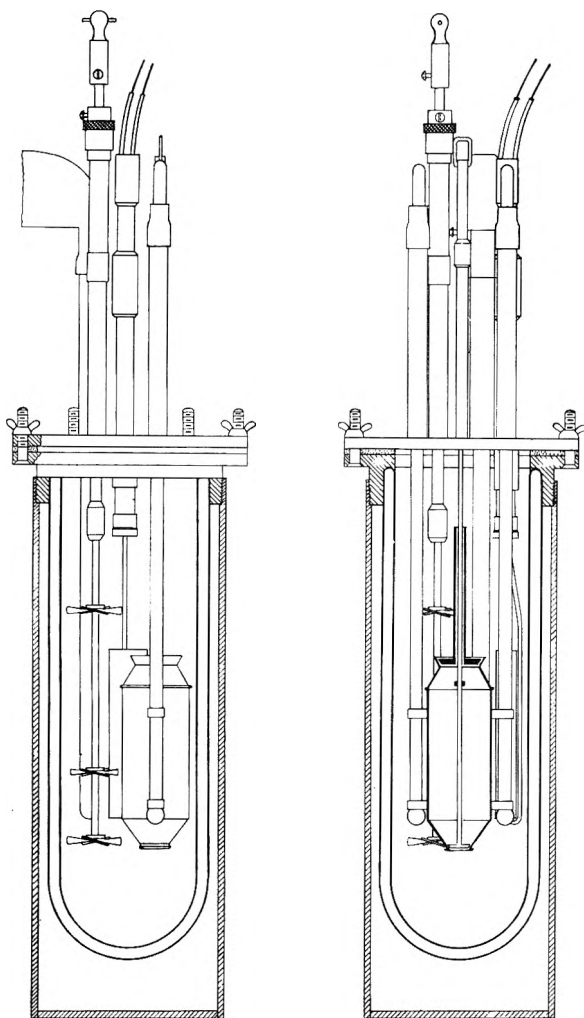


Fig. 6.—The calorimeter equipped with a pipet closed with ground stoppers.

The addition of equations 5 and 7 leads to

$$\Phi V = \frac{n_2\varphi_2 + n_3\varphi_3}{n_2 + n_3} + K\mu S(2)S(3) \quad (8)$$

in which K is an empirical constant. Calculations were carried out with both μ_V and μ_W . The value of K derived by trial from Wirth's data is -1.0×10^{-4} liter² mole⁻². This is the value to be used with μ_V . The constant to be used with μ_W is -0.8×10^{-4} liter kilogram mole⁻². The interchange of μ_V and μ_W each accompanied by its respective constant does not lead to expressions which are strictly equivalent mathematically. The discrepancies between theory and experiment, however, are not visibly different on the two plots. Either equation seems to represent the data within experimental error. The weight ionic strength was chosen as the independent variable for Fig. 5 in which the data are compared with equation 8. The single "interaction term" proves to be sufficient to bring the calculated values of ΦV into completely satisfactory agreement with experiment.

Apparent Molal Enthalpies.—The new mixture rule can be applied also to the heat contents of ternary mixtures but direct comparisons such as

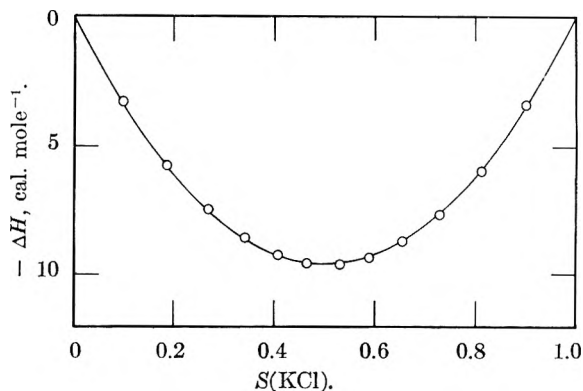


Fig. 7.—The heat absorbed, ΔH , when a solution containing $S(2)$ mole of KCl is mixed with one containing $S(3)$ mole of NaCl each in an m molal aqueous solution. The data shown are for 25° and $m = \text{unity}$. Note that ΔH is negative; heat is evolved. The line represents the enthalpy analog of equations 7 and 8.

those shown in Figs. 1 to 5 are not possible because we do not deal with absolute values of molal enthalpies; we work only with the changes in enthalpy which are observed when thermodynamic processes occur. Equations 5 and 8 therefore may be replaced by the statement that ΔH of mixing, *i.e.*, the heat absorbed, when two solutions of the same ionic strength are mixed is zero or small. Experiments made to test the rule result in direct determinations of the δ term.

Since no thermal data were available for comparison with these hypotheses several calorimetric investigations were made. The calorimeter (Fig. 6) was similar to one previously described¹⁵ but was equipped with a tantalum pipet closed with tantalum stoppers ground into seats at the ends of the pipet. A pull on the rod opened first the lower and then the upper stopper. The stoppers were sealed with a petroleum jelly which had been shown to impart no appreciable conductivity to water after prolonged contact. Because the volume of the pipet in the calorimeter was only about one-tenth of the total calorimeter volume, mixing experiments were arranged in a program of five or six steps. The ternary mixture produced in one step was subsequently mixed with a binary solution to produce the next ternary solution.

The heats of mixing of potassium chloride with sodium chloride are shown in Fig. 7. The heat effects are small¹⁶ and conform rather closely to equation 7. Data for the mixing of LiCl and NaCl are shown in Fig. 8. Again the curve has the general form represented by equation 7, though deviations from it are observable. Empirical equations which represent the observations more closely are

$$\text{For } \left\{ \begin{array}{l} \text{KCl} \\ \text{NaCl} \end{array} \right. \Delta H = -37.68S(\text{KCl})S(\text{NaCl})(1 + 0.030S(\text{KCl})) \quad (9)$$

$$\text{For } \left\{ \begin{array}{l} \text{LiCl} \\ \text{NaCl} \end{array} \right. \Delta H = \frac{+78.45S(\text{LiCl})S(\text{NaCl})}{1 - 0.1443S(\text{LiCl})} \quad (10)$$

(15) T. F. Young and J. S. Machin, *J. Am. Chem. Soc.*, **58**, 2254 (1936).

(16) They are small, for example, in comparison with the heat effect observed when 0.5 mole of Na_2SO_4 and 0.5 mole of HCl are mixed (ca. 2500 cal.) or in comparison with the heat of solution of one mole of NaCl in several kilograms of water (ca. 1000 cal.).

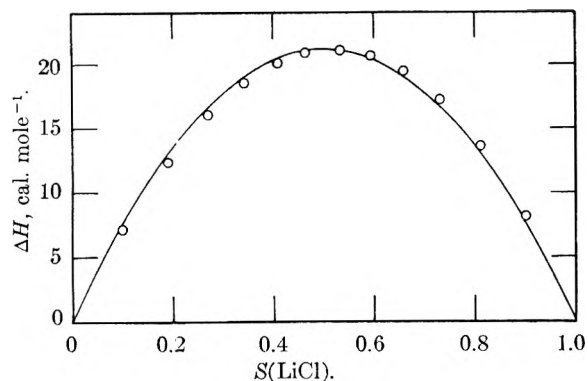


Fig. 8.—The heat absorbed, ΔH , when a solution containing $S(2)$ mole of LiCl is mixed with one containing $S(3)$ mole of NaCl each in an m molal aqueous solution. Note that ΔH is positive; heat is absorbed. The data shown are for 25° and $m = \text{unity}$. The line represents the enthalpy analog of equations 7 and 8.

The forms of these equations have no significance; they were chosen empirically solely to represent the observations.

Partial Molal Volumes.—If equation 4 be rearranged to present an explicit expression for V it may be differentiated and an equation for \bar{V} of each of the three constituents thus derived

$$\bar{V}_3 = \frac{\varphi_3 + w_3 \left[C_2 \frac{d\varphi_2}{d\mu_V} + C_3 \frac{d\mu_3}{d\mu_V} \right]}{1 + \frac{\mu_V}{1000} \left[C_2 \frac{d\varphi_2}{d\mu_V} + C_3 \frac{d\varphi_3}{d\mu_V} \right]} \quad (11)$$

In equation 11, the symbol w_3 denotes a factor dependent on the charge type of the electrolyte. It is unity for the purposes of this paper which deals with mixtures of electrolytes of the 1-1 charge type only. If n and μ_w be used as the concentration variables instead of C and μ_V the denominator becomes unity, and

$$\bar{V}_3 = \varphi_3 + w_3 \left[m_2 \frac{d\varphi_2}{d\mu_w} + m_3 \frac{d\varphi_3}{d\mu_w} \right] \quad (12)$$

If a δ term (equation 7) be included differentiation leaves

$$\bar{V}_3 = \varphi_3 + w_3 \left[m_2 \frac{d\varphi_2}{d\mu_w} + m_3 \frac{d\varphi_3}{d\mu_w} \right] + m_2 K \quad (13)$$

Equations 11, 12 and 13 were applied to Wirth's data for hydrochloric acid-sodium chloride mixtures with the aid of empirical equations derived by least square methods for the two binary solutions

$$\text{HCl in water: } \varphi V = 18.052 + 1.00096 \sqrt{\mu_w} - 0.06736 \mu_w \quad (14)$$

$$\text{NaCl in water: } \varphi V = 16.587 + 1.90065 \sqrt{\mu_w} + 0.01795 \mu_w \quad (15)$$

For solutions less concentrated than two molal, $\bar{V}(\text{HCl})$ was calculated from equation 11. The results are shown as lines in Fig. 9. The points represent Wirth's values calculated by differentiation of a set of empirical equations. Each had been derived to represent the density data corresponding to a curve representing a single series of experiments. The Wirth values will be referred to as "experimental" points. The agreement between the-

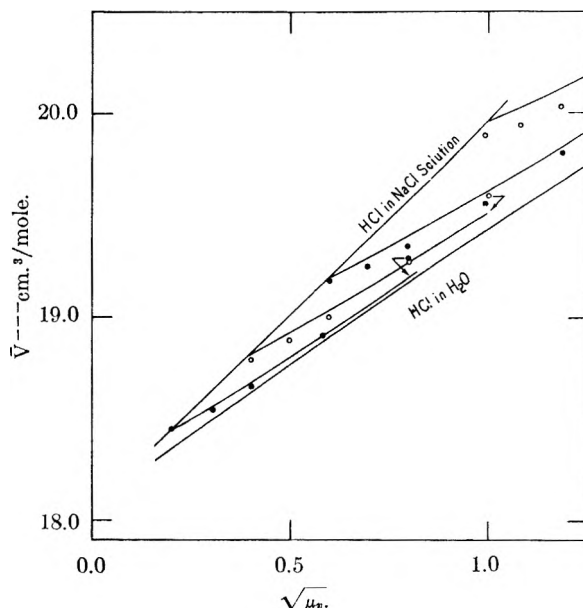


Fig. 9.—The partial molal volume of HCl in NaCl solutions calculated with equation 11 (without the δ term). The topmost line represents \bar{V} of HCl when the concentration of HCl approaches zero.

ory and "experiment" is excellent in Fig. 9 but not quite perfect. In Fig. 10 is a similar comparison of theory with Wirth and Collier's "experimental" values for HClO_4 - NaClO_4 solutions. There probably are no significant discrepancies. The unmodified rule seems to be as good as these very precise "experimental" data. In Fig. 11 the partial molal volumes of HCl in NaCl calculated

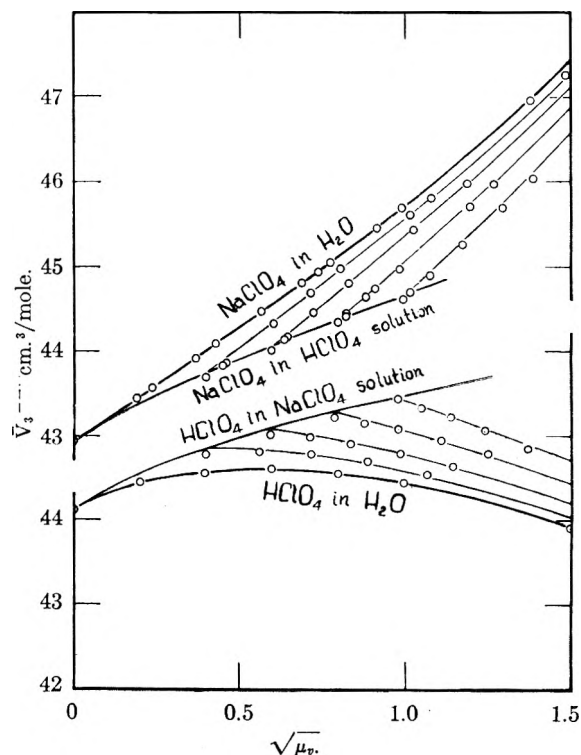


Fig. 10.—The partial molal volume of NaClO_4 in HClO_4 solutions and of HClO_4 in NaClO_4 solutions calculated with equation 11. The points are Wirth's experimental ones.

from equation 13, for concentrations as large as 2 molal, are compared with "experimental" values. The introduction of a single empirical constant (in the δ term) is, in this case, sufficient to eliminate all significant discrepancies. The agreement in Fig. 11 is essentially perfect.

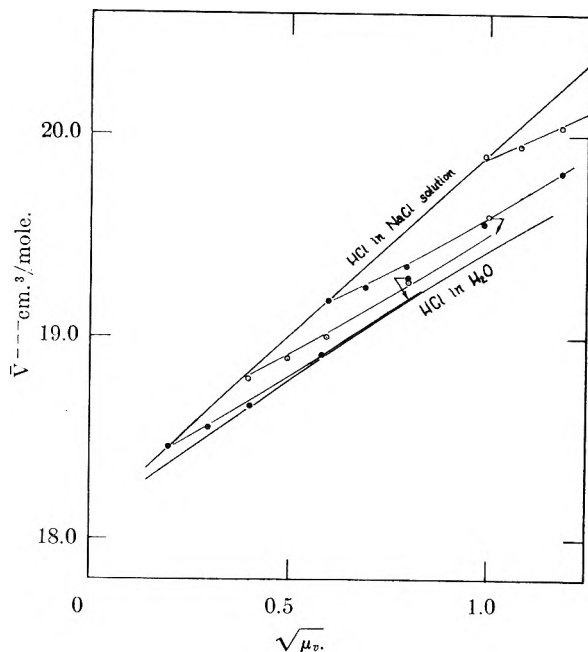


Fig. 11.—The partial molal volume of HCl in NaCl solutions calculated with equation 13 (with the δ term).

If the principle proposed here is basically correct we should expect it to become better as concentrations are decreased. It was somewhat disconcerting at first, therefore, to find appreciable deviations between theory and "experiment" for the most dilute solutions studied: note that the experimental points on two curves are slightly low over part of the range but that the last point in each series is so high that it appears to lie on the curve above the one on which it belongs. A glance at Figs. 3 and 5, however, reveals that no large discrepancy between theory and experiment exists in this concentration range. Careful examination revealed that equation 5 which possesses no empirical constant whatever represents Wirth's original density data for ternary solutions better than the three-constant empirical equation that had been derived originally to represent each of the two curves. In Fig. 11 as in Fig. 5 there seem to be no discrepancies which are significant.¹⁷

Wirth⁸ observed in his data evidence that \bar{V} is a linear function of C_2 or C_3 when μ_V is held constant. Both equation 12 and equation 13 predict such a linear relationship. Figure 12 shows a theoretical calculation (from equation 13) comparable to Fig. 3 in Wirth's article.

(17) The plot of \bar{V} of NaCl in HCl solutions on the other hand does reveal some discrepancies which are a little larger than was expected. These would be reduced materially if a curve for ϕ of HCl corresponding to the Redlich and Bigeleisen densities (ref. 14) were substituted for the Wirth values. This condition implies that the small error which afflicts the left end of Wirth's curve for hydrochloric acid in water does not seem to have affected his work with the ternary solutions containing dilute HCl.

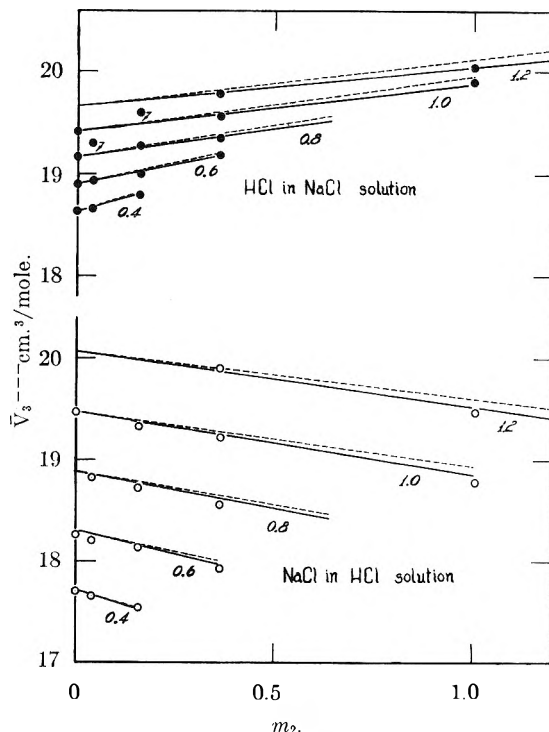


Fig. 12.—The variation of \bar{V} of HCl and NaCl at constant μ_w . The abscissas are m_{\pm} , the molalities of the respective solvent electrolytes. The dashed lines were calculated from equation 12, the solid lines from equation 13. The points are "experimental," *i.e.*, calculated by Wirth with the aid of empirical equations. All discrepancies are probably within the limits of error of the measurements. The two points distinguished by arrows represent the two observations similarly distinguished in Fig. 9 and Fig. 11.

It is instructive to compare the results of this treatment of the properties of ternary electrolytic solutions with other studies of mixtures. The mean apparent molal excess free energy is similar to a function defined and used by Scatchard¹⁸ in investigations of the properties of binary mixtures of non-electrolytes, the molal "excess free energy of mixing" which is the free energy of mixing minus the free energy calculated for the mixing of liquids forming ideal solutions of the same mole fractions. Some of his curves for the excess free energy and for the enthalpy of mixing of two non-electrolytes are similar in form to Figs. 7 and 8. It is important to observe, however, that not all of the curves are of that type.

Brönsted,¹⁹ in one of his celebrated papers on the "principle of the specific interaction of ions," discussed the variation of $\log \gamma_{\pm}$ of an electrolyte when the total concentration is held constant while the solvent electrolyte is changed continuously from one salt to another, *e.g.*, NaNO_3 to KNO_3 . He presented data supporting his arguments that $\log \gamma_{\pm}$ (and hence the partial molal free energy) is a linear function of the concentration of one of the electrolytes when the total ionic strength is

(18) G. Scatchard, *Chem. Revs.*, **8**, 321 (1931); G. Scatchard and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 1805 (1935); G. Scatchard, *Chem. Revs.*, **44**, 7 (1949).

(19) J. N. Brönsted, *J. Am. Chem. Soc.*, **45**, 2898 (1923); E. A. Guggenheim, *Phil. Mag.*, (7) **19**, 588 (1935); G. Scatchard and R. C. Breckenridge, *THIS JOURNAL*, **58**, 596 (1954).

mall and constant. Linear variations of $\log \gamma_{\pm}$ have been observed by Harned²⁰ and others even for very large constant ionic strengths. The solid lines of Fig. 13 are exact analogs of the Harned linear variations (the Harned rule). The dashed lines, on the other hand, are close analogs of the relationship discussed by Brönsted.

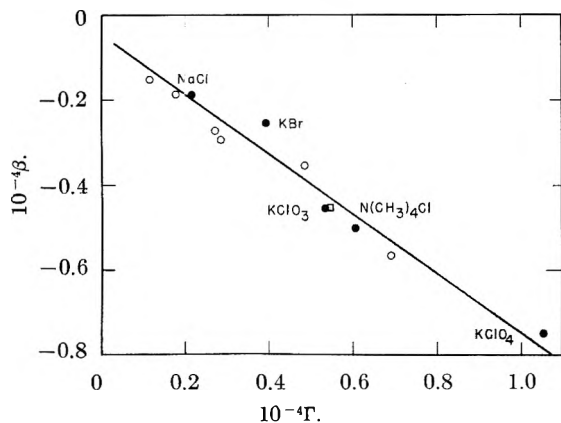


Fig. 13.— β versus Γ of equation 17 for electrolytes of the 1-1 charge type at 25°: O, NaCl, NaBr, NaClO₃, NaNO₃, NaBrO₃ and NaIO₃, respectively; ●, KCl, KBr, KClO₃, KNO₃ and KClO₄; □, N(CH₃)₄Cl.

The slopes of the dashed lines in the lower half of the figure are the negatives of the corresponding slopes of lines in the upper half; in other words, the sum of the two slopes corresponding to each ionic strength is zero. The sum of the slopes of

It must not be assumed that the deviations from any equation of the type of equation 5, can be represented by analogs of equation 7 or of the related equations 8 and 13. It has been shown by Harned and Harris,²² and by Harned and Cook²³ that solutions of sodium hydroxide in sodium chloride and potassium hydroxide in potassium chloride do not obey the free energy analog of equation 13. According to the point of view discussed here such results are to be expected. The calculations exhibited, however, indicate that equation 5 and its analogs will often serve as basic relations from which deviations can be represented by relatively simple expressions. Equation 7 is but one example of these.

Enthalpies of Binary Solutions.—The purpose of the mixture rule discussed in the preceding paragraphs is to facilitate the estimation of the properties of solutions containing two or more electrolytes. The use of the rule depends upon the availability of information concerning the binary solution from which the ternary ones may have been prepared. The last section of this paper is a report of useful relations that have been observed between the thermal properties of certain binary aqueous solutions of electrolytes.

The enthalpies of those electrolytes of the 1-1, 1-2 and 2-1 charge types which had been extensively investigated were shown by Young and Seligmann²⁴ to be representable by equations of the types

$$S = d \varphi H / d \sqrt{m} = S^{\circ} + \beta \sqrt{m} + \Gamma m + \dots \quad (16)$$

$$\varphi H = \varphi H^{\circ} = S^{\circ} \sqrt{m} + \beta m / 2 + \Gamma m^{3/2} / 3 + \dots \quad (17)$$

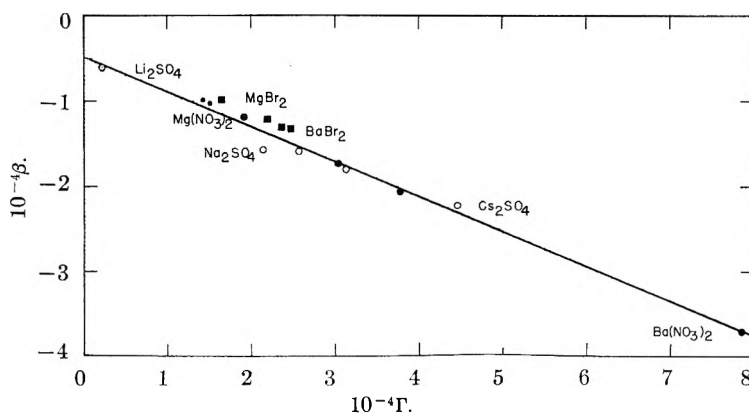


Fig. 14.— β versus Γ of equation 17 for electrolytes of the 1-2 and 2-1 charge types at 25°: O, Li₂SO₄, Na₂SO₄, K₂SO₄, Rb₂SO₄ and Cs₂SO₄; ●, Mg(NO₃)₂, Ca(NO₃)₂, Sr(NO₃)₂, Ba(NO₃)₂; ■, MgBr₂, CaBr₂, SrBr₂, BaBr₂; ●, SrCl₂, BaCl₂. The parameters for MgCl₂ and CaCl₂ have been omitted; they do not fall near the line.

the solid lines for each ionic strength is a constant, $2K$. The latter relationship between the experimental slopes for partial molal free energies has been pointed out by Glueckauf, McKay and Mathieson.²¹

(20) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, pp. 457-466.

(21) E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *J. Chem. Soc.*, S299 (1949); R. A. Robinson, "Electrochemical Constants," National Bureau of Standards Circular 524, 171 (1953).

Here S° , β and Γ are empirical constants determined from published calorimetric data by least square methods. The limiting derivative, S° , can also be computed from the limiting law of Debye and Hückel. Excellent agreement between the theory and experimental values was demonstrated.

(22) H. S. Harned and J. M. Harris, *J. Am. Chem. Soc.*, **50**, 2633, (1928).

(23) H. S. Harned and M. A. Cook, *ibid.*, **59**, 1890 (1937).

(24) T. F. Young and P. Seligmann, *ibid.*, **60**, 2379 (1938).

To increase the precision of estimates of β and Γ the constant S° was fixed at the theoretical value and a second set of empirical equations derived. Figure 13 shows β for all the salts of the 1-1 charge type plotted against Γ of the same salts. All of the values fall surprisingly close to a single line. This fact leads to the suspicion that the constants of equations 16 and 17 are more than empirical ones; it is probable that they will prove to have important theoretical significance. The suspicion is strengthened by the existence of a similar β - Γ plot for salts of the 1-2 and 2-1 charge types; Fig. 14.

If the constants do indeed have theoretical significance they may be expected to show interesting variations with constitution. So few data are available that few comparisons can be made at present. In Fig. 15 however β of four potassium

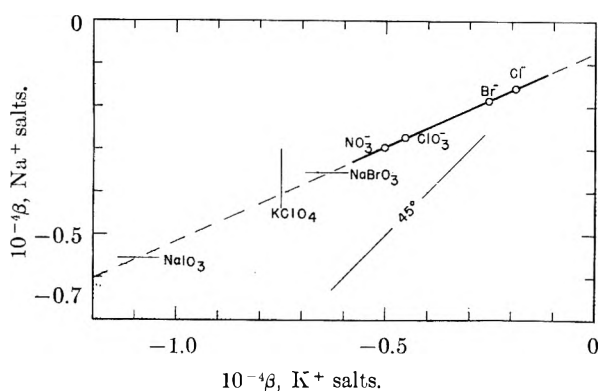


Fig. 15.— β of four sodium salts versus β of the corresponding potassium salts. β is indicated by lines for several other salts of sodium and potassium.

salts is plotted versus β of the corresponding sodium salts. To show the range of variation, values of β are indicated (by lines) for several salts whose counterparts in the other series have not been studied. If the difference between a potassium salt and the corresponding sodium salt were the same for each anion the property β would be described as an additive one. Additivity would imply a straight line having a slope of unity. The line in Fig. 15 is nearly straight throughout the short range in which a comparison is possible but the slope differs from unity by about a factor of two. The parameter β is therefore not an additive function of the ions.

Figure 16 is a plot of $1/\beta$ of the potassium salts against $1/\beta$ of the corresponding sodium salts. The slope is unity. For these eight salts therefore $1/\beta$ is an additive function of the ions.²⁵

Concerning the generality of the additivity of $1/\beta$ there is not enough information at present for much more than speculation. The existence of a simple relationship of any kind, however, supports the conclusion drawn from the orderliness observed in Figs. 13 and 14 that the parameter β is significant and worthy of extended study. When enough information has become available to establish general laws, those laws may be combined with

(25) T. F. Young, *Record Chem. Progress (Kresge-Hooker Sci. Lib.)*, **12**, 81 (1951).

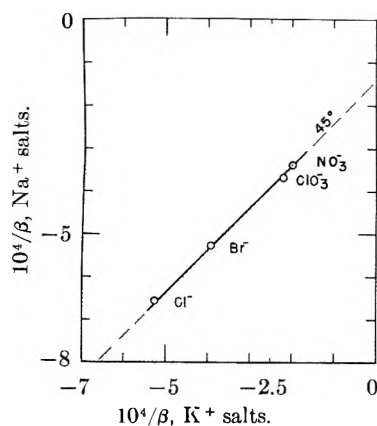


Fig. 16.—Reciprocal of β of four sodium salts versus $1/\beta$ of the potassium salts.

equations of the types of 5 and 8 for a better understanding of the thermodynamics of equilibria in solutions of electrolytes.

Acknowledgments.—The calculations reported here are extensive. Least square procedures were used throughout, and most of the volume calculations were made both for volume ionic strengths and weight ionic strengths. They were made at various times throughout an interval of more than ten years. We are especially grateful for the generous and thoughtful aid of Dr. Warren E. Henry, Dr. L. Margaret Kraemer, Dr. Helen E. Krizek, (Dr.) Sister Mary Dorcas Smith and Mr. Roger A. Pickering. The completion of the calculations needed for this paper was made possible by the Office of Naval Research, Department of the Navy.

DISCUSSION

B. B. OWEN (Yale University).—Professor Young's equations involving ΔV of mixing make it probable that apparent molal volumes in ternary mixtures could be determined most effectively by an experimental procedure similar to that of W. Geffcken, A. Kruis and L. Solana [*Z. physik. Chem.*, **B35**, 317 (1937)].

T. F. YOUNG.—The use of a method which makes it possible to measure directly the small δ term would facilitate the study of the volumes of mixtures. We should, of course, still want such methods as that used by Wirth for the investigation of the binary solutions. The first problems to be attacked might well be the determination of more details of functional relationship between the δ term μ and S for the solutions which were the subjects of Wirth's precise measurements.

M. EIGEN (University of Göttingen).—The slope curves of the heat of dilution of 1-1 and 1-2 electrolytes, shown by Professor Young, show negative deviations from the limiting law value. If the electrolyte is incompletely dissociated, a negative deviation corresponds to a positive heat of dissociation, while negative heats of dissociation must lead to positive deviations from the limiting law. Sound absorption and other measurements in solutions of 2-2 electrolytes seem to indicate an incomplete dissociation.* Davies, Jones and Monk (ref. 34, p. 711) calculated for these electrolytes negative heats of dissociation. I should like to ask Professor Young whether he has studied this case too and whether he has found for these electrolytes positive devia-

* The maxima of sound absorption—found in these solutions—can not be explained by normal ionic interaction effects due to the ionic atmosphere (cf. ref. 46, p. 713). The different maxima, however, seem to indicate that there may be several steps, including gain or loss of water, in the formation of the ionic complexes.

tions from the limiting law value opposite to those in 1-1 and 1-2 electrolytes.

T. F. YOUNG.—The deviations for magnesium sulfate, calcium sulfate, zinc sulfate, cadmium sulfate and copper sulfate are positive and large. The slope curves must pass through sharp maxima in the low-concentration region if the limiting law is to be approached. There is some evidence

that such maxima do exist, but they have not been demonstrated conclusively.

The largest positive deviations observed are in the heat-of-dilution curve for the 1-2 electrolyte, sulfuric acid. Some experimental determinations of the slope are as high as ten to fifteen times the limiting law value. For sulfuric acid we have a quantitative explanation of the experimental observations.

A CHAIN MODEL FOR POLYELECTROLYTES. I

BY FRANK E. HARRIS AND STUART A. RICE¹*Department of Chemistry, Harvard University, Cambridge, Mass.**Received March 26, 1954*

The various theories of polyelectrolyte behavior are examined and the nature of the approximations inherent in each are discussed. A new model of the polyion in solution is proposed and an outline is described for the evaluation of the free energy of the polyelectrolyte solution, including the effects of dissociation, binding and entropy of distribution of the un-ionized groups, ions and bound ion pairs. The binding of counter ions by the polymer is related to the pH, and comparison with experimental data of the theoretical relationship gives indications as to the nature of the binding process. The entropy of distribution among charged and uncharged sites on the polymer chain is evaluated, considering interaction between nearest neighboring sites, and is found to decrease markedly from its value for a random distribution, especially at intermediate degrees of neutralization. This large decrease in entropy as the degree of neutralization increases is responsible for the extensive binding of counter ions which is experimentally observed. These manifestations of non-ideal behavior make it impossible to use the previously accepted relationship between the pH of the solution and the thermodynamic properties of the polyion.

I. Introduction

In the past few years there have been several attempts to calculate the thermodynamic properties of polyelectrolyte solutions from some molecular model of the polyion in solution. In the earliest theories, the polyion was considered as a spherical distribution of charge, and the distribution of small ions in the system was assumed to be described by the Poisson-Boltzmann equation. Hermans and Overbeek² proceeded from this point by solving the Poisson-Boltzmann equation with the linearization approximation of Debye and Hückel,³ and calculating the electrostatic potential and free energy of the polyion as a function of its size and charge. Kimball, Cutler and Samelson,⁴ on the other hand, suggested that the effect of the electrostatic potential is not adequately approximated by the Debye-Hückel approximation, and in turn assumed that the distribution of small ions could be calculated using the Donnan condition that the term of the Poisson-Boltzmann equation involving derivatives of the potential could be neglected. Solution for the potential and polyion size could then be made, treating the polymer as a collection of charges bound by a central force. However, the maximum expansion which is permitted by this theory is only by a factor $\sqrt{2}$, which is far less than the experimental values.

Flory⁵ took a somewhat different approach and ignored the potential altogether, considering the system to be determined by the osmotic effects of the small mobile ions in the presence of the bound charges of the polyelectrolyte. The equilibrium value of the expansion is then found by minimizing the free energy of the system.

Both the Hermans-Overbeek and Flory theories predict expansions which are in qualitative accord with experiment, but the thermodynamic quantities computed from these theories are generally of the order of a factor of 100 too small.^{6,7} Another important drawback is the fact that the replacement of the polymer chain by a spherical model

modifies its properties in a manner which cannot even be approximately calculated, and no indication can be given as to the extent of error introduced.

The first attempt to deduce the properties of polyelectrolyte solutions from a chain model for the polymer was due to Kuhn, Künzle and Katchalsky.⁸ These authors assumed that the probability of the various possible configurations of the chain depended only upon its end to end distance and calculated the electrostatic interaction between the different charges of the chain as a function of the end-to-end distance. A most serious approximation of such a random chain model is the neglect of the fact that the probability of a given configuration of a charged chain will depend upon the distances between all pairs of links of the chain as well as the end to end distance, those configurations which place large amounts of the chain in close proximity occurring with far less than their random *a priori* probability. Another serious approximation is made by the assumption that the entire electrostatic energy is capable of causing expansion of the coil. However, a large portion of the electrostatic energy will arise from interactions between charges on adjacent monomers, and the fixed valence angles prevent these forces from producing any substantial expansion. Since each of these approximations materially overestimates the free energy available for producing expansion, it is not surprising that there is not even qualitative agreement between calculated and experimentally observed expansions.⁷ We must, therefore, regard the random chain model as providing only an initial approximation to the thermodynamic properties and mean configuration of the polyion as a function of its charge.

The use of the chain model described above for the calculation of the potential in the polyion solutions is subject to further important reservations. One of these resides in the assumption that the charge of the polyion is distributed uniformly along the polymer chain. Such an assumption might well be adequate for calculating the expansion because the most probable distribution of charge will indeed be uniform, markedly uneven distribution of the charge on the polymer skeleton being highly energetically unfavorable. However, the potentiometric properties of the polyion depend also upon

(1) Union Carbide and Carbon Fellow, 1953-1954.

(2) J. J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).(3) P. Debye and E. Hückel, *Physik. Z.*, **24**, 305 (1923).(4) G. Kimball, M. Cutler and H. Samelson, *THIS JOURNAL*, **56**, 57 (1952).(5) P. J. Flory, *J. Chem. Phys.*, **21**, 162 (1953).(6) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 458 (1952).

(7) N. Schneider, Thesis, Harvard University, February, 1954.

(8) W. Kuhn, O. Künzle and A. Katchalsky, *Helv. Chim. Acta*, **31**, 1994 (1948).

the entropy of distribution of its charged groups, and the electrical interactions will cause this entropy to deviate markedly from its value for random distribution. In fact, we shall show in the present communication that the free energy due to the distribution of charged and uncharged groups on the polymer chain becomes sufficiently large at intermediate degrees of dissociation that it is not possible to use the expressions for potentiometric titrations derived under the assumption that this free energy is adequately described by its value for random distribution.

An additional phenomenon which must have an important effect on the expansion and thermodynamic properties of polyions is the binding of counter ions by the polymer at higher degrees of neutralization. The bound counter ions will partially neutralize the charge of the polymer, and also will strongly affect the entropy of distribution discussed in the preceding paragraph. Since experimental data⁹ indicate that at complete neutralization as many as 60% of the counter ions of the polymer may be bound, this phenomenon must play an important role in the polyelectrolyte theory.

In the present communication is presented an outline for the evaluation of the free energy of a polyelectrolyte solution, including the effects of dissociation, binding and entropy of distribution of the un-ionized groups, ions and bound ion pairs among the possible configurations on the chain as well as the free energy due to the direct electrostatic interaction. We shall investigate the connection between the binding of counter ions and the other thermodynamic properties of the polyelectrolyte solutions. In addition, a calculation is made of the entropy of distribution of charged and uncharged sites, assuming, as a first approximation, that interactions occur whenever two adjacent sites are occupied by charged groups, sites occupied by bound ion pairs being regarded as uncharged. To this approximation, the problem is treated by the methods first developed for the magnetic spin systems of a one dimensional Ising lattice.

The succeeding paper will proceed to the evaluation of the direct electrostatic interactions whose value depends more critically upon finer details of the model adopted for the polymer. It will at that time be possible to compare the results obtained using the theory here developed with the results of experimental measurements of the pH, degree of binding and expansion in polyelectrolyte systems.

II. pH and Binding

We shall discuss for definiteness the properties of an aqueous solution of a polyacid. The extension to polymeric bases is completely analogous. Let the polymer chain be composed of Z dissociable groups, or, as they will be subsequently referred to, sites. Each of these sites is then assumed to be occupied either by an un-ionized group, a charged group or a bound ion counter ion pair. It is important to notice that in the foregoing assumption is included the notion that the sites for bound pairs are

the same sites as those for charged and for un-ionized groups.

Free Energy.—Consider the free energy, F , of the polyelectrolyte solution to be divided into three parts, one of which, F_1 , describes the free energy of the free hydrogen ions and counter ions eligible to take part in binding and neutralization phenomena. The remainder of the free energy will then be the contribution of the polyion itself. The first portion, F_2 , of this free energy will be the electrical free energy of the net charge of the polyion, regarding the ion pairs as uncharged sites completely equivalent to un-ionized groups. F_2 will thus include the interaction energy between portions of the net charge of the polymer, and the entropy associated with mixing charged and uncharged groups on the polymer chain. The remainder, F_3 , of the polyion free energy therefore includes the chemical free energy associated with the state of ionization and binding of the polymer, computed from a reference state in which the polyacid is in its completely undissociated form. Also included in F_3 will be the free energy of mixing of the bound ion pairs and un-ionized groups among the uncharged sites of the chain.

Let us define α to be the degree of neutralization of the polymeric acid, and f as the fraction of the dissociated sites occupied by bound ion pairs. It is then clear that the net fractional charge of the polyion, which we shall refer to as α' , will be $\alpha(1 - f)$, and the fraction of bound sites, referred to the total number of sites of the polymer, will be αf . From the way in which the various contributions to the free energy have been defined, we see that F_2 will be a function of the net charge of the polymer only, but that F_3 will depend upon the numbers of un-ionized sites and ion pair sites separately. F_1 is of course expressible in terms of the activities a_{H^+} , a_{c^-} of the free hydrogen ions and counter ions in the solution. We shall for simplicity assume the counter ions to be all univalent and of the same species. One may accordingly write

$$F = F_1(a_{H^+}, a_{c^-}) + F_2(\alpha') + F_3(\alpha, \alpha f) \quad (1)$$

Equilibrium Conditions.—The equilibrium hydrogen ion activity may now be determined by minimizing the free energy of the polymer solution with respect to the degree of neutralization of the polyacid. If the derivative is taken regarding α and αf as the two independent variables, we have

$$\left(\frac{\partial F_1}{\partial \alpha}\right)_{\alpha f} + F_2' + \left(\frac{\partial F_3}{\partial \alpha}\right)_{\alpha f} = 0 \quad (2)$$

where the notation F_2' refers to the derivative of F_2 with respect to its argument. Equation 2 may be simplified by introduction of the chemical potential of the hydrogen ions, μ_{H^+} . One may see that $(\partial F_1/\partial \alpha)_{\alpha f} = Z\mu_{H^+}$ since a change in α implies a change in the number of hydrogen ions in the solution, keeping the number of counter ions constant. The identification of $(\partial F_1/\partial \alpha)_{\alpha f}$ with $Z\mu_{H^+}$ is valid if changes in the charge of the polymer do not directly affect the activities of the small ions. Such a conclusion is reasonable under conditions such that the Debye-Hückel limiting law applies and that the charge attached to the polymer is not mo-

(9) J. R. Huizenga, P. F. Grieger and F. T. Wall, *J. Am. Chem. Soc.*, **72**, 2636, 4228 (1950).

ble and cannot contribute to the effective ionic strength of the solution.

In an entirely analogous manner the equilibrium degree of binding f can be determined from the requirement that the free energy be a minimum with respect to αf , at constant degree of neutralization α . In this case we recognize $-(\partial F_1/\partial \alpha f)_\alpha = Z\mu_{c^+}$ where the remarks of the preceding paragraph again apply. The negative sign arises from the definition of f , since f increases when the number of free counter ions diminishes. The equation corresponding to 2 is

$$\left(\frac{\partial F_1}{\partial \alpha f}\right)_\alpha - F_2' + \left(\frac{\partial F_3}{\partial \alpha f}\right)_\alpha = 0 \quad (3)$$

and the simplifications discussed above enable (2) and (3) to be written as

$$\begin{aligned} Z\mu_{H^+} + F_2' + \left(\frac{\partial F_2}{\partial \alpha}\right)_{\alpha f} &= 0 \\ Z\mu_{c^+} - F_2' + \left(\frac{\partial F_3}{\partial \alpha f}\right)_\alpha &= 0 \end{aligned} \quad (4)$$

The Term F_3 .—To proceed further it is necessary to introduce the specific nature of the free energy F_3 . We shall write F_3 in the form

$$F_3 = Z\alpha(\mu^0_{COO^-} - \mu^0_{COOH}) + Z\alpha f(\mu_{COO^-c^+} - \mu_{COO^-}) - TS_m \quad (5)$$

where S_m denotes the entropy of mixing of the ion pair and un-ionized groups. The standard chemical potentials μ^0 refer to states whose free energy does not include any interaction between the ions of the polymer and the atmospheres of small ions around them. These electrical interactions are, therefore, to be included in F_2 . We may simplify (5) by introducing equilibrium constants for the acid dissociation and ion pair formation processes. Treatment of the ion pair formation as an equilibrium is suggestive of the Bjerrum¹⁰ type ion association and may be regarded as a reasonable assumption if the intrinsic ion pair dissociation constant for an isolated acid anion can be assigned a large value. The acid dissociation constant can be determined by extrapolation of pH measurements to low values of α , for which it will be shown the theory can be greatly simplified. If we let K_a be the intrinsic dissociation constant for the acid and K_s for the ion pair, we may reduce F_3 to

$$F_3 = Z\alpha(-kT \ln K_a - \mu^0_{H^+}) + Z\alpha f(kT \ln K_s + \mu^0_{c^+}) - TS_m \quad (6)$$

We next use the definitions $\mu_{H^+} = \mu^0_{H^+} + kT \ln a_{H^+}$, $\mu_{c^+} = \mu^0_{c^+} + kT \ln a_{c^+}$ and differentiate equation 6 with respect to α and αf . Combining the result with equation 4

$$\begin{aligned} F_2' - ZkT \ln K_a + ZkT \ln a_{H^+} - T \left(\frac{\partial S_m}{\partial \alpha}\right)_{\alpha f} &= 0 \\ -F_2' + ZkT \ln K_s - ZkT \ln a_{c^+} - T \left(\frac{\partial S_m}{\partial \alpha f}\right)_\alpha &= 0 \end{aligned} \quad (7)$$

If a sufficiently detailed model had been adopted to permit evaluation of F_2 , the equations 7 could be used to obtain the potentiometric and binding properties of the polymer in terms of the electrical interactions between its charges. While such a

calculation will be discussed elsewhere¹¹ in conjunction with a specific model for F_2 , it is not necessary to adopt such a detailed model to secure useful results from equation 7. Adding the two equations 7, we obtain after rearrangement

$$pH + \log a_{c^+} = pK_a - pK_s - \frac{0.434}{Zk} \left[\left(\frac{\partial S_m}{\partial \alpha}\right)_{\alpha f} + \left(\frac{\partial S_m}{\partial \alpha f}\right)_\alpha \right] \quad (8)$$

where the pH is given in terms of quantities which are known if the degree of binding of the polyion has been measured.

Entropy of Mixing.—To use equation 8, it only remains to evaluate the entropy of mixing S_m . Since neither the un-ionized groups nor the ion pairs possess net charge, a reasonable first approximation to S_m might be achieved by considering a random distribution of un-ionized and ion paired groups. However, since the nature of the bound state is not understood in detail, it is certainly possible that all distributions of the bound pairs might not be equally probable. For random mixing

$$S_m = -Zk \left[(1 - \alpha) \ln \left(\frac{1 - \alpha}{1 - \alpha + \alpha f} \right) + \alpha f \ln \left(\frac{\alpha f}{1 - \alpha + \alpha f} \right) \right] \quad (9)$$

and the derivatives of S_m with respect to α and αf are

$$\begin{aligned} \left(\frac{\partial S_m}{\partial \alpha}\right)_{\alpha f} &= Zk \ln \frac{1 - \alpha}{1 - \alpha + \alpha f} \\ \left(\frac{\partial S_m}{\partial \alpha f}\right)_\alpha &= -Zk \ln \frac{\alpha f}{1 - \alpha + \alpha f} \end{aligned} \quad (10)$$

Substitution of these expressions for the derivatives into equation 8 yields

$$pH + \log a_{c^+} + \log \frac{1 - \alpha}{\alpha} - \log f = pK_a - pK_s = pK_1 \quad (11)$$

where pK_1 is defined by equation 11.

Comparison with Experiment.—Equation 10 can be compared with experimental results for polymethacrylic acid whose pH at varying degrees of neutralization and counter ion concentration has been measured by Oth and Doty.¹² These authors also studied the extent of binding of the counter ions, but we shall use for binding data the more accurate measurements obtained in polyacrylic acid solutions by Huizenga, Grieger and Wall⁹ based upon transference and diffusion measurements of radioactive sodium ions in the polymer solutions. The structure of polymethacrylic and polyacrylic acids differ only in details which, according to the theory here set forth, should not affect the degree of binding. Confirmation of the similarity in degree of binding between polymethacrylic and polyacrylic acids is available by comparison with the provisional binding data of Oth and Doty. Since the measurements of Oth and Doty were made without adding salt to the polymer solution, the concentration of sodium counter ions is equal to the net charge on the polymer and may be written as the stoichiometric concentration of Na^+ ions multiplied by the factor $1 - f$.

(10) N. Bjerrum, *Kgl. Danske Vid. Selsk., Math.-fys. Medd.*, **7**, no. 9 (1926).

(11) S. A. Rice and F. E. Harris, *This Journal*, **58**, 733 (1954).

(12) A. Oth and P. Doty, *ibid.*, **56**, 43 (1952).

It should be observed that the quantity actually desired for use in equation 11 is the activity of the sodium ions rather than their concentration. Since all the mobile ions in the solution are of the same sign, it is not clear that one should use the Debye-Hückel theory in its usual form to calculate ionic strengths and activity coefficients. Since the correct treatment of the ionic activities under these conditions is a more complicated problem, we defer its consideration and, for the present, replace the activities by concentrations. If the ionic activity coefficients depend significantly upon other parameters than the ionic strength, defined in terms of the mobile ions, the argument leading to equation 4 will also need to be re-examined.

Values of pK_1 , which according to the foregoing should be independent of α and c , were calculated from experimental data and equation 11 and are listed in Table I. The original pH data vary over a range of somewhat more than 3 pH units, and it can be seen that the present treatment has only managed to halve this spread, leaving significant differences between results at low and at high degrees of dissociation. Since the assumptions involved in the deduction of the theory are not strongly dependent in many respects upon the form of the interaction between the various charges of the molecule, one must conclude provisionally that either some important factor governing the behavior of the system has been omitted or that the assumptions regarding the nature of the counter ion binding are incorrect. It should be pointed out that the magnitude of the free energy changes associated with the electrostatic interactions, ionization and binding, do not enter into these conclusions, but that the important factors influencing the present considerations are the assumptions involved in enumerating the probable sites for the binding process.

TABLE I

VALUES OF pK_1 FOR POLYMETHACRYLIC ACID

g./100 cc.	pK_1				
	$\alpha = 0.08$	$\alpha = 0.20$	$\alpha = 0.35$	$\alpha = 0.50$	$\alpha = 0.75$
0.2166	3.90	4.42	4.55	4.90	5.51
.1083	3.73	4.28	4.45	4.81	5.46
.05415	3.59	4.16	4.31	4.65	5.39
.02707	3.35	4.00	4.17	4.48	5.29
.01353	3.20	..	4.03	4.35	5.09

One factor deliberately omitted from consideration was the deviation of the activity coefficients from unity. Although, as was mentioned earlier, we have no unambiguous way of calculating activity coefficients of ions when all the mobile ions are of the same sign, an estimate of the order of magnitude of the change to be expected in pK_1 due to inclusion of activity coefficients may be made by use of the Debye-Hückel theory. If such calculations are made, it is found that the variation of pK_1 with polymer concentration can be drastically reduced, but the change in pK_1 with degree of neutralization is much too large to be accounted for in this manner.

Another Approximation to S_m .—Another possible source of discrepancy between equation 11 and experimental results could reside in the assumption

of random distribution of the bound counter ions and the un-ionized hydrogens. If we retain the assumption that the free energy of the distribution of charges is governed by the distribution of only the net charge of the polyion, we then may introduce non-random mixing of the bound counter ions and hydrogens by assuming, for example, that a bound counter ion cannot be located adjacent to an un-ionized hydrogen. This assumption would be reasonable if the mechanism for binding required the presence of an adjacent ionized (but not necessarily unbound) site on either side of the site where the binding is to occur. Although the statistics of this problem are too difficult to solve in an entirely rigorous manner, an approximate indication may be obtained which will enable us to decide whether a mechanism of this type could explain the discrepancy. We approximate by assuming the centers of net charge to be equally spaced along the polymer chain. The proposed non-random distribution of counter ions and protons then corresponds to filling the spaces between a pair of centers of net charge all with the same species, and therefore the number of possible distributions of protons and counter ions will decrease as the average number of sites between centers of net charge increases. If we calculate the ratio of the number of possible distributions with and without the added restriction, the entropy change upon going from the random mixing to the more restricted situation may be found to be

$$\Delta S_m = Zk(1 - \alpha) \left(\frac{1}{1 - \alpha + \alpha f} - 2 \right) (f \ln f + (1 - f) \ln (1 - f)) \quad (12)$$

The use of equation 12 in addition to 9 causes the additional term

$$\frac{0.434}{Zk} \left[\left(\frac{\partial \Delta S_m}{\partial \alpha} \right)_{\alpha f} + \left(\frac{\partial \Delta S_m}{\partial \alpha f} \right)_{\alpha} \right] = \left(\frac{1}{1 - \alpha + \alpha f} - 2 \right) \left[\left(\frac{1 - f}{\alpha} - 1 \right) \log f - \frac{1 - f}{\alpha} \log (1 - f) \right] \quad (13)$$

to be added to the left-hand side of equation 11.

If the correction implied by (13) is made, the values of pK_1 increase very sharply at low values of α , while remaining substantially unchanged for $\alpha > 0.4$.

If a more moderate restriction of configurations than that which led to equation 13 is considered to be a more appropriate approximation to the true situation, we may employ a restriction on the occupation of sites in a manner which will effect a partial prohibition of occupation of the sites which were formally totally prohibited. If such an approximation were adopted, semi-quantitative calculations indicate that although pK_1 can be made substantially constant in the range $\alpha \leq 0.4$, no such approximation can completely account for the increase in pK_1 at higher degrees of neutralization. The methods outlined above have not led to a value of pK_1 constant to within less than 0.9 unit. The three treatments mentioned above are plotted in Fig. 1. Curve number 1 refers to the case of random mixing, curve 2 to total prohibition and curve 3 to partial prohibition of site occupation.

We, therefore, conclude that there yet remains a significant degree of difference between the model

adopted here for the binding of counter ions by polymeric ions, and the actual experimental situation, as observed in polymethacrylic and polyacrylic acids.

III

While the discussion of the preceding section indicated the close connection between the ionization to be expected of a polyion and the binding by it of counter ions, no indication was given as to the extent to which the binding should occur. While it is not our present task to fully calculate the free energy F_2 of a charged polymer chain, we can introduce forces between ionized groups on adjacent polymer sites, and calculate the entropy of the polymer arising from the distribution of its charge as a function of the net charge of the polyion. The calculations thus proposed do not depend upon the statistical treatment of the dimensions of the coiled polymer and will be valid when the interaction energy between adjacent sites is sufficiently large compared with that between sites further removed from each other. We thereupon write F_2 as a sum, $F_4 + F_5$, where F_4 is the free energy arising from the distribution of charged and uncharged sites, and F_5 is the remainder of F_2 .

We proceed by the method used by Kramers and Wannier for the solution of the very similar one-dimensional Ising spin lattice.¹³⁻¹⁵ Consider the polymer as a chain consisting of Z sites, each of which can be in one of two states, ionized or un-ionized. With each site let us associate a state variable $\eta_i, i = 1, \dots, Z$, where the sites are numbered consecutively along the chain. The η_i may have two values, 0 and 1, $\eta = 0$ referring to an un-ionized state, and $\eta = 1$ an ionized state. We next find it convenient to introduce a function related to a grand partition function, $G(\lambda, T)$

$$G(\lambda, T) = \sum_{\{u_i\}} e^{-\sum u_{i,i+1}/kT} \lambda^{\sum \eta_i} \quad (14)$$

where the summation is to be carried out over all possible values of the η_i . The quantity $u_{i,i+1}$ is the energy of interaction between sites i and $i + 1$, and is equal to χ if both sites i and $i + 1$ are ionized and zero otherwise. Obviously, $u_{i,i+1} = \chi \eta_i \eta_{i+1}$ is a satisfactory form for $u_{i,i+1}$. The quantity λ plays a role analogous to that of an absolute activity serving as a parameter whose value will be determined by the number of charges on the polymer chain.

The evaluation of equation 14 may be performed by the methods used for the one-dimensional Ising lattice. The summations over $\eta_2, \dots, \eta_{Z-1}$ may be regarded as the expression of the matrix product V^{Z-1} , where the matrix V is defined as

$$V_{\eta\eta'} = \lambda^{(\eta+\eta')/2} e^{-\eta\eta'\chi/kT} \quad (15)$$

When the definition equation 15 is used, equation 14 becomes

$$G(\lambda, T) = \sum_{\eta_1, \eta_Z} (V^{Z-1})_{\eta_1, \eta_Z} \lambda^{(\eta_1+\eta_Z)/2} \quad (16)$$

Since the chain is very long, end effects may be neg-

(13) H. A. Kramers and G. H. Wannier, *Phys. Rev.*, **60**, 252 (1941).

(14) L. Onsager, *ibid.*, **65**, 117 (1944).

(15) G. F. Newell and E. W. Montroll, *Revs. Mod. Phys.*, **25**, 353 (1953).

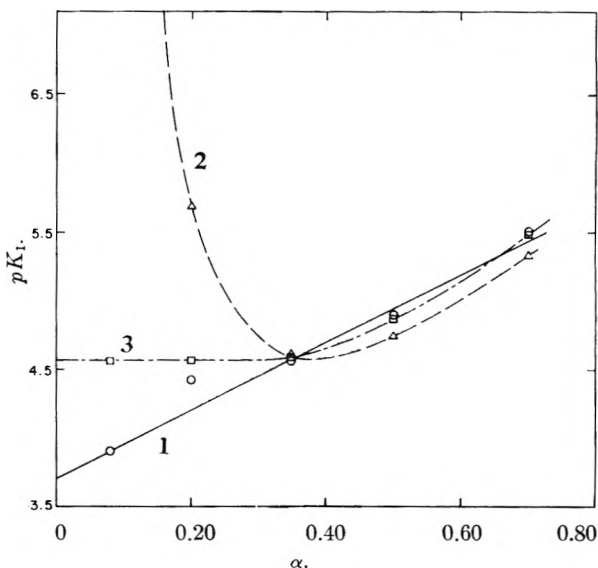


Fig. 1.—Dependence of pK_1 on degree of neutralization. Curve 1 is for random distribution of bound ion pairs and un-ionized sites. Curve 2 is for complete prohibition of occurrence of bound ion pairs on sites adjacent to un-ionized sites, and curve 3 applies when such configurations are permitted with reduced probability chosen to secure optimum constancy of pK_1 .

lected, and quantities which will not produce a large change in $\log G$ may be omitted without error. Therefore, the expression 16 for G may be approximated in terms of the largest eigenvalue, φ , of the matrix V .

$$G(\lambda, T) \sim \varphi^Z \quad (17)$$

The details of proceeding from equation 16 to equation 17 are amply discussed in several places and will not be elaborated upon at this time.^{13,14}

The necessary eigenvalue, φ , of V , is readily obtained by solving the secular equation

$$\begin{vmatrix} 1 - \varphi \lambda^{1/2} & \\ \lambda^{1/2} & \lambda e^{-\chi/kT} - \varphi \end{vmatrix} = 0 \quad (18)$$

Since the elements of V are all positive, the larger eigenvalue is

$$\varphi = 1/2[\lambda u + 1 + \sqrt{(\lambda u + 1)^2 - 4\lambda(u - 1)}] \quad (19)$$

where

$$u = e^{-\chi/kT} \quad (20)$$

Returning to the definition equation 14 of G and using standard statistical mechanical methods,¹⁶ it is possible to see that

$$\left(\frac{\partial \ln G}{\partial \ln \lambda}\right)_T = \alpha' Z \quad (21)$$

using the fact that the most probable value of $\sum_i \eta_i$ may be identified with $\alpha' Z$, the net number of charges of the polyion. One may also find that the free energy may be expressed in the form

$$-F(\alpha') = kT \ln G - \alpha' Z kT \ln \lambda \quad (22)$$

Differentiation of equation 22 with respect to T ,

(16) For a simple discussion see G. S. Rushbrooke, "Introduction to Statistical Mechanics," Oxford Univ. Press, New York, N. Y., 1949.

keeping α' fixed, enables one to obtain the following equation for the entropy

$$S(\alpha') = - \left(\frac{\partial F(\alpha')}{\partial T} \right)_{\alpha'} = k \ln G + kT \left(\frac{\partial \ln G}{\partial T} \right)_{\alpha'} - \alpha' Z \left(\frac{\partial}{\partial T} (kT \ln \lambda) \right)_{\alpha'} \quad (23)$$

Introducing, from equation 17, $\ln G = Z \ln \varphi$, equation 23 becomes

$$S(\alpha') = Zk \ln \varphi + \frac{ZkT}{\varphi} \left(\frac{\partial \varphi}{\partial T} \right)_{\alpha'} - Zk\alpha' \ln \lambda - \frac{Z\alpha'kT}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_{\alpha'} \quad (24)$$

The condition 21, determining λ , may be similarly transformed into

$$\frac{\lambda}{\varphi} \left(\frac{\partial \varphi}{\partial \lambda} \right)_T = \alpha' \quad (25)$$

Equation 24, however, is not yet a convenient form for computation since φ is given by equation 19 in terms of the variables T and λ , whereas the differentiation of φ is required in (24) at constant α' . Accordingly, observing the identity

$$\left(\frac{\partial \varphi}{\partial T} \right)_{\alpha'} = \left(\frac{\partial \varphi}{\partial T} \right)_{\lambda} + \frac{\varphi\alpha'}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_{\alpha'} \quad (26)$$

which follows from the basic rule for partial differentiation and the use of equation 25, we rearrange equation 24 to the form

$$S(\alpha') = Zk \ln \varphi - Zk\alpha' \ln \lambda + \frac{ZkT}{\varphi} \left(\frac{\partial \varphi}{\partial T} \right)_{\lambda} \quad (27)$$

For the quantities in which we are interested, it is necessary to know $1/Z(\partial S(\alpha')/\partial \alpha')_T$. By suitable manipulation of equation 24 and the use of 25, one obtains

$$\frac{1}{Z} \left(\frac{\partial S(\alpha')}{\partial \alpha'} \right)_T = -k \ln \lambda - \frac{kT}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_{\alpha'} \quad (28)$$

Again there appears on the right hand side of (28) a derivative which cannot be taken by direct means. But upon introducing the identity

$$\left(\frac{\partial \lambda}{\partial T} \right)_{\alpha'} = - \left(\frac{\partial \alpha'}{\partial T} \right)_{\lambda} / \left(\frac{\partial \alpha'}{\partial \lambda} \right)_T \quad (29)$$

(28) may be conveniently evaluated.

The resulting equations are

$$\alpha' = \frac{\lambda[u + (\lambda u^2 - u + 2)J^{-1/2}]}{\lambda u + 1 + J^{1/2}} \quad (30)$$

$$J = (\lambda u + 1)^2 - 4\lambda(u - 1)$$

$$\frac{T}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_{\alpha'} = \frac{-u \ln u [1 - \alpha' - \alpha'(\lambda u - 1)J^{-1/2} + J^{-1/2} \{ (2\lambda u - 1)(\lambda^2 u^2 - 2\lambda u + 4\lambda + 1) - (\lambda^2 u - \lambda)(\lambda u^2 - u + 2) \}]}{\alpha'(\lambda u + 1 + J^{1/2}) \left[\frac{1 - \alpha'}{\lambda} + J^{-1/2} (u - (\lambda u^2 - u + 2) J^{-1/2}) \right]} \quad (31)$$

The free energy F_4 is to be defined as arising only from the entropy of the distribution of configurations and is, therefore, given by $-TS(\alpha')$ and not by $F(\alpha')$. The energy terms associated with the interaction between nearest neighbors would have been included in F_4 by directly using the expression of equation 22, but if this energy were included, it would be more difficult to adopt a simple approximation to the energy of interaction F_5 between all the charges of the polymeric chain.

IV

Using the equations 28, 30 and 31, one may proceed to evaluate the contribution of the adjacent

site interaction to the entropy of polyion systems. For a random distribution, $u = 1$, $\alpha' = \lambda/(\lambda + 1)$, and

$$\frac{1}{Z} \left(\frac{\partial S(\alpha')}{\partial \alpha'} \right)_T = -k \ln \frac{\alpha'}{1 - \alpha'} \text{ (random)} \quad (32)$$

The limiting behavior for small u , corresponding to large nearest site interactions, is somewhat more complex. If u is set equal to zero, which implies absolute prohibition of the occupation of adjacent sites by charge, $(\partial S(\alpha')/\partial \alpha')_T$ tends strongly to $-\infty$ as α' approaches 0.5. This behavior is to be expected from the assumed impossibility of charging adjacent sites, in addition to which the charging of alternate sites produces an extremely well ordered state. As will become more apparent when actual numerical values of u are computed, we shall be interested in values of u sufficiently small that the qualitative behavior of $(\partial S(\alpha')/\partial \alpha')_T$ is a great deal like the limiting case just discussed. We, therefore, consider the region $1 \gg u > 0$ in detail.

Equation 30, relating α' with λ , can be simplified for most values of α' . If λ is such that $\lambda u \ll 1$, equation 30 reduces essentially to

$$\alpha' = \frac{2\lambda}{1 + 4\lambda + (1 + 4\lambda)^{1/2}} \quad (33)$$

and the corresponding value of $(T/\lambda)(\partial \lambda/\partial T)_{\alpha'}$ contributes negligibly to the entropy. Inspection of equation 33 shows that values of α' from zero up to nearly 0.5 are included in the range of applicability of equation 33 for sufficiently small u . When $\lambda u = 1$, equation 30 indicates an exact value of $\alpha' = 0.5$ and $(T/\lambda)(\partial \lambda/\partial T)_{\alpha'} = -\ln u$. On the other hand, when λ becomes sufficiently large that $(\lambda u)^2 \gg 0(\lambda)$, equation 30 simplifies to

$$\alpha' = \frac{\lambda u + [(\lambda u)^2 + 2\lambda][(\lambda u)^2 + 4\lambda]^{1/2}}{\lambda u + [(\lambda u)^2 + 4\lambda]^{1/2}} \quad (34)$$

and the equation corresponding in this event to (31) is

$$\frac{T}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_{\alpha'} = \frac{-\lambda u \ln u}{\alpha'(\lambda u + [(\lambda u)^2 + 4\lambda]^{1/2})} \times \left[\frac{1 - \alpha' - \frac{\alpha' \lambda u}{\sqrt{(\lambda u)^2 + 4\lambda}} + \frac{\lambda u(\lambda^2 u^2 + 6\lambda)}{((\lambda u)^2 + 4\lambda)^{3/2}}}{1 - \alpha' + \frac{(\lambda u - (\lambda^2 u^2 + 2\lambda)(\lambda^2 u^2 + 4\lambda)^{-1/2})}{\sqrt{(\lambda u)^2 + 4\lambda}}} \right] \quad (35)$$

It is also apparent that this formulation applies for

values of α' ranging downward from unity to quite close to 0.50.

It should be observed that for any value of u the behavior to be expected in the limit of low α' will approach that of a chain without interaction between charged sites. Therefore, $(\partial F_4/\partial \alpha')_T$ approaches $-T(\partial S(\alpha')/\partial \alpha')_T$ (random), where the latter quantity is given by equation 32. In addition, $(\partial S_m/\partial \alpha')_{\alpha'}$ approaches zero since the number of bound sites goes to zero as may be seen formally from equation 10. The portion of $(\partial F_5/\partial \alpha')_T$ depending upon interactions between charges on the polymer will also vanish in the limit of low α'

TABLE II^a

α'	ENTROPY OF NON-RANDOM DISTRIBUTION OF CHARGE SITES						
	0.25	0.30	0.40	0.444	0.476	0.50	0.75
$-\frac{1}{Zk} \left(\frac{\partial S}{\partial \alpha'} \right)_T$	-0.28	+0.25	+1.80	+2.99	+4.60	+79.6	+160
$-\frac{1}{Zk} \left(\frac{\partial S(\text{random})}{\partial \alpha'} \right)_T$	-1.10	-0.85	-0.41	-0.22	-0.09	0	+1.10
$-\frac{1}{Zk} \left(\frac{\partial(S - S(\text{random}))}{\partial \alpha'} \right)_T$	0.82	1.10	2.21	3.21	4.69	79.6	159

^a $u = 5 \times 10^{-18}$.

and the only contribution to F_2' remaining will be terms of $(\partial F_5/\partial \alpha')_T$ depending upon the interaction of charges of the polymer with their respective ion atmospheres. Because the binding of counter ions becomes unimportant at low degrees of neutralization, α approaches α' and the two quantities may be regarded as interchangeable. In this limit equation 7 simplifies to the equation

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha} + \frac{0.434}{ZkT} \left(\frac{\partial F_5}{\partial \alpha} \right)_T \quad (36)$$

originally derived by Overbeek.¹⁷

V

It is now necessary to investigate the range of u which will actually arise in polyelectrolyte solutions. In polymethacrylic acid (PMA), the carboxyl groups are separated by a distance of approximately 2.5 Å. To complete the calculation of u , it is also necessary to know what value to assign the local dielectric constant of the region between charges on neighboring sites. If adjacent carboxylate ions are in a configuration which places them on opposite sides of the polymer skeleton, the space between them will be occupied by organic matter of dielectric constant of the order of 2.¹⁸ On the other hand, if the charges are in a configuration such that only water could be between them, at most one water molecule would be able to squeeze into the small space between the two large negative ions, and any such water molecule would be unable to orient cooperatively with neighboring water to effect the large dielectric polarization characteristic of the pure substance. In view of this situation, we have chosen the value 5.5 for the local dielectric constant¹⁹ because it is of the order of magnitude of the polarization which may be attributed to water molecules not free to orient in an electric field. Since the dielectric constant of the polymer skeleton is less than 5.5, the value chosen provides a useful lower bound to the energy of interaction. Furthermore, the calculations will be found to be not at all sensitive to the exact value chosen for the interaction energy when it is large compared with kT . In PMA the interaction energy will be $\chi = \epsilon^2/Dr = 39.8kT$. The corresponding value of u is 5×10^{-18} .

A few values for $(\partial S(\alpha')/\partial \alpha')_T$ calculated from equations 28 and 33 to 35 are shown in Table II. The values clearly indicate a large decrease in entropy as the fraction of charged sites approaches

0.5, and show that the reduction of net charge by binding of counter ions can effect a substantial decrease in free energy from the entropy of mixing of charged and uncharged sites.

The treatment of the entropy of mixing of charged and uncharged sites described here is based on the assumption that only charges on adjacent sites can interact. The inclusion of the effect of forces between sites not immediately adjacent to each other will, of course, further increase the free energy at higher fractions of net charge but by amounts which should be much less than the corresponding quantities in Table II since the greater distance between sites and the increased effective dielectric constant at this distance will greatly reduce the magnitude of the interaction. Due to the difficulty of the calculation, we have not been able to more quantitatively estimate the error made by omission of further interactions.

The deviations of the free energy of mixing from the values obtained in the absence of interaction between sites are also shown in Table II. If equation 36 is used to proceed from experimental pH data to values of $1/Z(\partial F_5/\partial \alpha')_T$ and the latter identified with $\epsilon\psi$, where ψ is the "potential" in the solution, values of $\epsilon\psi/kT$ are obtained. Many approximations involving electrostatic interactions in the solution depend for their validity, or rapid convergence, upon the magnitude of $\epsilon\psi/kT$. We are now in a position to observe that the actual values of $\epsilon\psi/kT$, assuming that all the contributions to F_5 are electrical in nature and that the identification $1/Z(\partial F_5/\partial \alpha')_T = \epsilon\psi$ is a good approximation will be lower than the value calculable using equation 36 by the deviation in the entropy of mixing of charged and uncharged sites from its ideal value. By consultation of Table II, we can see that there will be a large difference between values of $\epsilon\psi/kT$ calculated including, or neglecting, the non-ideality of the entropy of mixing.

VI

The preceding discussion which has dealt first with the general framework of the thermodynamics of polyelectrolyte solutions, and secondly with the entropy of mixing of charged and uncharged sites upon the polymer, indicates clearly the general pattern of behavior of the polyions. From the relations between the degree of binding to be expected of a polyion and its neutralization characteristics, it has been possible to see that the presence of extensive binding must be symptomatic of strong electrostatic forces which must be considered if an adequate theory of polyelectrolyte systems is to

(17) J. T. G. Overbeek, *Bull. soc. chim. Belges*, **57**, 252 (1948).

(18) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

(19) J. B. Hasted, D. M. Ritson and C. H. Collie, *ibid.*, **16**, 1 (1948).

be formulated. An attempt was made to quantitatively relate the potentiometric and binding data for a polyacid, and the lack of total success in so doing must be taken as an indication that not all significant factors pertinent to the theory have been completely evaluated.

The entropy of mixing of charged and uncharged sites on the polymer chain was evaluated using a nearest neighbor approximation and showed that this effect is large enough to be of great importance. Since this contribution to the free energy is omitted if the conventional expression 36 for the potential is used, potentials calculated in that manner will be too high by a very significant amount. It is apparent from the discussion of the present paper that the most desirable procedure would be to compare the theory with an experimental result such as the pH rather than to compare with another quantity whose calculation depends upon assumptions as tenuous as the main body of the theory itself.

In the following paper we proceed to evaluate the free energy term, F_6 , and calculate the expansion and degree of binding of some polyelectrolyte solutions, making the additional assumptions necessary to more completely describe a satisfactory model for the polyion systems.

Acknowledgments.—We wish to thank Drs. Bartholemew Hargitay and Alfred Holtzer for a valuable discussion of the contents of this paper. We are also indebted to Professor Paul M. Doty for his interest in this work and for critically reading the manuscript.

DISCUSSION

H. MORAWETZ (Polytechnic Institute of Brooklyn).—The binding of counter-ions quoted by Professor Wall is an operational concept defined in terms of an electrophoresis experiment. As a matter of fact, the fraction of counter-ions found to travel with the polyions would probably be appreciably sensitive to the potential gradient used. It seems to me, therefore, that it is rather difficult to correlate these results with the equilibrium properties of a polyelectrolyte. In any case, we certainly do not know how close an

approach of the counter-ion to the poly ion charge is implied by the "binding" as defined by Wall's experiments.

F. E. HARRIS.—The model used by us for counter-ion binding is admittedly crude and, as we pointed out, does not completely reproduce the experimental situation. However, the main purpose of the present exposition is to discuss qualitatively, or at best semi-quantitatively, the various contributions to the thermodynamic functions arising from binding so as to see whether the gross properties of polyelectrolyte solutions can be explained in terms of concepts now understood. While the "binding free energy" will certainly depend upon the exact distance of closest approach between counter ions and polymer, many features of the present development depend only upon an assumed correspondence between sites for ionization and for binding. In fact the binding free energy was left as a parameter to be determined from the experimental data. We believe that, as also pointed out by Prof. Hermans (see discussion after the next paper) a more serious question could be raised as to the adequacy of the site hypothesis for the binding.

R. A. MARCUS (University of Maryland).—I should like to mention another treatment (THIS JOURNAL, 58, 621 (1954)) similar in several respects to the one presented here. It considered the titration behavior of these polymeric acids from the viewpoint of nearest neighbor repulsions between like charges on the polymer chain. It was felt there that such an approximation would be justified only at the higher ionic strengths for only then would this interaction between the fixed charges fall off sufficiently rapidly with distance r_1 roughly as e^{-kr}/r . Further, with certain reservations, it is to be expected that the change in the pK value of the polymeric acid going from 0 to 100% neutralization would be related to the difference of the first and second dissociation constants of the corresponding dibasic acid. This was observed to be the case at higher ionic strengths. Under such conditions the difference between the Ising model and the simpler model which assumes a random mixing of neutralized and unneutralized acid groups on the polymer chain was estimated there to be small.

In connection with the remark concerning the "binding" of the counter-ions of a polyelectrolyte, as reflected by the electrical transference properties observed by Wall (*J. Am. Chem. Soc.*, 72, 2636 (1950)), a somewhat different approach toward this behavior also might be used. In many of the theoretical models of these systems, one usually regards the polymeric ion and its counter-ions as being in a volume equal to the total volume of solution divided by the number of macro-ions. If ψ denotes the potential difference (arising from these ionic charges) between the boundary of this volume and any region within it, then it seems reasonable to regard as "bound" all counter-ions within regions for which $|e\psi/kT| = 1$, as a rough approximation.

A CHAIN MODEL FOR POLYELECTROLYTES. II

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The chain model for polyelectrolytes proposed in the preceding paper is further developed by considering in more detail the electrostatic interaction energy between the charges of the polymer. It is pointed out that not all of the electrostatic energy is effective in expanding the polymer and that the weighting of the probability of the configurations must depend upon factors other than their end-to-end distances. Expansions are calculated assuming that only nearest neighboring links of the polymer chain interact to alter the distribution of lengths. Calculated and experimental expansions are compared for carboxymethylcellulose and polymethacrylic acid. The results for CMC are in good agreement with the theory while those for PMA deviate in the direction expected if significant higher order interactions were omitted. The degree of binding of counter ions is also calculated and compared with experimental values for polyacrylic acid. It is found that the calculated degree of binding is not very sensitive to the approximations used and semi-quantitative agreement with experiment is obtained. The discrepancy is of the right sign and magnitude to be interpreted in terms of further interactions whose effect was neglected in the present calculations.

I. Introduction

In a preceding paper² it has been pointed out that the use of spherical models of polyions modifies the free energy in a manner which cannot be quantitatively calculated. In addition, the models employed by Hermans and Overbeek,³ Kimball, Cutler and Samelson,⁴ Flory,⁵ and Kagawa⁶ lead to results which are not altogether in satisfactory agreement with experiment. On the other hand, the use of a chain model in which the probability of any configuration is assumed to depend only upon its end-to-end extension is also found to lead to results which differ markedly from experiment.⁷ The two most objectionable approximations of this random chain model are, first, the inclusion with undiminished statistical weight of all configurations of the polyion with the same end to end distance, and, second, the assumption that it is the total electrostatic interaction energy which is capable of causing the polyion to expand. In actuality, the configurations will be weighted according to the amount of local kinking, those configurations which place large amounts of chain close together occurring with far less than their random *a priori* probability. When using the concept of statistical element, care must be taken that one does not think that the last monomer in a given element is independent of the first in the next element. Such a conclusion, of course, is not true since there is a constant bond angle between the two monomer units. However, it is just such interactions as these between charges situated on adjacent monomers that constitute a large part of the total electrostatic interaction energy. Therefore, far less than the total interaction energy is effective in expanding the polymer coil.

In order to remove the first of these approximations, we shall find it advantageous to proceed

by introducing, step by step, the interaction between the charges of the polyion, rigorously calculating the change in the distribution of configurations at each step of the process. The method we shall employ to introduce interactions between the charges will be to consider, first, pairwise interactions between nearest neighbor links of the polymer chain, then those between the charges on next nearest neighbor links, and so forth. While we will be unable to evaluate the results of the higher approximations, such a scheme will provide, conceptually at least, a mechanism by which any desired approximation to the actual behavior of the polyion chain can be calculated. By the use of the methods of statistical mechanics, the angular correlation between a link of the polymer chain and the preceding links can be evaluated, and the theory of random flight processes with partial correlations⁸ employed to calculate the resulting distribution of molecular lengths. These statistical mechanical methods will also enable us to evaluate the thermodynamic functions of the polymer coil.

When calculating the expansion of the polyion from the extension characteristic of an uncharged polymer chain, it is assumed that the actual distribution of charges on the polymeric chain can be replaced by an average distribution characterized by an equal spacing between the charges of the polyion. Although such an approximation should be relatively good for most purposes, since this uniformly charged configuration is also the most probable one, the approximation is not adequate for calculating the entropy arising from the various possible choices of charged and uncharged ionizable groups. It is, therefore, necessary when evaluating the thermodynamic functions of polyelectrolyte solutions to include in the entropy of the chain molecule the contribution arising from the actual distribution of charged and uncharged sites on the polyion. The methods by which this aim can be accomplished have been discussed in the preceding paper of this series.

The calculations of the preceding paper indicate that the entropy decreases so rapidly at high degrees of ionization that binding of counterions by the polyion must occur when a large proportion of the ionizable portions of a polyacid are removed. The entropy involved when binding occurs is so

(1) Union Carbide and Carbon Fellow, 1953-1954.

(2) F. E. Harris and S. A. Rice, *THIS JOURNAL*, **58**, 725 (1954), hereinafter sometimes referred to as part I.(3) J. J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).(4) G. E. Kimball, M. Cutler and H. Samelson, *THIS JOURNAL*, **56**, 57 (1952).(5) P. J. Flory, *J. Chem. Phys.*, **21**, 162 (1953).(6) F. Osawa, N. Imai and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1954).(7) (a) W. Kuhn, O. Künzle and A. Katchalsky, *Helv. Chim. Acta*, **31**, 1994 (1948); A. Katchalsky, O. Künzle and W. Kuhn, *J. Polymer Sci.*, **5**, 283 (1950); A. Katchalsky and S. Lifson, *ibid.*, **11**, 409 (1953), and references quoted therein; (b) F. E. Harris and S. A. Rice, *ibid.*, **12**, in press (1954).(8) C. M. Tchen, *J. Chem. Phys.*, **20**, 214 (1952).

far from that of a random distribution of ionized and un-ionized groups that there is a serious question as to the significance of comparing thermodynamic data with theoretical quantities calculated omitting a good treatment of this effect. Since such a treatment depends crucially upon the interaction energy between ions at very small separations along the polymer chain, it is not justifiable to approximate the interaction as that between point charges in a continuous dielectric.

II

The model for a polyion upon which the following discussion will be based consists of a chain of N "statistical elements" or links, each of length A and net number of charges ζ , connected together at the ends by universal joints. By a statistical element is meant a number of monomer units such that the mean square length h_0^2 of a similar but uncharged polymer coil is correctly given by the random flight formula⁹

$$h_0^2 = NA^2 \quad (1)$$

The statistical element will differ from the real monomer unit in such a way as to take into consideration fixed bond angles, hindered rotation, etc., but not the effect of the charges. Since the idea of a statistical element has been introduced to take into account the local orientational order caused by forces common to both the charged and uncharged polymer, it would be contrary to the spirit of the present model to assume that the behavior of a statistical element when charged should affect its length.

If we consider each possible configuration of the chain as being built up by successively adding links to the chain, the probability of adding the j th link in a given relative orientation to the preceding links will be governed by the energy of interaction of the charge of the j th link with links $j - 1, j - 2, \dots$. If the interaction between links falls off sufficiently rapidly as they become separated on the chain, the sequence of approximations to the distribution of configurations generated by successively considering interactions between sets of segments separated on the chain by increasing numbers of units will converge. The first such approximation, after that of the completely random chain, is provided when one assumes the configuration of each link to depend only upon the one added immediately before it. Such a dependence generates a Markoff process,¹⁰ and it can be concluded that the distribution of lengths becomes gaussian in the limit of large N with the average end-to-end distance increasing as $N^{1/2}$. The higher approximations are also Markoff processes but with the number of polymer segments per Markoff unit increasing to two, three, etc. These approximations, therefore, correspond to Markoff chains in higher dimensional vector spaces.

One must not conclude, however, that in general a sequence of approximations of the type described, each defining a Markoff process, converges to a Markoff process in the limit of increasing number of

interacting links. We are assuming here that the interaction between successive links falls off sufficiently rapidly to render such a conclusion tenable. Similar considerations indicate that the limiting dependence upon the degree of polymerization of the size of chain molecules composed of links of non-zero volume cannot be ascertained by this type of approximation unless the method is known to be convergent to a Markoff process.

In view of the rapidly increasing mathematical complexity as one proceeds to higher approximations, we shall confine the more detailed discussion to the case of nearest neighbor interaction only. After finding to what extent modification of the random flight distribution occurs, one may then ask whether proceeding to higher approximations is worthwhile. It should be emphasized, however, that proceeding to higher approximations requires no fundamentally new development, but merely necessitates more tedious calculations.

In order to complete the specification of the model described here, it is necessary also to consider the interactions between the charges on monomer units of the same statistical element. These interactions will of necessity depend upon the net degree of ionization of the polymer and when there are several charges per statistical element, intra-element interactions will make the major contribution to the potential. Means of evaluating the interaction energy within a statistical element will be discussed individually for the various polymeric species concerned.

III

We are now ready to consider more explicitly the nearest neighbor approximation. We find it convenient to discuss separately the end to end extension of the polyion and its free energy.

Expansion of Polyions.—Since the only interaction between links of the polymer is assumed to be the electrostatic force directed along the lines connecting the charges of a pair of neighboring links, the distribution of orientations of any link will be axially symmetric with respect to the preceding link. In this case the correlation between the orientations of successive links can be defined as the average value of the cosine of the angle γ between the vectors specifying the directions of the successive elements. Writing $\langle \cos \gamma \rangle = c$ it is possible to show⁸ that the average square length h_1^2 approaches, for large N , the value

$$h_1^2 = h_0^2 \left(\frac{1+c}{1-c} \right) \quad (2)$$

Since the distribution of lengths is Gaussian, it is given by the formula⁸

$$V(h) dh = \left(\frac{3}{2h_1^2} \right)^{3/2} \frac{4h^2}{\sqrt{\pi}} e^{-\frac{3h^2}{2h_1^2}} \quad (3)$$

where $V(h) dh$ is the probability that the end-to-end distance is in the range from h to $h + dh$. It should be emphasized that the simple formula 2 only applies when there is axial symmetry.

The evaluation of c may be accomplished by the standard methods of statistical mechanics,¹¹

(9) For a discussion of random flight processes, see S. Chandrasekhar, *Revs. Mod. Phys.*, **15**, 1 (1943).

(10) J. Doob, "Stochastic Processes," John Wiley and Sons, Inc., New York, N. Y., 1953.

(11) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940.

$$c = \langle \cos \gamma \rangle = \frac{\int \cos \gamma e^{-u(\gamma)/kT} d\Omega}{\int e^{-u(\gamma)/kT} d\Omega} \quad (4)$$

where $u(\gamma)$ is the potential energy of interaction between the charges on adjacent chain segments. The integral of (4) is understood to be extended over all orientations, and $d\Omega$ is the element of solid angle. If the interaction energy $u(\gamma)$ is written as the sum of the contributions of pair potentials, and the interactions between a pair of charges is approximated by a screened Coulomb potential

$$u(\gamma) = \sum_{i,j} \frac{\epsilon_i \epsilon_j e^{-\kappa r_{ij}(\gamma)}}{D r_{ij}(\gamma)} \quad (5)$$

where the summations are to be extended over all net charges i on one statistical element, and all net charges j of the other, ϵ_i is the magnitude of charge i , D the dielectric constant of the medium, and $r_{ij}(\gamma)$ is the distance between charges i and j when the angle between their statistical elements is γ . The screening constant may be taken as the reciprocal Debye length, κ , and is given by¹²

$$\kappa^2 = \frac{4\pi e^2}{DkTV} \sum_i n_i \quad (6)$$

where the n_i refer to the number of ions of type i in the solution, per macromolecule, and V is the volume per polymer molecule.

Equation 5 is not in a convenient form for actual use in finding $u(\gamma)$ and, more important, the exact location of the various charges on the statistical element is not generally known. We, therefore, will approximate equation 5 by moving all the net charge of each statistical element to its center. In this approximation

$$u(\gamma) = \frac{\zeta^2 e^2 e^{-\kappa r_{ij}(\gamma)}}{D r_{ij}(\gamma)} \quad (7)$$

$$r_{ij}(\gamma) = A \cos \left(\frac{\gamma}{2} \right)$$

The extent of the approximation in going from equation 5 to equation 7 depends upon at least two factors. The first of these resides in the approximation inherent in the use of the concept of "statistical element," and is due to the fact that the charges near the end of a statistical element cannot have their full effect as indicated by equation 5 in forcing orientation of the next statistical element because the actual molecule cannot bend sharply at a given point while the model can. Indeed though a major portion of the electrostatic interaction energy arises from the interactions of adjacent charges, this part of the energy is completely ineffective in expanding the polyion due to the constant bond angle between adjacent monomers. In fact the first segment on which the interaction can have any orienting effect at all is a next nearest neighbor and this effect may be markedly reduced if there is a large potential restricting rotation about the monomer-monomer bond. A second approximation which we can qualitatively evaluate is the change in electrostatic interaction which occurs when a group of charges, situated at points of the statistical element, are replaced by the sum of their charges at their centroid. Since, as mentioned earlier, charges less than a sta-

tistical element apart cannot exert their full force toward expanding the chain, the approximation of lumping the charge should largely cancel that of overestimating the effective interaction of neighboring charges. To examine the probable size of this effect which will decrease the electrostatic interaction, we may approximate the location of the charges of each statistical element by a set of equally spaced charges on a line. The difference between $u(\gamma)$ as calculated by a single charge model and the distributed charge model is discussed in connection with the various experimental results.

Thermodynamic Functions of Polyions.—While treatment of the polyion expansion as a Markoff process enables its distribution of lengths to be determined, such considerations do not facilitate determination of the thermodynamic functions. For this purpose we will divide the free energy of the polyelectrolyte solution into a number of parts in the manner indicated in the preceding paper. We shall at once specialize to polyacids, noticing that for polymeric bases an analogous development can be made.

The first contribution to the free energy, F_1 , is that of the free hydrogen ions and counter ions eligible to take part in binding and neutralization phenomena. The second term, F_2 , is the sum of the contributions of the electrostatic interactions of the polyion with itself and with the small ions. The third term, F_3 , is the free energy change that accompanies the processes of binding and dissociation, together with the contribution of the entropy of mixing of bound and undissociated sites.

The division of the free energy of the polymer into parts F_2 and F_3 depends upon the assumption that the electrostatic effect of binding can be regarded merely as a reduction in net charge of the polymer. In addition the evaluation of F_3 requires further assumptions regarding the binding process. The nature of these assumptions and the probable extent of their validity have been discussed in part I.

F_1 will be a function of a_{H^+} , the activity of the free hydrogen ions in the solution, and a_{c^+} , that of the counter ions. F_2 will be expressible in terms of the net fraction of charge, α' , of the polymer chain. α' is related to α , the degree of dissociation of the polymer, by the formula $\alpha' = \alpha(1 - f)$, where f is the fraction of the dissociable groups bound by counter ions. In this notation, ζ , the number of charges per statistical element is expressible as $\zeta = \alpha'Z/N$. F_3 will depend upon α and f separately as well as upon the dissociation constants, K_a and K_b for the acidic groups and bound ion counter ion pairs, respectively. We may summarize much of the above in the equation

$$F = F_1(a_{H^+}, a_{c^+}) + F_2(\alpha') + F_3(\alpha, f, K_a, K_b) \quad (8)$$

Following the notation of the previous paper we will further subdivide F_2 such that

$$F_2 = F_4 + F_5 = F_4 + F_6 + F_7 + F_8 \quad (9)$$

where F_4 is the contribution to the free energy arising from the entropy of the statistical distribution of the net charge of the polymer among the sites on the chain. F_6 arises from the interaction between statistical elements and here will be approximated

(12) See for example H. Falkenhagen, "Electrolytes," Oxford University Press, New York, N. Y., 1934.

as being satisfactorily described by terms including only the interaction of nearest neighboring statistical elements. To calculate F_6 , it is convenient to consider the set of angles $\{\gamma_{i,i+1}\} \equiv \{\gamma_i\}$ between the orientation of the succeeding statistical elements. The $\{\gamma_i\}$ are independent, as follows immediately from the limitation of interaction to nearest neighboring elements. In addition, the $\{\gamma_i\}$ suffice to determine the energy of the system of interacting links. They are, therefore, suitable quantities to use in a statistical mechanical ensemble. We may define a configuration partition function, Q , by the formula

$$Q = \int e^{-u(\gamma)/kT} d\Omega \quad (10)$$

and the change in free energy, F_6 , resulting from the introduction of the interaction $u(\gamma)$ will be¹¹

$$F_6 = -NkT(\ln Q - \ln Q^0) \quad (11)$$

where Q^0 refers to the value of Q when $u(\gamma)$ is zero. By direct integration we know $Q^0 = 4\pi$, so

$$F_6 = -NkT \ln \left(\frac{Q}{4\pi} \right) \quad (12)$$

F_7 is the free energy change accompanying the building up of ion atmospheres about each of the ions of the system. We take this as¹²

$$F_7 = - \frac{\epsilon^2 \kappa \alpha' Z}{3D} \quad (13)$$

It must be emphasized that equation 13 probably holds when the ionic strength is due to added salt. When the only ionic strength is that due to the counterions of the polyion itself, the situation is not presently clear as to the proper status of equation 13. This uncertainty arises from the use of the Debye-Hückel equation when the negative ions are immobile. Thus, though each fixed negative ion may have an atmosphere of positive ions about it, the positive ions do not have an atmosphere of negative ions about them in the manner prescribed by the Debye-Hückel theory.

Finally, it is necessary to add the free energy, F_8 , of the electrostatic interaction within the statistical elements. The explicit form of F_8 will be determined by the model chosen for the statistical element. To calculate F_8 , we use a crude model in which the charges are assumed to be equally spaced in a straight line along the statistical element. F_8 is then given by the sum over all pairs of the pair interaction energy and may be conveniently written as

$$F_8 = \frac{Ne^2 \zeta}{DA} \sum_{j=1}^{\zeta} \left(\frac{\zeta - j}{j} \right) e^{-j\kappa A/\zeta} \quad (14)$$

To proceed to a calculation of the potentiometry or degree of binding of the polyion, we shall find it necessary to obtain derivatives of the various terms of F_2 with respect to the fraction of net charges α' . Carrying out the indicated differentiations we obtain

$$\frac{\partial F_6}{\partial \alpha'} = \frac{2Z}{\zeta} \frac{\int u(\gamma) e^{-u(\gamma)/kT} d\Omega}{\int e^{-u(\gamma)/kT} d\Omega} \quad (15)$$

$$\frac{\partial F_7}{\partial \alpha'} = - \frac{\epsilon^2 \kappa Z}{3D} \quad (16)$$

$$\frac{\partial F_8}{\partial \alpha'} = \frac{\epsilon^2 Z}{DA} \sum_{j=1}^{\zeta} \left(\frac{2\zeta}{j} - 1 - \kappa A + j \frac{\kappa A}{\zeta} \right) e^{-j\kappa A/\zeta} \quad (17)$$

It should be noted that equations 14 and 17 are not well defined for non-integral values of ζ and are to be regarded as replaced by appropriate continuous functions for non-integral ζ .

The remaining contribution to $\partial F_2/\partial \alpha'$, namely $\partial F_4/\partial \alpha'$, is given by equations 28, 30 and 31 of part I. The conditions determining the potentiometry and the binding of counter-ions of the polymeric electrolyte are obtained by minimizing the free energy under appropriate conditions. The results are given in equation 7 of part I.

$$- \frac{\partial F_2}{\partial \alpha'} + ZkT \ln K_s - ZkT \ln a_{e^+} - T \left(\frac{\partial S_m}{\partial \alpha'} \right)_{\alpha} = 0 \quad (18)$$

$$+ \frac{\partial F_2}{\partial \alpha'} - ZkT \ln K_a + ZkT \ln a_{H^+} - T \left(\frac{\partial S_m}{\partial \alpha'} \right)_{\alpha_f} = 0$$

The terms involving S_m , the entropy of mixing of bound ions and undissociated sites, arise from the free energy term F_3 . Expressions for the derivatives indicated in equation 18 may be found as equation 10 of Part I.

IV

The experimental quantities usually compared with a theory of polyelectrolyte behavior are the expansion of the polyion as a function of ionic strength, and the potential as determined from a relation between the pH of the solution, a constant characteristic of the dissociating group, and the free energy of mixing of the ionized and un-ionized sites. The expansion of the polyions is a good test of the theory since its experimental determination is completely independent of any assumptions concerning the behavior of polyelectrolytes in solution. On the other hand, the usual comparison of theoretical and experimental potentials is not a good test. The accepted relation between the thermodynamic functions of the polyion, the pH and the degree of dissociation is¹³

$$pH = pK_0 - \log \frac{1 - \alpha}{\alpha} + 0.434 \frac{\epsilon \psi}{\kappa T} \quad (19)$$

where K_0 is the ionization constant of the dissociating groups in the absence of the interference of electrostatic interactions and ψ is the electrostatic potential of the polyion. The potential as defined by (19) is related to the electrostatic free energy (i.e., F_5 of the present development) by $(\partial F_5/\partial \alpha)_{\kappa} = Z\epsilon\psi$. Equation 19 implies random distribution of charged and uncharged sites, and we have shown² on the basis of a model employing interactions between neighboring charge groups that the entropy of mixing of such a system, while approaching the ideal value for low degrees of ionization, deviates considerably and to an increasing extent as the degree of ionization increases. In order to calculate the potential, it is necessary to account quantitatively for the entire electrostatic free energy of the polyion. To do this correctly, the treatment must include those contributions arising from binding and other non-ideal effects as well as the more obvious electrostatic terms. However, it is not suitable merely to reduce the degree of neutralization to compensate for the binding and then use equation 19 since the binding is symptomatic of something fundamentally wrong with the assumptions inher-

(13) J. T. G. Overbeek, *Bull. soc. chim. Belges*, **57**, 252 (1948).

ent in the use of equation 19. Thus, all of the data in the literature obtained from experimentally observed pH values which were then converted to values of $e\psi/kT$ by means of relation 19 are certainly at best inapplicable to test any theory and at worst completely incorrect. The correct relation between the pH and the electrical properties of the polyion was discussed in paper I of this series.

The potential has been shown² to be intimately related to the degree of binding of counter ions by the polyion and, therefore, it suffices to compare either the pH of the solution or the degree of binding with experimentally observed values. The second test of the theory to be applied here, then, will be the agreement of the calculated values of the binding with those directly observed experimentally by transference or diffusion measurements.

Binding.—The extent of binding was evaluated assuming that the entropy of mixing, S_m , of bound ion pairs and un-ionized sites is given by the ideal solution expression. $(\partial S_m/\partial \alpha)_{af}$ is then given by equation 10 of paper I. Equation 18 of the present paper was then solved by an iterative procedure assuming a value of 10 for K_s . It was found that the value of K_s chosen does not seriously affect the results since $(\partial F_2/\partial \alpha')$ varies extremely rapidly with α' for the values of α' with which we are concerned. The major contributions to $(\partial F_2/\partial \alpha')$ are found to arise from the interactions within the statistical element included in F_3 , and from the non-random mixing term F_4 . For this reason the amount of binding will increase sharply as the distance between neighboring charges is decreased. One might, therefore, expect that the amount of binding in carboxymethylcellulose (CMC), where the sites are 5 Å. apart,¹⁴ would be less than that observed under corresponding conditions for polyacrylic acid (PAA) where the sites are separated by but 2.5 Å. A serious difficulty in evaluation of the necessary free energy terms depends upon the choice to be made for the effective dielectric constant between a pair of charges only a few angstroms apart. This small space will undoubtedly be partially occupied by other portions of the polymer molecule, which as Kirkwood and Westheimer¹⁵ have indicated, should be recognized explicitly as having a much lower dielectric constant than the bulk of the aqueous medium. It should also be remembered that even in the absence of polymer chain between charges the decrease in dielectric constant for the water molecule in such close proximity to ions would be most important.¹⁶ For the reasons enumerated in the preceding paper, we have chosen the value 5.5 for the local dielectric constant.

Binding for PAA calculated according to the above discussion is listed together with the experimental values¹⁷ in Table I. It will be observed that the calculated binding decreases faster than

the experimental findings indicate it should. A possible explanation of this deviation is the neglect of higher order interactions between the charged groups. At high α' this omission makes little difference since there is a large decrease in the pair interaction energy on going from nearest to next nearest neighboring pairs. This decrease is due to both the increased distance between the charges and the increase in effective dielectric constant at the larger distance. On the other hand, at low α' , the charges are on the average further apart, and the further neighbors contribute proportionally more of the total interaction. Since the difficulty of extending the calculations to include next nearest neighboring sites is considerable, we must be content with the eminently satisfactory qualitative agreement now obtained.

TABLE I
COMPARISON OF THE CALCULATED AND OBSERVED BINDING
IN POLYACRYLIC ACID

	$\alpha = 1$	$\alpha = 0.5$	$\alpha = 0.2$
Exptl. ¹⁷	0.63	0.45	0.20
Calcd.	0.65	0.36	~0.0

Expansion. 1. **Sodium Carboxymethylcellulose.**—Data on CMC were taken from the work of Dr. N. Schneider¹⁸ who has conducted an extensive investigation of the size and shape of CMC as a function of ionic strength using light scattering, viscometric, potentiometric and various other appropriate techniques. A short description of the methods we used to obtain the data required for the calculation is not out of place at this time.

From the observed weight average molecular weight and assuming that the polydispersity could be adequately accounted for as a Flory distribution,¹⁹ the z average molecular weight was calculated from the relation $M_z = 1.5M_w$. From the z average molecular weight, the z average contour length L was obtained. The value of the unperturbed polymer size was determined by extrapolation of the light-scattering data to infinite ionic strength and was found to be 2100 angstroms for a polymer of weight average molecular weight 435,000. The Kuhn statistical element length²⁰ can then be calculated by solving the simultaneous equations

$$\begin{aligned} h_0^2 &= NA^2 \\ L &= NA \end{aligned} \quad (20)$$

In this manner A was found to be 335 angstroms. The polymer was characterized as possessing 1.1 carboxyl groups per 5.1 angstroms and the degree of neutralization was 0.96.

The expansion factor h_1/h_0 was calculated by the use of equations 2 and 4. The integrals necessary to evaluate (4) were computed numerically by means of a 20-point interpolation formula, and equation 7 was used for the function $u(\gamma)$. D was taken as 80. A comparison of the experimental values of h_1/h_0 with the ones calculated assuming no binding is given in Table II. It can be seen that

(18) N. Schneider, Thesis, Harvard University, February, 1954.

(19) For a discussion of the distribution of molecular weights arising from condensation polymerization see P. M. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(20) W. Kuhn, *Kolloid Z.*, **76**, 258 (1936); **87**, 3 (1939).

(14) The properties of this sample of CMC are further discussed in succeeding paragraphs.

(15) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(16) J. B. Hasted, D. M. Ritson and C. H. Collie, *ibid.*, **16**, 1 (1948).

(17) J. R. Huizenga, P. F. Grieger and F. T. Wall, *J. Am. Chem. Soc.*, **72**, 2636, 4228 (1950).

at low ionic strengths the calculated expansion is too large in spite of the fact that the method used would be expected to give a lower value than that actually observed. But we have already seen in part I that the interactions between neighboring charge sites on the polymer chain will make it impossible to remove all the sodium ions from the chain. This binding reduces the effective charge per statistical element, thereby decreasing the interaction between elements. In Table II we have also listed the calculated expansions for 33% and 67% binding and have plotted all the data of the table in the accompanying graph (Fig. 1).

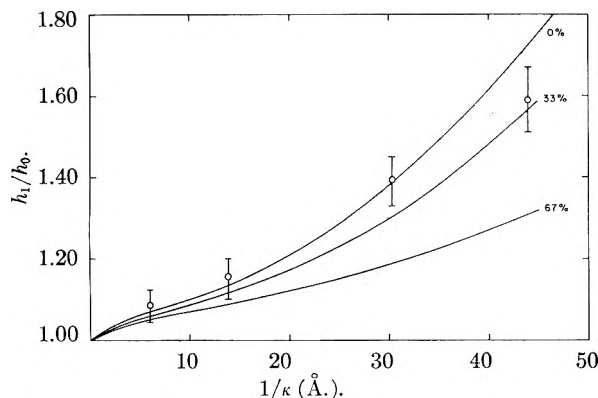


Fig. 1.—Expansion of sodium carboxymethylcellulose as a function of ionic strength. The curves are calculated assuming the amounts of counter ion binding indicated. The circles are experimental points.¹⁸ Top curve, 0%; middle curve, 33%; bottom curve, 67%.

While the experimental error of approximately 10% does not permit a decisive choice at higher ionic strengths, the data at low ionic strength points to a small amount of binding, probably somewhat less than 33%. This conclusion is in accord with our discussion of binding where we suggested that the extent of binding in CMC should be less than that in PAA. The extent of binding observed for PAA at complete stoichiometric neutralization is about 63%.¹⁷

TABLE II

COMPARISON OF THE CALCULATED AND EXPERIMENTAL EXPANSION FACTORS h_1/h_0 FOR SODIUM CARBOXYMETHYLCELLULOSE

Columns 1, 2 and 3 are calculated on the basis of the theory presented in this paper. Column 4 is based on the theory of Katchalsky and Lifson^{7b} and column 5 is based on the theory of Hermans and Overbeek.³ Column 6 presents the experimental results of Schneider.¹⁸

$1/\kappa$	No binding	Binding 33%	Binding 67%	K.L.	H.O.	Exptl.
6	1.07	1.07	1.06	2.00	1.41	1.09
13.8	1.13	1.11	1.09	4.16	1.81	1.16
30.4	1.38	1.30	1.19	10.9	2.45	1.39
44	1.72	1.57	1.31	13.8	2.87	1.59
50	1.91					

It is quite clear that the present calculation treats the electrostatic interactions in a quite different way than the more random model of Kuhn, Künzle and Katchalsky. The effect of the modifications introduced in the present theory may be seen by comparing results computed using the formula of Katchalsky and Lifson^{7a} with the other entries in

Table II.²¹ Also listed in the table are the expansions calculated from the spherical model of Hermans and Overbeek.³ A substantial improvement over all these theories has been realized.

2. Polymethacrylic Acid.—The only structural difference between the monomeric group in polymethacrylic acid (PMA) and polyacrylic acid (PAA) is the presence of a methyl group on the carbon atom α to the carboxyl group in PMA. In both polymers the spacing between charged sites is 2.5 ångströms so that to the approximation involved in the theory described here with the possible exception of the statistical element length, there should be little difference between PMA and PAA. The major contributions to the electrostatic free energy arise from the non-random free energy of mixing and the interaction between nearest neighbor charge groups. The interaction between the statistical elements is a small additional term which, even if the statistical elements in PMA and PAA are not identical, cannot be very different for the two polymers. Recognizing this similarity between the polymers, we have assumed that the extent of binding in PMA will be the same as the extent of binding in PAA which is 63% at complete neutralization.¹⁷

The calculated expansions for PMA in the absence of added salt are compared with the experimental values of Oth and Doty²² in Table III. It is easily seen that the calculated values, even for zero binding, fall below the experimental value.

TABLE III

COMPARISON OF THE CALCULATED AND EXPERIMENTAL EXPANSION FACTORS h_1/h_0 FOR SODIUM POLYMETHACRYLATE $A = 10. \text{Å}$.

No binding	60% binding	Exptl. ²²
3.26	1.64	6.0

The model employed in this theory neglects interactions between segments further separated than nearest neighbors. In CMC where the statistical element is 335 ångströms long, the shielding radius $1/\kappa$ is only about one eighth the element length even at the lowest ionic strength investigated. In this case the neglect of higher order interactions is not serious. In PMA the statistical element is only 10 ångströms long and the experimental lengths listed in Table III were determined under conditions such that the shielding radius $1/\kappa$ was never less than 30 ångströms. Under these circumstances it is to be expected that higher order interactions will be important and that the calculated expansions will be smaller than the experimental values.

Since the statistical element length in PMA corresponds to only four monomer units,²² it is possible to make an estimate of the decrease in electrostatic energy when we replace the discrete ensemble of charges spaced in some manner along the element with one large charge at the centroid. In principle

(21) Katchalsky and Lifson's equation (21) for h_1/h_0 has been shown to be incorrect. However, the correction does not seriously influence the results of the theory under the experimental conditions for which it has been used. A discussion of this point may be found in reference 7b.

(22) A. Oth and P. M. Doty, *THIS JOURNAL*, **56**, 43 (1952).

one may write the exact solution to the interaction between the pairs of charges on adjacent segments, but this expression is inconvenient for numerical calculations due to its great complexity when there are a large number of charges on a statistical element. For the element of four monomers, with equally spaced charges, the error involved in replacing the four charges with one of magnitude four is of the order of 25% at moderate ionic strengths and decreases at low ionic strength. It is to be expected that the error involved in overestimating the interaction energy due to the model being able to bend sharply is in the opposite direction and is probably of the same order of magnitude.

V. Acknowledgments.—We acknowledge interesting discussions with Drs. Bartholemew Hargitay and Alfred Holtzer. We also wish to thank Dr. Nathan Schneider for making available to us before publication the experimental results quoted in this paper, and Professor Paul Doty for critically reading the manuscript.

DISCUSSION

J. J. HERMANS (University of Groningen).—The papers by Harris and Rice represent a very interesting attempt to account for ion binding. The concept of *specific sites* may prove very useful in the treatment of this problem, but I believe that it has been somewhat overemphasized in their papers.

I have two further comments in connection with earlier theories. In the first place it is not, I think, quite sure that the calculations of Kuhn and Katchalsky and of Katchalsky and Lifson are the only ones that preserve the chain-like character of the molecule. In the spherical model the chain-like character is preserved completely as far as the statistical treatment is concerned. The sphericity plays a part only

in the calculation of the electrical free energy, and it was shown that the result is almost independent of the charge distribution in the sphere: if the dimensions are defined in terms of the radius of gyration,* the result for the electrical free energy in the absence of counter-ions is $0.60 Z^2 e^2 / \epsilon R$ for uniform charge, $0.63 Z^2 e^2 / \epsilon R$ for a Gaussian distribution and $0.70 Z^2 e^2 / \epsilon R$ for a simple exponential decay. What is more, it does not change much with the shape of the particle, either. For an axial ratio of 2, one finds $0.69 Z^2 e^2 / \epsilon R$; for an axial ratio of 3 the result is $0.71 Z^2 e^2 / \epsilon R$. The situation in the presence of counter-ions is similar.

For this very reason the approximation involved in the assumption that the probability of a configuration is dependent only on the over-all dimensions of the molecule is not quite so serious as the authors appear to believe.

J. R. VAN WAZER (Monsanto Chemical Company).—In the discussion of this and previous papers, emphasis has been placed on the "binding" of simple cations by the high charge of the polyanion. I wish to emphasize that there can also be covalent binding of the cations, which are then held in the form of a "complex." Work on the chain phosphates (polyphosphates) indicates that both types of binding are found for all of the common metal ions with these polyanions. For metals such as sodium, the charge interaction predominates over the covalent type of binding; but, for transition metals, the reverse is true.

From the published papers and recent undisclosed studies in our laboratories, it seems that the various methods of determining the amount of cation bound by the polyphosphates will lead to different results, depending on the method. Some measurements include the entirety, or a large part, of the counter-ion atmosphere, whereas others dig down into this ionic atmosphere and differentiate the close, covalently bound cations from the rest of the counter ions. Thus, the method by Schindewolf and Bonhoeffer [*Z. Elektrochem.*, **57**, 216-21 (1953)] appears to cover the ionic atmosphere, whereas the methods of Van Wazer and Campanella [*J. Am. Chem. Soc.*, **72**, 655-63 (1950)] seem to primarily detect the covalently bound ions. Probably there will be considerable argument during the next few years between the proponents of various methods, as to which gives the "true" amount of bound cations.

* Ref. 2 in Harris and Rice, Paper I.

CONDUCTANCE OF POLYELECTROLYTES UNDER PRESSURE¹

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The conductivities of dilute aqueous solutions of potassium chloride, hydrochloric acid, acetic acid, polyacrylic acid, styrene-maleic acid copolymer, polyvinyl potassium sulfate and a series of sodium phosphates were measured at 25° and pressures up to 1000 bars. The degree of dissociation of polyacrylic acid was observed to be a linear function of pressure with the pressure coefficient a function of the concentration. The results are treated thermodynamically to obtain volume changes attending the process of ionization. The volume change associated with the ionization of polyacrylic acid at zero degree of ionization is -17.7 ml. per mole of carboxyl groups, but with increasing degree of dissociation the volume change becomes less negative. The data are interpreted theoretically on the basis of a simple spherical model for the polyion. The sodium phosphates studied show an increasing pressure coefficient of conductance with increasing chain length.

Introduction

The effect of pressure on conductivity of solutions of simple electrolytes has been a subject of investigation for a number of years. The usual pressure range was from one to 3,000 bars, although Zisman² records results to 10,000 kg./cm.². Investigations have also been made on the pressure dependence of the ionization constants of weak acids; the most recent of these studies was that of Brander,³ who has reviewed the field in considerable detail. Studies of this type have led to calculations of the volume changes associated with the ionization of a weak acid and the results so obtained generally compared favorably with estimates made by independent methods.⁴ In such calculations, approximations must be made to obtain the degrees of dissociation at different pressures. Such approximations can be made quite accurately by using Onsager's⁵ equation, which relates the equivalent conductance to the concentration and other properties of the electrolytic solutions.

The dependence of conductivity upon pressure is rather complex because of the following factors: (1) the increase of concentration accompanying increased pressure; (2) the anomalous pressure effect on the viscosity of water; and (3) the marked influence of pressure on the degree of ionization of weak electrolytes. The behavior of simple electrolytes under pressure suggested that interesting results might be obtained for polymeric electrolytes,

particularly polyacids and polybases. To this end we chose to study dilute solutions of such electrolytes, with particular emphasis on the effect of pressure on the intraionic electrical free energy.

Experimental

A. Pressure System.—The high pressure components of the apparatus used for this study consisted of a pressure injector, gages, a high pressure bomb and appropriate connections.⁶ A 10,000 p.s.i. Heise gage was employed for the low pressure readings (up to 500 bars), and a 50,000 p.s.i. Ashcroft gage was used for the higher readings. Both gages were calibrated against a dead weight gage. Electrical leads entered the pressure bomb through the piston-like bomb head, using the conventional cone, follower and nut technique.

B. Conductance Bridge and Cell.—The conductivity bridge assembly was constructed following the plans of Luder,⁷ with certain modifications. Six-volt tubes were used and the amplifier was connected to the voltage supply instead of to batteries. A VI-C7 variable inductor, made by United Transformer Corporation, was used in place of the honey-comb coil arrangement specified in the original plans. This inductor allowed a precise setting to be made at the desired oscillator frequency (1000 cycles). The balance point of the bridge was detected by an oscilloscope. A General Radio type 1432-N decade resistance box served for readings to 11,000 ohms. Higher resistances were measured by using in addition a group of 10,000 ohm precision G-R resistors as described by Luder. The sensitivity of this apparatus was one part in one hundred thousand.

The conductance cells used in earlier high pressure investigations generally followed the design of Körber⁸ and Tammann.⁴ Zisman² used a cell for which changes of cell constant with pressure could be calculated from geometric considerations. Adams and Hall⁹ described a cell for use with relatively concentrated solutions; they employed a layer of "Nujol" oil to transmit the pressure to the solution, instead of the mercury seal used by Körber.

With these earlier studies in mind we designed a cell for use in our work (see Fig. 1). Electrodes, made from sheet platinum (0.004" thick) fashioned into bands of 2.0 cm. diameter and 1 cm. width, were centered axially in a 3-cm. Pyrex tube approximately 5 cm. apart and were supported by indentations in the tube. Platinum wires, sealed through the glass walls, served as electrical connections. Standard taper (12/18) joints were attached to the ends of the glass tube to facilitate closing the cell. The cell was standardized on several occasions, both before and after use, utilizing standard KCl solutions described by Jones and Bradshaw.¹⁰ The reproducibility of the standardization was within 0.1%.

When a pool of mercury was used to transmit the pressure, reasonable results were obtained for 0.01 *N* solutions, but marked irreversibility was encountered for more dilute

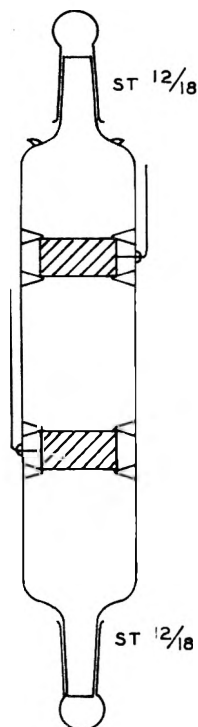


Fig. 1.—Conductance cell. Top cap is removed when in use with Nujol layer.

(1) The work discussed herein was supported in part by the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) W. A. Zisman, *Phys. Rev.*, **39**, 151 (1932).

(3) E. Brander, *Soc. Sci. Fennica Commentationes Phys. Math.*, **6**, 1 (1932).

(4) G. Tammann and A. Rohmann, *Z. anorg. allgem. Chem.*, **183**, 1 (1929); **182**, 353 (1929).

(5) See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 128.

(6) The apparatus is described by P. B. Hill, Ph.D. Thesis, Univ. of Ill., 1953.

(7) W. F. Luder, *J. Am. Chem. Soc.*, **62**, 89 (1940).

(8) F. Körber, *Z. physik. Chem.*, **67**, 340 (1909).

(9) L. H. Adams and R. E. Hall, *This Journal*, **35**, 2145 (1931).

(10) G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933).

solutions. We concluded, as Lad Körber, that mercury contaminates the solution. We further noted that the reaction is strongly pressure dependent.

The method of Adams and Hall, in which a "Nujol" layer is used to transmit the pressure, was also investigated and found to give results consistent to $\pm 0.2\%$ even for extremely dilute solutions. For this arrangement, which was the one employed in the studies here reported, the bottom of the cell is closed off and the "Nujol" layer is placed on top of the solution.

An appreciable length of time had to elapse after each pressure setting for the system to reach thermal and chemical equilibrium. One hour was sufficient for all of the systems studied, except for the phosphates for which an hour and one-half proved to be necessary. Temperature measurements using a thermistor indicated that thermal equilibrium is obtained in approximately 40 minutes. The temperature outside the bomb was maintained by a temperature control bath at $25.00 \pm 0.02^\circ$.

C. Chemicals and Standardization.—The PAA (polyacrylic acid) was made by the organic preparations section at the University of Illinois. The SMAC (hydrolyzed styrene-maleic anhydride copolymer) was prepared by the method described by Wall and de Butts.¹¹ Concentrations of the polymer solutions were determined by drying aliquot portions and by determining pH titration curves with a Beckman Glass Electrode pH meter, model G. The latter method gave results accurate to 0.2% for the PAA and to 0.4% for the SMAC. The drying method agrees exactly with the titration for PAA, but deviates 1% for the SMAC. Since our interest was in the number of functional groups, the titration method was believed to give more dependable results.

The PVS (polyvinyl potassium sulfate) was supplied by Dr. Hiroshi Terayama of this Laboratory. Solutions of this polymer were standardized by the conventional sulfate determination.

Solutions of reagent grade sodium phosphate and sodium pyrophosphate were standardized by pH titrations. Sodium tripolyphosphate was obtained from Professor L. F. Audrieth and solutions of the same were prepared from weighed amounts of the hexahydrate material. The sodium polymetaphosphate had been prepared from directions found in "Inorganic Syntheses."¹² Aqueous solutions were prepared from weighed amounts of the material, and an average chain length of 70 units was determined by titration of the end groups using the method of Van Wazer and Holst.¹³

All of the solutions were made from water redistilled over potassium permanganate. The water so prepared had a specific conductance of $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25° .

Treatment of Data

For calculating changes in concentration with pressure, it was assumed that the solutions obeyed the Tait equation for the compressibility of pure water. At 25° this equation is¹⁴

$$\frac{V_0(P)}{V_0(1)} = 1 - 0.3150 \log \left\{ \frac{2996 + P}{2997} \right\} \quad (1)$$

where $V_0(P)$ is the specific volume of water at 25° under a pressure P expressed in bars. If $\Lambda^{(P)}$ and $R^{(P)}$ denote, respectively, the equivalent conductance and the resistance at pressure P , then we can also write that

$$\frac{\Lambda^{(P)}}{\Lambda^{(1)}} = \frac{R^{(1)}V_0(P)}{R^{(P)}V_0(1)} \quad (2)$$

By combining equations 1 and 2, one can calculate the equivalent conductances from resistance measurements. In making the calculations it was assumed that the cell constant was independent of pressure, although a small correction (0.1%) might

be applied at 1000 bars. In calculating the ratio $R^{(1)}/R^{(P)}$, the initial $R^{(1)}$ reading was used for ascending pressure settings and the final $R^{(1)}$ for descending settings. In all cases the initial and final values agreed within 0.5%. A correction for solvent conductance was applied to the KCl solutions. Comparison of results for KCl and HCl at 25° (see Fig. 2) with the value obtained by interpolation between Körber's experiments at 20° and those of Zisman at 30° showed excellent agreement (within 0.1%) at 500 and 1000 kg./cm.² For dilute solutions it was found that $\Lambda^{(P)}/\Lambda^{(1)}$ was independent of concentration.

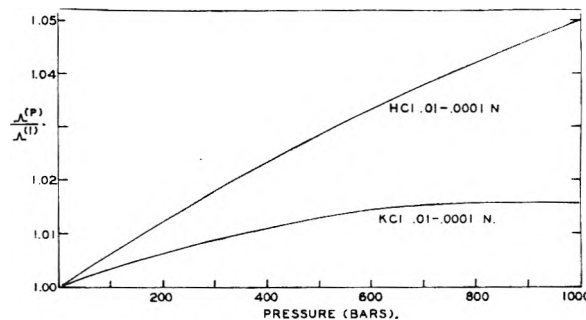


Fig. 2.—Relative equivalent conductance of dilute solutions of HCl and KCl versus pressure.

To calculate the degree of dissociation of a polymeric acid at different pressures, it is necessary to know the equivalent conductance of the hydrogen ion at those pressures. Values were obtained by applying Onsager's equation for the equivalent conductance of HCl and KCl¹⁵ in conjunction with equation 2 and the relation

$$\Lambda_{H^+}^{(P)} = \Lambda_{HCl}^{(P)} - t_a \Lambda_{KCl}^{(P)} \quad (3)$$

where t_a is the anion transference number of KCl, with a value of 0.510 at 25° and 1 atm.¹⁶ It was supposed that t_a is independent of pressure, which is not an unreasonable assumption.^{15a}

The value of the degree of dissociation, α , for acetic acid was calculated by assuming for the equivalent conductance at infinite dilution

$${}^0\Lambda_{HAc}^{(P)} = \frac{\Lambda_{HCl}^{(P)}}{\Lambda_{HCl}^{(1)}} \times {}^0\Lambda_{HAc}^{(1)} \quad (4)$$

The value of ${}^0\Lambda_{HAc}^{(1)}$, namely 390.7, was taken from Kortüm and Bockris,¹⁵ and α was calculated by the approximate relation

$$\alpha = \Lambda_{HAc}^{(P)}/{}^0\Lambda_{HAc}^{(P)} \quad (5)$$

For PAA on the other hand, α was calculated using the equation

$$\Lambda_{H^+}^{(P)} = \frac{t_c \Delta P_{PAA}^{(P)}}{\alpha} \quad (6)$$

We assumed t_c , the transference number of the hydrogen ion in PAA, to be a function of α only, and applied an approximate correction for the effect of α on transference number using the relation of Wall, Stent and Ondrejcin.¹⁷

$$t_c = 1.008 - 2\alpha \quad (7)$$

(15) G. Kortüm and J. O'M. Bockris, "Electrochemistry," Elsevier Press., Houston, Texas, 1951, p. 696.

(15a) Recent measurements in our laboratory indicate that the transference number of KCl is slightly pressure dependent but not enough to affect our calculations appreciably.

(16) L. G. Longworth, *J. Am. Chem. Soc.*, **54**, 2741 (1932).

(17) F. T. Wall, G. S. Stent and J. J. Ondrejcin, *THIS JOURNAL*, **54**, 979 (1950).

(11) F. T. Wall and E. de Butts, *J. Chem. Phys.*, **17**, 1330 (1949).

(12) L. F. Audrieth, Editor, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1947, p. 91.

(13) J. R. Van Wazer and K. A. Holst, *J. Am. Chem. Soc.*, **72**, 639 (1950).

(14) See B. B. Owen, *J. Chem. Educ.*, **21**, 59 (1944).

Combining equations 6 and 7 we obtain

$$\alpha = \frac{1.008\Lambda_{PAA}^{(P)}}{\Lambda_{H^+}^{(P)} + 2\Lambda_{PAA}^{(P)}} \quad (8)$$

For the styrene-maleic acid copolymer, similar equations were used.¹⁷

$$t_{-SMAC} = \alpha \quad (9)$$

$$\alpha = \frac{\Lambda_{SMAC}^{(P)}}{\Lambda_{H^+}^{(P)} + \Lambda_{SMAC}^{(P)}} \quad (10)$$

The equivalent conductance and the degree of dissociation were observed to be linear functions of pressure for acetic acid and polyacrylic acid (see Figs. 3, 4 and 5). The data for polyacrylic acids

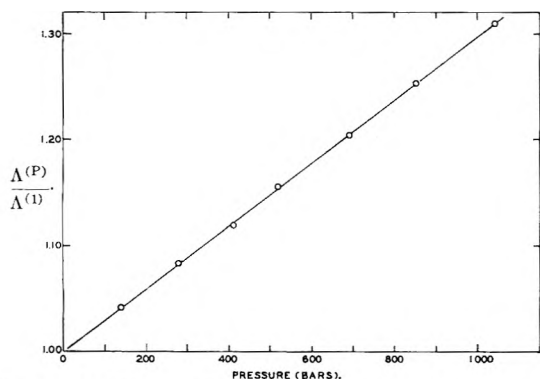


Fig. 3.—Relative equivalent conductance of 0.00994 *N* acetic acid versus pressure.

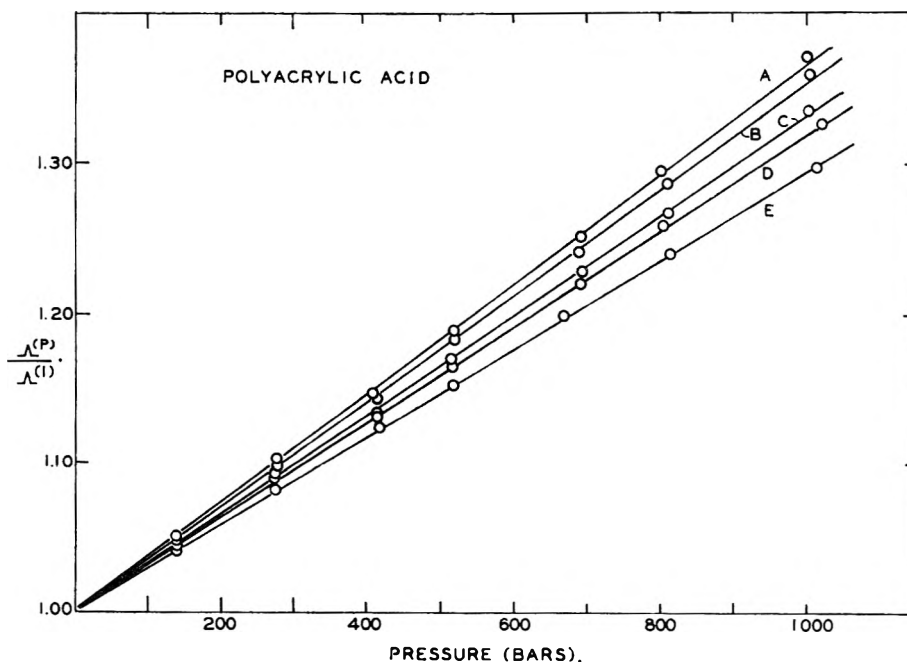


Fig. 4.—Relative equivalent conductance of polyacrylic acid versus pressure: A, 1.741×10^{-1} *N*; B, 6.96×10^{-2} *N*; C, 1.738×10^{-2} *N*; D, 8.69×10^{-3} *N*; E, 1.734×10^{-3} *N*.

were fitted to the following equations by least squares with standard deviations less than 0.3%

$$\frac{\Lambda^{(P)}}{\Lambda^{(1)}} = 1 + b\Delta P \quad (11)$$

$$\frac{\alpha^{(P)}}{\alpha^{(1)}} = 1 + m\Delta P \quad (12)$$

In the above equations, ΔP equals the excess pressure above one atmosphere. The coefficient, m ,

which appears in equation 12 is a function of c_0 , the concentration of the solution when $\Delta P = 0$. It follows, therefore, that m can be regarded as an implicit function of $\alpha(c_0)$. If $1/m$ is plotted *vs.* $\alpha(c_0)$ for $\Delta P = 0$, a straight line is obtained with an intercept $1/m_0$ corresponding to $\alpha = 0$ (see Fig. 6). This result can be expressed in the form

$$\frac{1}{m} = \frac{1}{m_0} + k\alpha(c_0) \quad (13)$$

An analysis of the graph shows that $1/m_0$ equals 3000 bars for PAA and that $k = 4.179 \times 10^4$ bars.

Equivalent conductances of solutions of SMAC, PVSK, sodium phosphate, sodium pyrophosphate, sodium tripolyphosphate and sodium polyphosphate are plotted *versus* pressure in Figs. 7 and 8.

Discussion

As noted above, equivalent conductance and degree of dissociation of a weak acid such as acetic acid are linear functions of pressure up to 1000 bars, a result observed previously by Fanjung.¹⁸ The dependence of dissociation constant on pressure can be used to calculate the change in volume attending the dissociation of a weak acid as follows. Since

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \quad (14)$$

and

$$K = \alpha^2 c / (1 - \alpha) \quad (15)$$

we conclude that

$$\Delta V = -RT \left(\frac{\partial \ln c}{\partial P} + \frac{2 - \alpha}{1 - \alpha} \frac{\partial \ln \alpha}{\partial P} \right) \quad (16)$$

Equation 16 yields values of ΔV at one bar equal to -12.57 , -12.97 and -12.94 cc. for acetic acid of concentrations 9.92×10^{-4} , 9.94×10^{-3} , 9.95×10^{-2} *N*, respectively.

(18) I. Fanjung, *Z. physik. Chem.*, **14**, 697 (1894).

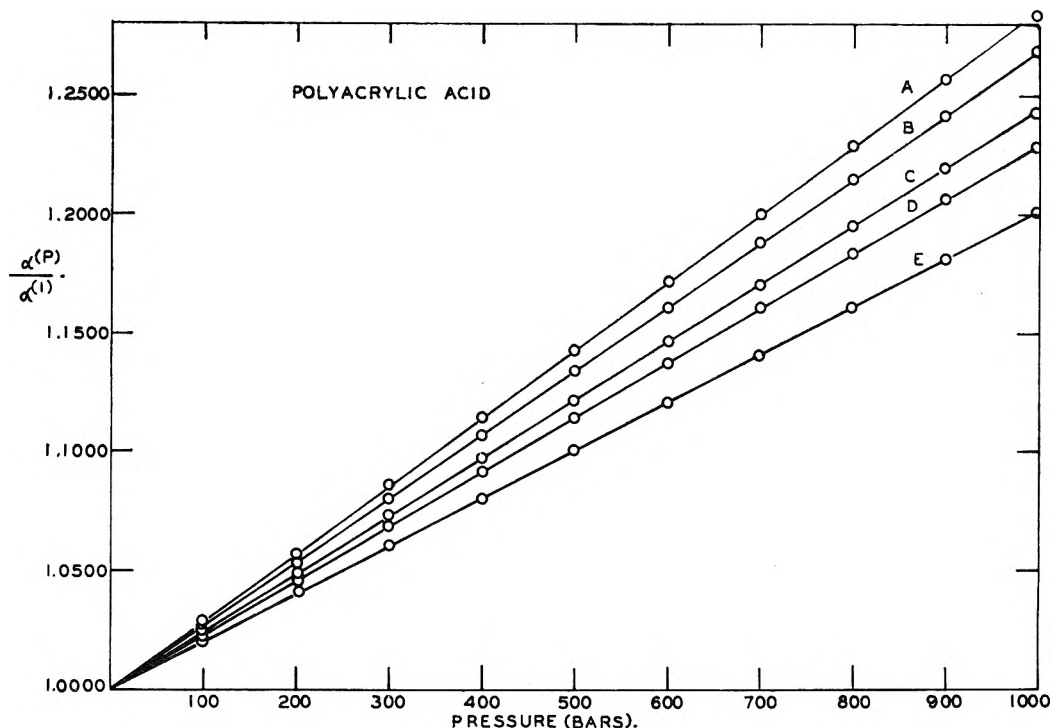


Fig. 5.—Relative degree of ionization of polyacrylic acid versus pressure: A, $1.741 \times 10^{-1} N$; B, $6.96 \times 10^{-2} N$; C, $1.738 \times 10^{-2} N$; D, $8.69 \times 10^{-3} N$; E, $1.734 \times 10^{-3} N$.

Application of equation 16 to a polymeric acid involves several difficulties, the most serious of which is the fact that a spectrum of dissociation constants is necessary to describe the system. This problem can be resolved by use of Bjerrum's equation¹⁹ for successive dissociation constants of a polybasic acid. This equation, which has been successfully applied to polymeric acids, is

$$K = K_0 \exp(-\Delta F_{el}/RT) \quad (17)$$

where K_0 is the "inherent dissociation constant," ΔF_{el} is the excess free energy of dissociation because of the increased charge, and K is the effective dissociation constant of the polyacid. (ΔF_{el} is really the change in electrical free energy per unit ionization.) More detailed theories of polyelectrolytes have been worked out by Kuhn, Künzle and Katchalsky,²⁰ as well as by Hermans and Overbeek.^{21,22}

Volume changes associated with the process of ionizing a polymeric acid can be calculated by using equation 14 in conjunction with certain empirical equations for polyacrylic acid describing the effect of pressure upon its degree of dissociation. Substitution of equation 15 into equation 17, followed by differentiation with respect to P holding T constant, yields

$$\frac{\partial \ln c}{\partial P} + \frac{2 - \alpha(P,c)}{1 - \alpha(P,c)} \frac{\partial \ln \alpha(P,c)}{\partial P} = -\frac{\Delta V_0}{RT} - \frac{\Delta V_{el}}{RT} = -\frac{\Delta V}{RT} \quad (18)$$

In equation 18, ΔV_0 is the "inherent volume

(19) N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

(20) W. Kuhn, O. Künzle and A. Katchalsky, *Helv. Chim. Acta*, **31**, 1994 (1948).

(21) J. J. Hermans and J. Th. C. Overbeek, *Bull. soc. chim. Belg.*, **57**, 154 (1948).

(22) J. Th. C. Overbeek, *ibid.*, **57**, 252 (1948).

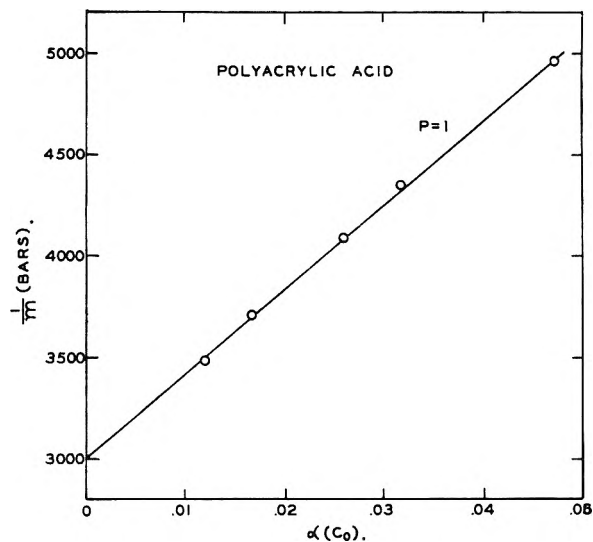


Fig. 6.— $-1/m$ versus degree of ionization for polyacrylic acid at one bar.

change," ΔV_{el} is the additional volume change attributable to the intra-polyion charge effect, and ΔV is the over-all volume change for the process. In making the calculations it was stipulated that ΔV_{el} must vanish for zero degree of dissociation and so under those limiting circumstances ΔV_0 becomes equal to ΔV . Hence allowing α to approach zero in equation 18 one obtains

$$\frac{\partial \ln c}{\partial P} + 2 \left[\frac{\partial \ln \alpha(P,c)}{\partial P} \right]_{\alpha=0} = -\frac{\Delta V_0}{RT} \quad (19)$$

Making use of equations 12 and 13 we observe that

$$\left[\frac{\partial \ln \alpha(P,c)}{\partial P} \right]_{\alpha=0} = \frac{m_0}{1 + m_0 \Delta P} \quad (20)$$

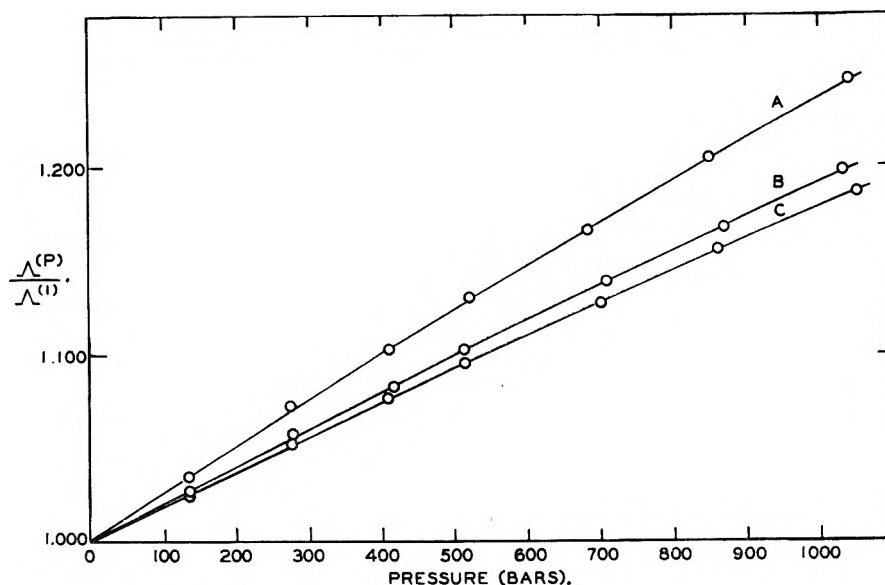


Fig. 7.—Relative equivalent conductance of styrene-maleic acid copolymer *versus* pressure: A, $2.01 \times 10^{-1} N$; B, $2.77 \times 10^{-2} N$; C, $2.77 \times 10^{-3} N$.

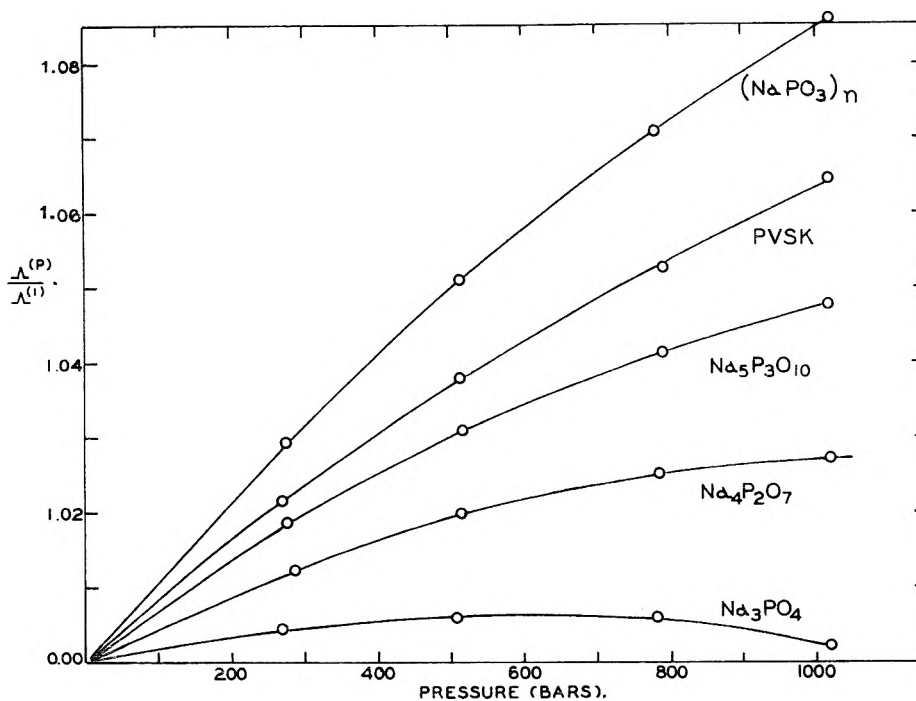


Fig. 8.—Relative equivalent conductance *versus* pressure for polyvinyl potassium sulfate and a series of linear phosphates.

Substituting equation 20 into equation 19 yields

$$\Delta V_0 = -RT \left[\frac{\partial \ln c}{\partial P} + \frac{2m_0}{1 + m_0 \Delta P} \right] \quad (21)$$

Equation 21 can be simplified through use of an approximate form of equation 1 to give for PAA the following

$$\Delta V_0 = \frac{-2.137RT}{2099 + P} \quad (22)$$

Since RT equals 2.48×10^4 bar-cm.³ at 298°K., at a pressure of one bar $\Delta V_0^{(1)}$ equals -17.65 ml.

From equations 21 and 18, we further obtain

$$\Delta V_{el} = -RT \left[\frac{2 - \alpha(P,c) \partial \ln \alpha}{1 - \alpha(P,c) \partial P} - \frac{2m_0}{1 + m_0 \Delta P} \right] \quad (23)$$

which allows a calculation of ΔV_{el} from experi-

mentally known quantities. Values of ΔV_{el} at one bar are plotted as a function of α in Fig. 9.

For the purpose of interpreting these results, it is worthwhile to consider theoretically the dependence of ΔF_{el} upon certain of the parameters of the system. For this purpose let us consider the simple model of Hermans and Overbeek^{21,22} consisting of spherical anion particles, homogeneously charged, at infinite dilution. For this case, the change in free energy brought about by increasing the charge on the sphere by one unit is given by

$$\Delta F_{el} = \frac{6Z\epsilon^2}{5rD} \quad (24)$$

where Z is the number of electronic charges, ϵ , throughout a sphere of radius r in a medium of di-

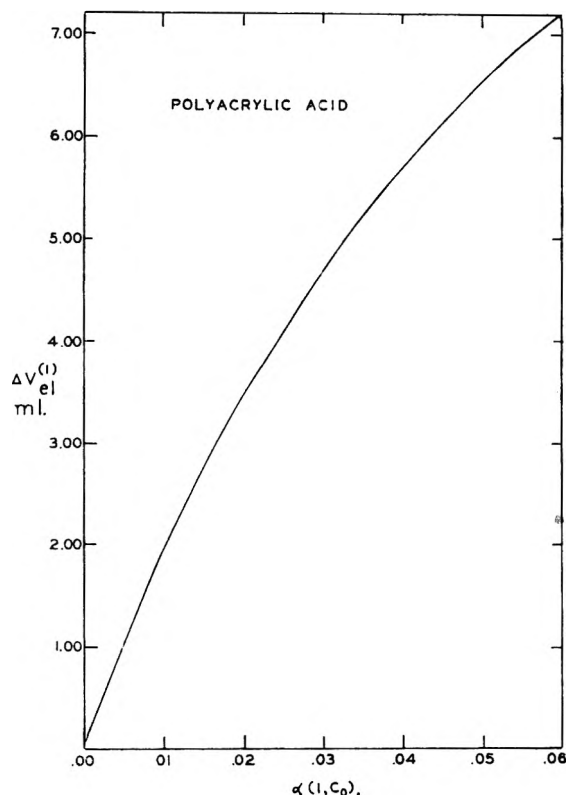


Fig. 9.— ΔV_{e1} versus degree of ionization for polyacrylic acid at one bar.

electric constant D . (For the sake of simplicity, we do not use the more complex expression of Kuhn, *et al.*²⁰) Equation 24 can be rewritten as

$$\Delta F_{e1} = \text{const} \times \frac{\alpha}{\tau D} \quad (25)$$

and will now be applied to PAA solutions with de-

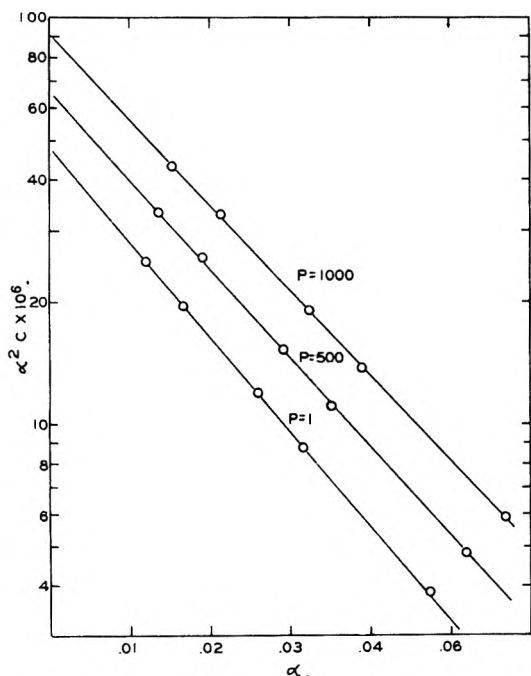


Fig. 10.—Semi-logarithmic plot of $\alpha^2 c$ versus degree of ionization for polyacrylic acid.

grees of dissociation from 0.01 to 0.05. For low α , equations 17 and 25, combine to give

$$\ln \alpha^2 c \cong \ln K_0 - \text{const} \frac{\alpha}{\tau D R T} \quad (26)$$

A semi-log plot of experimental values of $\alpha^2 c$ vs. α for PAA (Fig. 10) is linear, which means that equation 25 adequately describes the behavior of PAA at low α . Evidently ΔF_{e1} depends principally upon α , and the relative change in τ with α is minor in this range. The intercept (4.83×10^{-5}) at $\alpha = 0$ must equal K_0 , a quantity of the same order of magnitude as the dissociation constant for simple acids.

Assuming equation 24 contains the most important factors, the relative change of τ with pressure can now be calculated. This calculation involves the determination of

$$\frac{\partial \ln \Delta F_{e1}}{\partial P} = \frac{-\Delta V_{e1}}{RT \ln \frac{\alpha^2 c}{(1-\alpha)K_0}} \quad (27)$$

A plot of this derivative vs. α for PAA is given in Fig. 11.

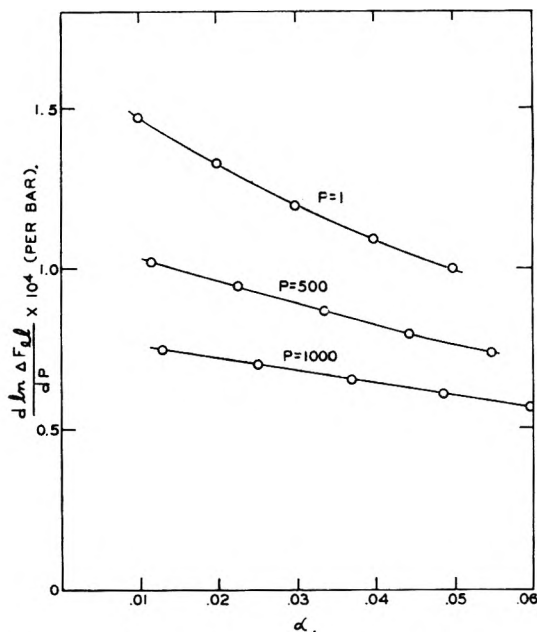


Fig. 11.— $\partial \ln \Delta F_{e1} / \partial P$ versus degree of ionization for polyacrylic acid.

From equation 25 it follows that

$$\frac{\partial \ln \tau}{\partial P} = \frac{\partial \ln \alpha}{\partial P} - \frac{\partial \ln D}{\partial P} - \frac{\partial \ln \Delta F_{e1}}{\partial P} \quad (28)$$

$\partial \ln \tau / \partial P$ was evaluated for PAA using the formula for the pressure derivative of the dielectric constant of water²³ and our experimental results for α as a function of pressure. These values are plotted in Fig. 12. It is interesting to note that for a given α , the relative increase in τ becomes greater with increasing P . This can be explained by the increasing compression of the polymer assuming that for a given α the radius of the anion will be less the greater the pressure. Further increase in pressure

(23) B. B. Owen and S. R. Brinkley, Jr., *Ann. N. Y. Acad. Sci.*, **51**, 760 (1949).

to produce a change in α will then simultaneously produce a larger relative change in r .

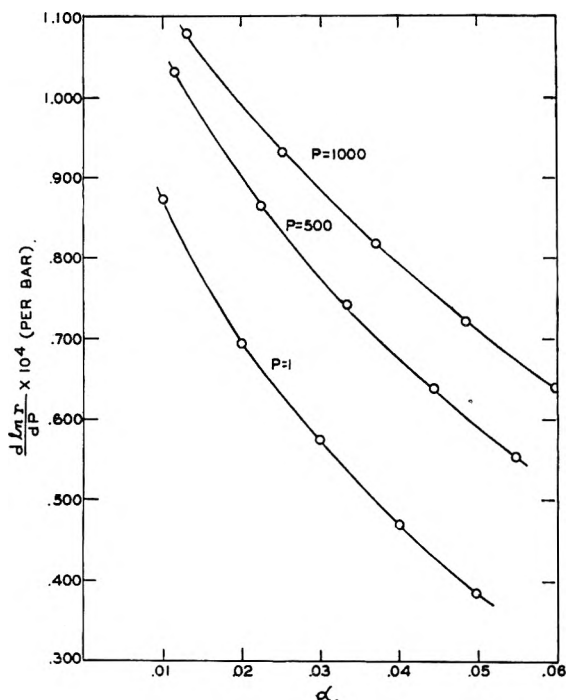


Fig. 12.— $\frac{d \ln r}{dP}$ versus degree of ionization for polyacrylic acid.

The value of $\Delta V_0^{(1)}$ for PAA (−17.7 ml.) is considerably more negative than the value for acetic acid. The reason for the difference is indicated by values which Fanjung determined for a series of simple acids, namely: formic, −8.66 ml. at 15°; acetic, −10.63 at 14°; propionic, −12.39 at 14°; and butyric −13.44 at 16°. Although these values may not be too accurate, they show that the longer the acid molecule the larger the volume change. Hence the value −17.7 ml. should not be unreasonable for an infinitely long chain fatty acid. At higher temperatures (25°) the volume change is even more negative.

Measurements on the styrene–maleic acid copolymer indicate a dependence of equivalent conductance on pressure similar to that for polyacrylic acid, although equation 12 does not appear to hold. It should be pointed out that the degrees of dissociation of this acid were considerably greater than for PAA which suggests a reason for this departure.

The measurements on the sodium phosphate compounds are plotted in Fig. 8 along with those for polyvinyl potassium sulfate. It is interesting to note that as the phosphate chain length increases, the slope of these plots increases. This behavior can be explained by the fact that the longer the chain, the less the initial dissociation. Hence there are more groups available to respond to the effect of pressure. As the phosphate chain length increases, the number of sodium ions attached to the chain also increases. This observation is in agree-

ment with conclusions reached from exchange studies on these compounds.²⁴

DISCUSSION

Dr. HELFFERICH.—In measuring the electrical conductivity of polyelectrolytes, an interesting effect has been discovered by U. Schindewolf²⁵ and K. Heckmann²⁶ in our institute and independently by B. Jacobson²⁷ in Sweden.

The conductivity of flowing solutions of polyelectrolytes containing non-spherical poly-ions is anisotropic, if there is a gradient in the flowing velocity. In a glass tube or a Couette apparatus the conductivity of the flowing solution is greater than that of the resting solution when measured in direction of flow, smaller than that of the testing solution when measured perpendicular to the flow. The change in conductivity may be 20% or more; of course there is a dependence on the velocity gradient, but the effect approaches a limiting value with increasing gradient.

We suggest a simple explanation: the poly-ions will be oriented, by the velocity gradient, nearly parallel to the direction of flow (this can be seen from birefringence measurements on such systems). Now a chain-, rod-, or plate-shaped poly-ion will move more easily forth and back than sideways—similar to a ship. Thus the measurements could be accounted for, though other effects may have their part, which the authors will discuss in more detail elsewhere.

The change in conductivity is greater the higher the molecular weight of the polyelectrolyte, that is to say the longer the chains. On the other hand, it decreases with increasing concentration and decreases when salt (for instance NaCl) is added. The chains stretched in dilute solution by electrostatic action of their fixed charges will then coil, because the counter-ion atmosphere becomes denser and the charges will be more effectively shielded one from another. This effect is well known.

Schindewolf studied polyphosphates, Jacobson thymonucleic acid, whereas Heckmann obtained similar results with sodium oleate. There, of course, micelles instead of poly-ions are present.

Using a Couette apparatus consisting of two concentric cylinders, one of which rotates, the solution being in the slot between the cylinders, it should be possible, by suitable sets of electrodes, to detect whether a poly-ion or micelle is chain- or plate-shaped. But quantitative data are not yet at hand.

PAUL DOTY (Harvard University).—Do you consider ΔV_{e1} to arise from an increase in the partial molal volume of polymer or in the spacial expansion of the polyion when ionization occurs? What would be the effect on ΔV_{e1} of added salt? If the expansion of the polyion does play a role, does this imply that an extended configuration has a larger molecular volume than a smaller configuration?

F. T. WALL.—When a monobasic acid undergoes ionization in aqueous solution, there is a diminution of volume that can be attributed to shrinkage accompanying the hydration of ions. In the case of a polyelectrolyte there will be somewhat less hydration about each of the charged sites in the polyion because of the proximity of like charges. An isolated charge will have associated with it a certain number of solvent molecules, but in the polyion the charges compete with each other, thus diminishing the tendency for a given solvent dipole to orient itself about a particular charge. This results in less shrinkage of total volume, and is the source of what we call ΔV_{e1} , a quantity of opposite sign to ΔV_0 . The expansion of the polyion is incidental to all this, and I believe it would be difficult to relate the over-all molecular configuration to ΔV_{e1} . I cannot predict the effect of added salt on ΔV_{e1} .

(24) F. T. Wall and R. H. Doremus, *J. Am. Chem. Soc.*, **76**, 868 (1954).

(25) U. Schindewolf, *Naturwissenschaften*, **40**, 435 (1953); *Z. physik. Chem.*, (neue Folge) **1**, 128 (1954).

(26) K. Heckman, *Naturwissenschaften*, **40**, 478 (1953).

(27) B. Jacobson, *Nature (London)*, **172**, 666 (1953); *Rev. Sci. Instruments*, **24**, 949 (1953).

THE TRANSITION FROM TYPICAL POLYELECTROLYTE TO POLYSOAP.

I. VISCOSITY AND SOLUBILIZATION STUDIES ON COPOLYMERS OF 4-VINYL-N-ETHYLPYRIDINIUM BROMIDE AND 4-VINYL-N-*n*-DODECYLPYRIDINIUM BROMIDE

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Received March 15, 1954

Poly-4-vinyl-N-ethylpyridinium bromide and four polysoaps, prepared by quaternizing 6.7, 13.6, 28.5 and 37.9% of the nitrogens of poly-4-vinylpyridine with *n*-dodecyl bromide and the remainder with ethyl bromide, were compared by viscosity and solubilization studies in aqueous solutions. While the reduced viscosity showed a more than hundred-fold over-all decrease in going from the first to the last of these compounds, the decrease did not occur uniformly with the increase in dodecyl group content, but several irregularities appeared. Thus extraordinarily high reduced viscosities were reached by the "6.7%" polysoap at higher concentrations, while η_{sp}/C for the "28.5%" polysoap was lower than for the "37.9%" polysoap. The greatest reduced viscosity decrease occurred in going from the "6.7%" to the "13.6%" polysoap. Solubilized *n*-decane, benzene and 1-heptanol influenced η_{sp}/C as follows: decane and benzene behaved as with previously studied polysoaps, but the benzene maximum was absent in some instances. Heptanol showed both a maximum and a minimum in concentrated solutions of the "28.5%" and the "37.9%" polysoaps. With decreasing polysoap concentration the maximum disappeared but the minimum remained. Deviations from this behavior appeared with the "13.6%" polysoap. The viscosity results are interpreted in terms of two fundamental properties of the polysoap molecule, its effective size and the hydrophobic fraction of its surface. The best solubilizer for the three additives was the "37.9%" polysoap. Decane solubilization dropped off extremely rapidly with decreasing dodecyl group content, reaching a value of zero for the "13.6%" polysoap. The solubilization limits of benzene and heptanol decreased by factors of ten and two, respectively, from the "37.9%" to the "13.6%" polysoap. Dilute solutions of the "6.7%" polysoap or the polyvinylethylpyridinium bromide solubilized neither benzene nor heptanol to any measurable extent.

Introduction

In several recent studies¹⁻⁴ it has been shown that polysoaps (which are defined as polymers to whose chain structure soap⁵ molecules are chemically attached) differ considerably in their physical properties from the conventional synthetic polyelectrolytes.⁶ These differences must be due to the presence of the long hydrophobic side chains in the polysoap molecules, for it is only in this respect that the two types of substances are chemically distinct. It is then of interest to study the gradual transition from typical polyelectrolyte to polysoap by progressively attaching a greater number of such side chains to the flexible backbone of a macro-ion.

The ethyl bromide addition product of poly-4-vinylpyridine was chosen as the typical polyelectrolyte. Four polysoaps were prepared from this same sample of poly-4-vinylpyridine by quaternizing 6.7, 13.6, 28.5 and 37.9% of the nitrogens with *n*-dodecyl bromide and the remaining nitrogens with ethyl bromide. In this way the dodecyl group content could be varied while at the same time the electrolyte density along the polymer chain was held constant. An exploratory study of the viscosity and solubilization properties of these compounds in aqueous solution was then undertaken, and the results of this study are presented and compared in this paper.

Experimental

Materials.—Poly-4-vinylpyridine (our sample No. G 13) was prepared at 49° by the emulsion polymerization of 400

g. of 4-vinylpyridine (b.p. 56–56.5° at 11 mm.) with 0.4 g. of benzoyl peroxide and 1 g. of Nekal AEMA in 800 g. of water according to the method of Fitzgerald and Fuoss.⁷ The yield was 360 g. Nitrogen⁸ was 13.55%, theoretical 13.33%. The portion which was to be used for the characterization of the polymer was dissolved in *t*-butyl alcohol in order to remove a slight amount of insoluble material⁹ by filtration. After freeze-drying, the intrinsic viscosity in 92.0 weight per cent. ethanol (density = 0.8080 at 25°) was 4.88 at 25°. From this value we estimate the degree of polymerization to be about 6000.

Each of the four dodecyl bromide addition compounds (our samples No. G 335, G 137 A, G 137 B, G 137 C) was prepared as follows: one part of the poly-4-vinylpyridine was dissolved in 28 parts of a 1:1 nitromethane–nitroethane mixture, and after filtering out the slight amount of insoluble gel⁹ 50 parts of *n*-dodecyl bromide (b.p. 140° at 11 mm.) were added at 49°. After allowing the reaction to proceed for the desired time (2, 5, 9.7 and 17.7 hours, respectively), the reaction mixture was poured into three volumes of ethyl acetate at 0°. The precipitated polymer was dried *in vacuo* and purified by precipitation from a 5% solution of a butanone–ethanol mixture (containing just enough ethanol to dissolve the polymer) into four volumes of ethyl acetate¹⁰ at 0°.

Polymers G 335, G 137 A, G 137 B and G 137 C were analyzed for bromide ion content by potentiometric titration with silver nitrate and for hydrogen ion content by potentiometric titration with sodium hydroxide in 50% ethanol solution. Bromide ion was 0.543, 1.083, 1.697, and 1.995 meq./g., respectively, and hydrogen ion 0.028, 0.130, 0.121, 0.121 meq./g., respectively. Nitrogen⁸ was 10.8, 9.78, 7.73, 6.93%, respectively. The bromide ion to nitrogen atom ratio gives the fraction of the pyridine groups which are substituted. The hydrogen ion to nitrogen atom ratio determines how much of this substitution is due to hydrogen bromide. The difference (multiplied by 100) gives the percentage of pyridine groups quaternized with dodecyl bromide. These values are 6.7, 13.6, 28.5 and 37.9%, respectively.

Each of the four polysoaps (our sample No. G 339, G 147, G 146, G 145) was prepared by refluxing three parts

(7) E. B. Fitzgerald and R. M. Fuoss, *Ind. Eng. Chem.*, **42**, 1603 (1950).

(8) All nitrogen analyses reported in this paper were performed by W. Manser, Mikrolabor der E. T. H., Zurich, Switzerland.

(9) Approximately 2% of the polyvinylpyridine was cross-linked.

(10) In the case of polymer G 335 a 1:1 ethyl acetate–isooctane mixture was used instead of the ethyl acetate.

(1) U. P. Strauss and E. G. Jackson, *J. Polymer Sci.*, **6**, 649 (1951).
 (2) E. G. Jackson and U. P. Strauss, *ibid.*, **7**, 473 (1951).
 (3) L. H. Layton, E. G. Jackson and U. P. Strauss, *ibid.*, **9**, 295 (1952).
 (4) U. P. Strauss, S. J. Assony, E. G. Jackson and L. H. Layton, *ibid.*, **9**, 509 (1952).
 (5) The term *soap* is used here in its broader sense including both cationic and anionic detergents.
 (6) R. M. Fuoss, *Science*, **108**, 545 (1948).

of the desired intermediate polymer (No. G 335, G 137 A, G 137 B and G 137 C, respectively) with 13 parts of ethyl bromide in 68 parts of nitromethane at 49° for 72 hours. The reaction mixture was poured into three volumes of ethyl acetate¹¹ at 0°, and the precipitated polysoap was purified several times by precipitation from dilute ethanol solution into an excess of ethyl acetate¹² at 0°.

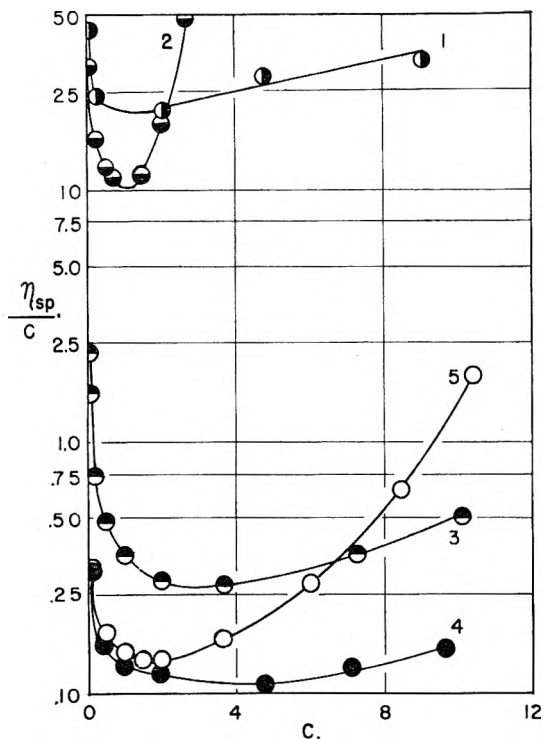


Fig. 1.—Effect of dodecyl group content on reduced viscosity of polyelectrolytes: 1, polyvinyl-N-ethylpyridinium bromide; 2, "6.7%" polysoap; 3, "13.6%" polysoap; 4, "28.5%" polysoap; 5, "37.9%" polysoap.

The analytical results and the composition values which were calculated as above (using the dodecyl bromide substitution of the appropriate intermediate polymer) are given as follows.

"6.7%" Polysoap (our sample No. G 339): N, 6.30%; Br⁻, 4.29 meq./g.; H⁺, 0.094 meq./g.; 6.7% of pyridine groups substituted with *n*-dodecyl bromide, 86.4 with ethyl bromide, 2.1 with hydrogen bromide, 4.8 free.

"13.6%" Polysoap (our sample No. G 147): N, 6.18%; Br⁻, 4.15 meq./g.; H⁺, 0.159 meq./g.; 13.6% of pyridine groups substituted with *n*-dodecyl bromide, 77.0 with ethyl bromide, 3.6 with hydrogen bromide, 5.8 free.

"28.5%" Polysoap (our sample No. G 146): N, 5.37%; Br⁻, 3.79 meq./g.; H⁺, 0.149 meq./g.; 28.5% of the pyridine groups substituted with *n*-dodecyl bromide, 66.6 with ethyl bromide, 3.9 with hydrogen bromide, 1.0 free.

"37.9%" Polysoap (our sample No. G 145): N, 5.33%; Br⁻, 3.57 meq./g.; H⁺, 0.146 meq./g.; 37.9% of pyridine groups substituted with *n*-dodecyl bromide, 52.1 with ethyl bromide, 3.8 with hydrogen bromide, 6.2 free.

Poly-4-vinyl-N-ethylpyridinium bromide (our sample No. G 254) was prepared from the polyvinylpyridine (No. G 13) and ethyl bromide in a similar manner as a butyl bromide analog previously described.¹³ Nitrogen was 6.35%, bromide ion 4.53 meq./g., and hydrogen ion 0.087 meq./g. indicating that 97.8% of the pyridine groups were substituted with ethyl bromide, 1.8 with hydrogen bromide while 0.4 remained free.

(11) In the case of polysoap G 339 a 1:1 ethyl acetate-iso-octane mixture was used instead of the ethyl acetate.

(12) In the case of polysoap G 339 dry dioxane was used instead of the ethyl acetate.

(13) R. M. Fuoss and U. P. Strauss, *Ann. New York Acad. Sci.*, **61**, 836 (1949).

The solubilizes, benzene (thiophene free), *n*-decane and 1-heptanol (Eastman Kodak white label products) were redistilled before use.

Procedure.—Viscosities were measured in a Bingham viscometer¹⁴ whose constant (pt_0) for water at 25° was 7506 gram seconds per square centimeter.

Previously described methods were used for preparing and equilibrating the polysoap solutions containing the desired amounts of solubilize.³⁻⁴

Results and Discussion

Reduced Viscosities.—The way in which the number of soap molecules attached to the polymer chain affects the viscosimetric behavior in aqueous solution is shown in Fig. 1, where for each of the five samples η_{sp}/C , the reduced viscosity, is plotted against C , the polymer concentration in g. per 100 ml. Starting our discussion with the polyelectrolyte containing no dodecyl side chains (sample No. G 254), which is represented by curve 1, we find the by now familiar pattern for such a polyelectrolyte: the reduced viscosity which is very large at high dilutions because of the highly extended configuration of the flexible polyions decreases with increasing polymer concentration as the electrostatic repulsions between ionized groups are diminished; at still higher concentrations, the reduced viscosity increases again because of the short range interactions between proximate polyions. Curve 2 illustrates the behavior of the "6.7%" polysoap which may be imagined as having been created from the polyelectrolyte of curve 1 by replacing the ethyl side chains of 6.7% of the pyridine nitrogens with *n*-dodecyl side chains.¹⁵ The effect of this change is striking and manifests itself in two ways, both of which may be explained in terms of the van der Waals attractive forces between the long hydrophobic side chains. In the dilute region the reduced viscosity is depressed by about 30 to 50% which may be ascribed to a contraction of the flexible polymer coils brought about by the attractions between dodecyl groups belonging to the same polyion. In the concentrated region, on the other hand, curve 2 rises much more steeply than curve 1, which may be ascribed to aggregate formation of the polymer molecules brought about by the attractions between dodecyl groups belonging to different polyions. This apparent "stickiness" of the polysoap molecules is very sensitive to temperature changes: while a 5% solution of this polymer is practically a stiff gel at 25°, it is quite fluid at 50°. Evidently the intermolecular attractions are reduced as the opposing thermal forces become larger.

Curve 3 shows the behavior of the "13.6%" polysoap which contains just about twice as many dodecyl groups as the polysoap of curve 2. This change in composition is seen to produce a reduced viscosity depression amounting to more than an order of magnitude. The large contraction of the polysoap molecules, which is indicated by this viscosity change, also decreases the extent to which the polysoap molecules fill the solution volume and hence the extent of contacts between them.

(14) E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922.

(15) The small differences in the hydrogen bromide content and in the number of unquaternized pyridine groups should have a negligible effect and are therefore ignored in the discussion.

As a consequence of this decrease in intermolecular interactions curve 3 is seen to rise far less steeply than curve 2 in the region of higher polysoap concentrations.

The behavior of the "28.5%" polysoap is represented by curve 4. The change from curve 3 to curve 4 is in the expected direction, and the reduced viscosity reaches values only slightly higher than 0.1 which is quite low for a polymer whose molecular weight is of the order of 10^6 . The van der Waals forces are seen to contract these polysoap molecules to almost protein-like compactness.

As still more dodecyl groups are introduced into the polysoap molecules the hithertofore observed decreasing trend in the reduced viscosity is reversed. Curve 5 which represents the "37.9%" polysoap is seen to lie above curve 4. The steep rise of curve 5 in the high concentration region indicates that this reversal in trend is due to increased interactions between polysoap molecules. Apparently the "28.5%" polysoap molecules are already so compact that a further increase in dodecyl group content increases their "stickiness" much more than their compactness.

Solubilization.—It has been shown that the reduced viscosity of solutions of polysoaps derived from poly-2-vinylpyridine is affected in different ways depending on whether aliphatic or aromatic hydrocarbons are solubilized.³ As increasing amounts of aliphatic hydrocarbons are added, the reduced viscosity decreases uniformly until hydrocarbon saturation is reached; on the other hand, with aromatic hydrocarbons the reduced viscosity goes first through a maximum. The same behavior is observed with a 6% solution of our 4-vinylpyridine derived "37.8%" polysoap as is shown in Fig. 2 where the effects of *n*-decane and benzene are illustrated by curves 1 and 2, respectively. In this and similar following figures the abscissa *K* repre-

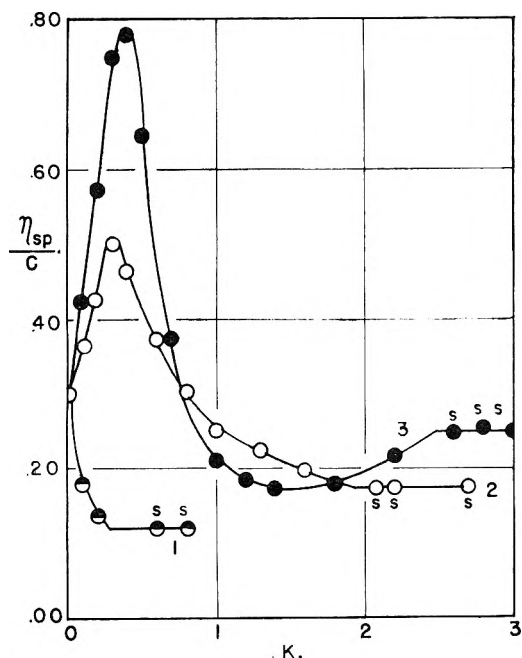


Fig. 2.—Effect of three solubilizates on the reduced viscosity of a 6% solution of the "37.9%" polysoap: 1, decane; 2, benzene; 3, heptanol.

sents the concentration of additive in units of g./100 ml., while the experimental points labeled with the symbol S correspond to saturated solutions containing a visible excess of additive. Curve 3 illustrates the effect of 1-heptanol on the reduced viscosity of the same solution. As increasing amounts of heptanol are solubilized, the reduced viscosity passes first through a maximum similar to, though higher than, that due to benzene and then through a minimum before heptanol saturation is reached. To find out more about the nature of these effects, studies were also made at lower concentrations of the same polysoap. In Fig. 3, curves 1, 2 and 3 show the influence of decane, benzene and heptanol, respectively, on the reduced viscosity of a 2% polysoap solution. It is seen that the lowering of the polysoap concentration has caused the benzene maximum to completely disappear, thus further supporting the previously reached conclusion³ that this maximum is caused by interactions between polysoap molecules.¹⁶ In the case of heptanol the maximum is just barely present in the 2% polysoap solution and completely absent in a 0.5% polysoap solution as is shown in curve 4. The reduced viscosity minimum, however, persists at all polysoap concentrations. These results suggest that the maximum, just as in the case of benzene, is caused by interactions between the polysoap molecules while the minimum reflects changes in their size. These points can be seen somewhat more clearly, if the data are presented in a somewhat different form. In

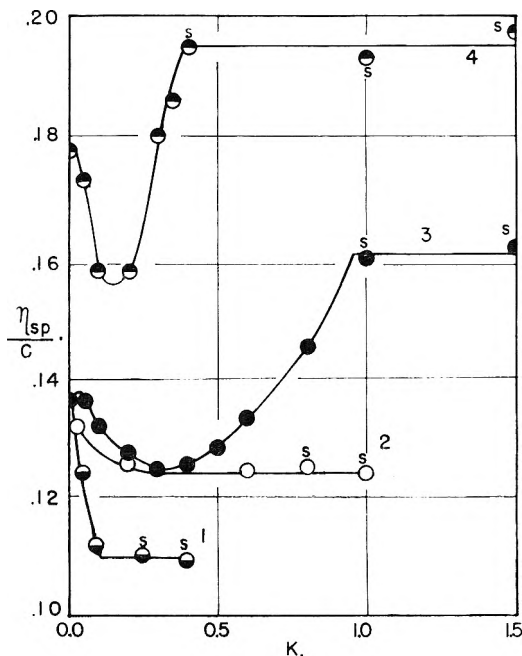


Fig. 3.—Effect of three solubilizates on the reduced viscosity of dilute solutions of the "37.9%" polysoap: 1, decane; 2, benzene; 3, heptanol; 4, heptanol in 0.5% polysoap solution.

(16) In contrast, the maximum is still quite pronounced in 2% solutions of polysoaps derived from poly-2-vinylpyridine.³ This difference between the two types of polysoaps is probably due to the greater stiffness of the poly-2-vinylpyridine chain which causes the polysoap molecules derived from this parent polymer to be less compact, which in turn produces a greater number of intermolecular contacts and hence more interaction between different polysoap molecules.

Fig. 4 each curve represents a reduced viscosity against polysoap concentration plot. Curve 1 represents the polysoap without added heptanol. When 0.058 g. of heptanol per g. of polysoap has been solubilized,¹⁷ curve 2 results. The fact that this curve starts out below curve 1 at low concentrations and then rises sharply above it as the polysoap concentration increases indicates that the solubilization of this small amount of heptanol has on the one hand made the polysoap molecules more compact and on the other has enormously increased their tendency to interact with one another. As more heptanol is solubilized the steepness of the curves at the higher concentrations decreases again. Curve 3 which corresponds to a solubilization of 0.217 g./g. and curve 4 which corresponds to heptanol saturation (0.387 g./g.) are seen to be relatively flat, indicating that the interactions between polysoap molecules have become quite weak. The reduced viscosity increase from curve 3 to curve 4 may therefore be interpreted as due to a swelling of the polysoap molecules.

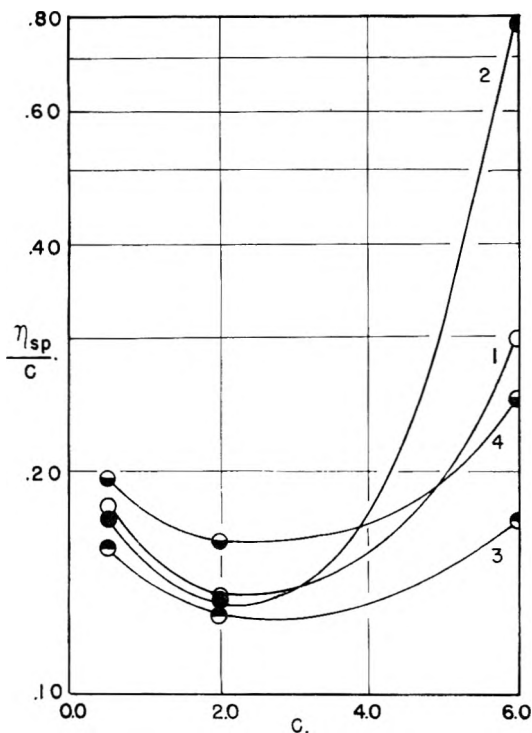


Fig. 4.—Effect of solubilized heptanol on plot of reduced viscosity against concentration of “37.9%” polysoap; grams of heptanol solubilized per g. of polysoap: (1) 0.000; (2) 0.058; (3) 0.217; (4) 0.387.

The way in which the heptanol brings about these changes is somewhat difficult to understand. However, the following mechanism seems reasonable: at first the heptanol molecules are predominantly solubilized with their hydroxyl groups located in the polar region near the polymer backbone and

(17) This and similar values appearing later have been corrected for the amount of heptanol which is dissolved in the water with the assumption that for a given polysoap solution the distribution ratio of heptanol between the polysoap molecules and the water is constant for all heptanol concentrations. This distribution ratio is calculated at heptanol saturation from the known solubility of heptanol in water and from the measured solubility in the polysoap solution.

with their aliphatic chains extending into the hydrocarbon region of the polysoap molecule. This will contract the polar region which therefore will be less able to shield the hydrocarbon region from the aqueous medium. The hydrocarbon which is thus exposed at the surface of the polysoap molecule will be attracted by van der Waals forces to similarly exposed hydrocarbon of other polysoap molecules, with the result that the polysoap molecules will tend to stick to one another. These interactions are responsible for the initial viscosity increase in the 6% solution, while the simultaneous contraction of the polysoap molecules causes the initial viscosity decrease in the 0.5% solution. In order to explain what happens when more heptanol is added, we have to assume that the heptanol molecules also can be solubilized at the hydrocarbon-water interfaces in such a way that the hydroxyl groups are in the water while the aliphatic chains are anchored in the hydrocarbon region of the polysoap molecules. In this manner the exposed hydrocarbon becomes shielded by the hydroxyl groups and the “stickiness” decreases. The resulting decrease in the interactions is responsible for the decline in the reduced viscosity beyond the maximum in the 6% solution. The same type of mechanism may also reduce the van der Waals forces between different parts of the same polysoap molecule. This would explain the swelling of the polysoap molecules which is indicated by the reduced viscosity increase beyond the minimum.¹⁸

Similar effects are observed with the “28.5% polysoap” as is shown in Fig. 5. Curve 1 illustrates the influence of solubilized heptanol on a 1% polysoap solution. After a slight decrease the reduced viscosity increases above its original value, reflecting corresponding changes in the size of the polysoap molecules. In curve 2 which shows the effect of heptanol on a 3.98% polysoap solution, the interaction maximum is present again. The minimum occurs when the interactions become small again. It is seen that at this point the polysoap molecules are already swollen beyond their original size. For comparison the small decrease of the reduced viscosity of this solution brought about by decane is shown by curve 3.

The effects of the various solubilizes on both a dilute and a concentrated solution of the “13.6%” polysoap are shown in Figs. 6 and 7, respectively. The curves 1 indicate that decane is not solubilized by this polysoap. In view of the fact that the molecules of this polysoap are more than twenty times as compact as those of the polyelectrolyte without the dodecyl groups, it is surprising that the dodecyl groups which bring about this compactness are unable to bring about the solubilization of decane. The significance of this result may be that a dense hydrocarbon region of a definite minimum size in the interior of the polysoap molecules is necessary for solubilization of aliphatic hydrocarbons to take place.

(18) In those cases where the viscosity first goes through a maximum the swelling may begin while the interactions are decreasing. As a consequence, the viscosity minimum will appear at a higher heptanol concentration than the one corresponding to the beginning of the swelling.

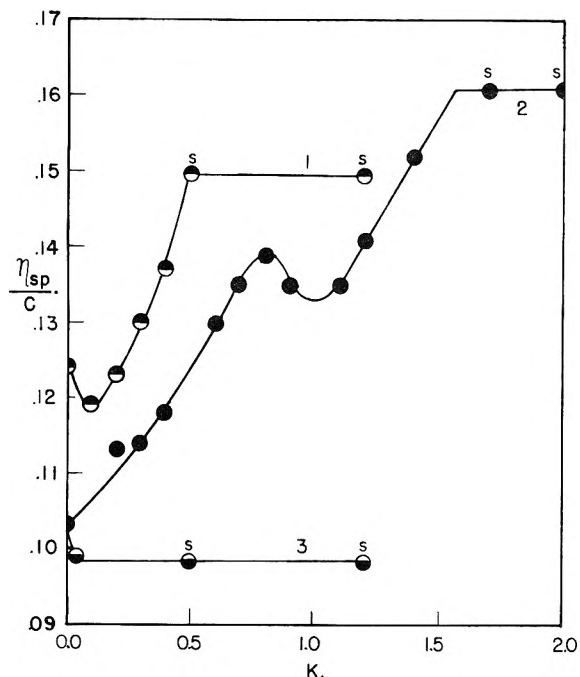


Fig. 5.—Effect of heptanol and decane on the reduced viscosity of the "28.5%" polysoap: 1, heptanol in 1% polysoap solution; 2, heptanol in 3.98% polysoap solution; 3, decane in 3.98% polysoap solution.

The curves 2 in Figs. 6 and 7 illustrate the effect of benzene. The reduced viscosity is seen to decrease until saturation is reached, and no viscosity maximum appears. Apparently the relatively few dodecyl groups are shielded by the polar region even when the latter is contracted by the solubilized benzene. The same reason would account for the absence of the viscosity maxima in the curves 3 which illustrate the influence of heptanol. The absence of the viscosity minimum in the 1.88% polysoap solution is more difficult to explain. The fact that considerably less heptanol can be solubilized per g. of polysoap in this solution than in the 7% polysoap solution where the minimum does appear may have a bearing on this problem. Possibly the polysoap molecules are not compact enough in the 1.88% solution to allow for the type of heptanol solubilization which in the more compact polysoap molecules produce the final increase in size.

The solubilizing powers of the "37.9%," "28.5%" and "13.6%" polysoaps at various concentrations, C , are compared in Table I. The quantities marked S represent the amount of organic substance solubilized by the polysoap per 100 ml. of solution. S is obtained by subtracting the solubility in water (decane, 0.000 g./100 ml.¹⁹; benzene, 0.179 g./100 ml.²⁰; 1-heptanol, 0.18 g./100 ml.²¹) from the solubility in the polysoap solution which is determined in the usual manner from the η_{sp}/C against K plot.^{2,3} The values of S/C , which represent the solubility per g. of polysoap, are seen to

(19) J. W. McBain and P. H. Richards, *Ind. Eng. Chem.*, **38**, 642 (1946).

(20) R. L. Bohon and W. F. Clausen, *J. Am. Chem. Soc.*, **73**, 1571 (1951).

(21) J. A. V. Butler, D. W. Thomson and W. H. MacLennan, *J. Chem. Soc.*, 674 (1933).

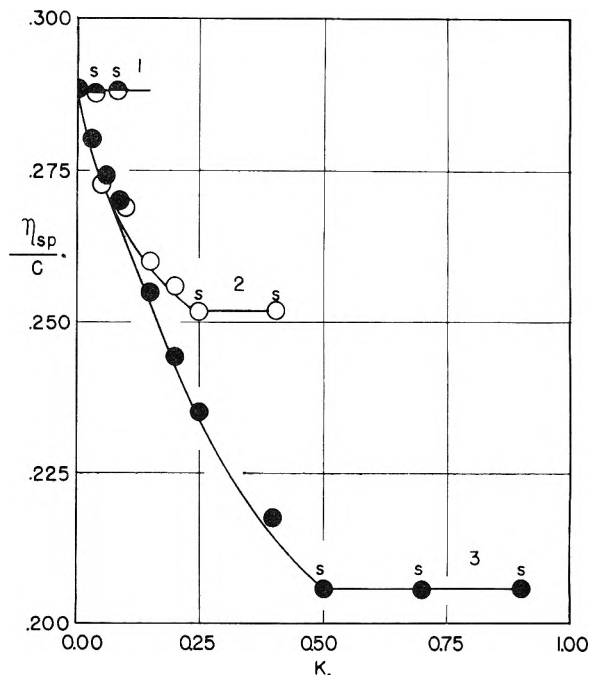


Fig. 6.—Effect of three solubilizates on the reduced viscosity of a 1.88% solution of the "13.6%" polysoap: 1, decane; 2, benzene; 3, heptanol.

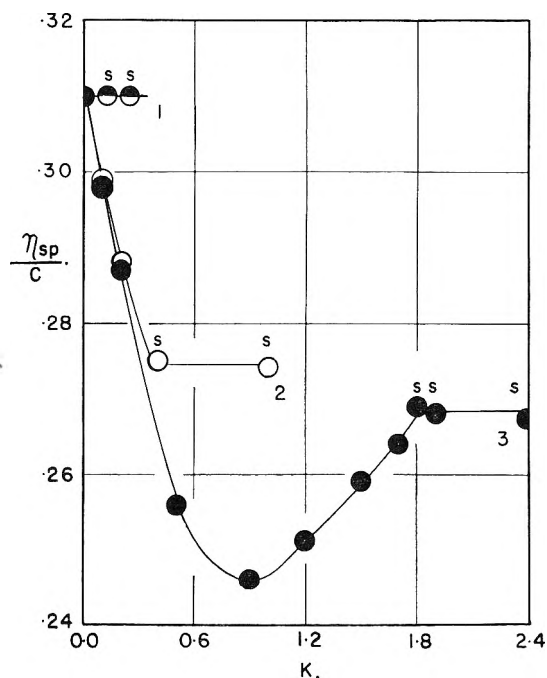


Fig. 7.—Effect of three solubilizates on the reduced viscosity of a 7% solution of the "13.6%" polysoap: 1, decane; 2, benzene; 3, heptanol.

decrease for all solubilizates as the number of dodecyl groups per polysoap molecule decreases. In this connection it should be pointed out that by visual inspection the solubilities of both benzene and heptanol in 1% solutions of the "6.7%" polysoap were found to be less than 0.01 g. per g. of polysoap. The same results were also found for the polyelectrolyte without dodecyl groups.

Since these results clearly indicate that it is the presence of the dodecyl groups which causes the

TABLE I
 SOLUBILIZATION LIMITS

Polysoap	Decane			Benzene			1-Heptanol			
	C_1 , g./100 ml.	S_1 , g./100 ml.	S/C_1 , g./g.	T_1 , moles/ mole C_{12}	S_2 , g./100 ml.	S/C_2 , g./g.	T_2 , moles/ mole C_{12}	S_3 , g./100 ml.	S/C_3 , g./g.	T_3 , moles/ mole C_{12}
"37.9%"	0.50	0.195	0.39	2.3
	2.00	0.11	0.055	0.27	0.52	0.26	2.3	0.77	.39	2.3
	6.00	.35	.058	.28	1.76	0.29	2.6	2.32	.39	2.3
"28.5%"	1.00	0.30	.30	2.4
	3.98	.06	.015	.10	1.36	.34	2.7
"13.6%"	1.88	.00	.00	.00	0.056	0.030	0.64	0.31	.17	2.4
	7.00	.00	.00	.00	0.20	0.029	0.62	1.60	.23	3.3

solubilization to take place, it is of interest to calculate T , the number of solubilize molecules which are solubilized per dodecyl group. The sharp decline of this number for both decane and benzene as the amount of dodecyl groups per polysoap molecule decreases is noteworthy and indicates that it is the synergistic effect of a large number of dodecyl groups in the same polysoap molecule which controls the solubilization of these hydrocarbons.²²

In the case of heptanol, on the other hand, the values of T seem to increase with decreasing dodecyl content of the polysoaps. The reason for this is not clear. Moreover, while in all other instances variations in the polysoap concentration had no observable effect on T (within the precision limits of about 10%), in the case of the "13.6%" polysoap the increase of T with increasing polysoap concentration is much larger than the experimental uncertainty. This increase of T with increasing polysoap concentration may be due either to interactions between polysoap molecules or to their greater compactness at the higher concentrations. In view of the viscosity behavior which has already been discussed the latter view is favored at present. Further work involving other long chain alcohols and electrolytes as additives is necessary before these difficulties can be resolved.

Acknowledgment.—This investigation was supported by research grants from the Office of Naval Research and the Rutgers Research Council.

DISCUSSION

PAUL DORY (Harvard University).—Do you not have to consider that the distribution of substitution may be so wide that dodecyl-rich molecules may solubilize dodecyl-poor molecules? Have you any independent evidence that the solutions are molecularly disperse?

U. P. STRAUSS.—The polysoap molecules discussed in this paper become more hydrophobic with increasing dodecyl group content, but they all are soluble in water. For these reasons, solubilization of dodecyl-poor molecules by dodecyl-rich molecules is unlikely. On the other hand, studies involving the effect of electrolytes on the solubility of these polysoaps show some polydispersity of the "13.6%" and the "28.5%" polysoaps with respect to dodecyl content. Since the amount of hydrocarbon which can be solubilized has been shown to increase much faster than linearly with the dodecyl content of the polysoap molecules, one may expect that a polydisperse "X%" polysoap will solubilize more hydrocarbon than a monodisperse "X%" polysoap. The preparation of reasonably monodisperse polysoaps is in progress in order to test this point.

R. M. FUOSS (Yale University).—How does the conductance of polysoaps depend on the amount of solubilized oil?

(22) This, of course, does not imply that decane and benzene are solubilized by the same mechanism.

U. P. STRAUSS.—No electrolytic conductance of the polysoaps described in this paper has been measured. However, the conductance of aqueous solutions of a polysoap derived from poly-2-vinylpyridine decreased slightly with the addition of decane, much more so with the addition of benzene, and first decreased and then increased slightly with the addition of octanol (U. P. Strauss and S. Slowata, unpublished results). The observation that the conductance decreased uniformly while the viscosity went through a maximum for both benzene and octanol indicates that the viscosity maximum is not caused primarily by changes in the electrical charge of the polysoap ion.

J. J. HERMANS (University of Groningen).—It might be possible to distinguish between the effect of size and the effect of interaction on viscosity if the experiments were carried out in the presence of small amounts of electrolytes, especially if use is made of the technique of "iso-ionic dilution" (D. T. F. Pals, Thesis, Groningen, 1951).

U. P. STRAUSS.—Such studies with electrolytes are in progress. However, there are two reasons which indicate that such a procedure is not as simple with polysoaps as with conventional polyelectrolytes. First, it is experimentally difficult to work at low polysoap concentrations, especially in the presence of electrolytes, because of the very small values of the reduced viscosity. Second, the addition of electrolytes does not always cause a decrease of the interactions between polysoap molecules but in some cases causes an increase.

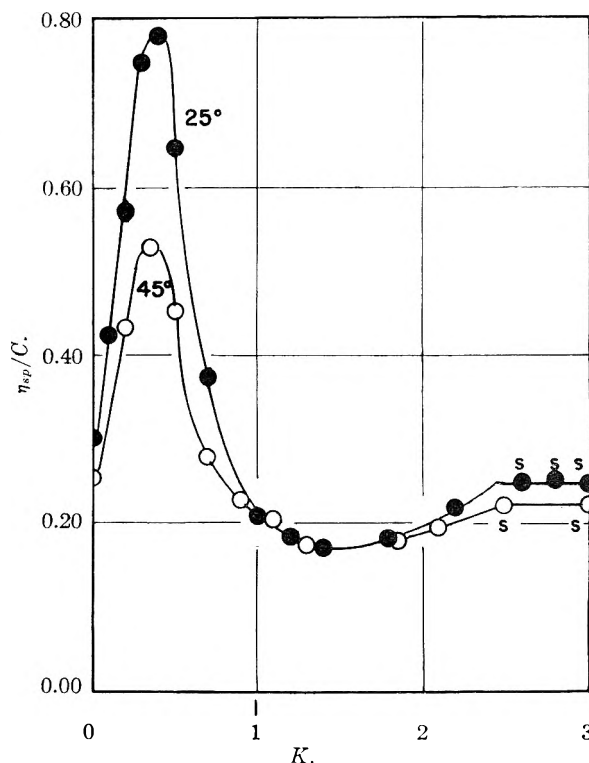


Fig 8.—Effect of heptanol on the reduced viscosity of a 6% solution of the "37.9%" polysoap at 25° and at 45°.

H. MORAWETZ (Polytechnic Institute of Brooklyn).—What is the temperature dependence of the viscosity maxima and minima which you have obtained.

U. P. STRAUSS.—The effect of temperature on the reduced viscosity of a 6% solution of the "37.9%" polysoap with solubilized heptanol is shown in Fig. 8. The viscosity maximum is seen to be strikingly reduced by a temperature rise from 25 to 45°. It has been shown previously that a 20° temperature rise hardly affects the reduced viscosity of polysoap solutions when the reduced viscosity is predominantly a measure of the size of the polysoap molecules [L. H.

Layton and U. P. Strauss, *J. Colloid Sci.*, **9**, 149 (1954)]. Therefore the large viscosity decrease at the viscosity maximum is further evidence for the conclusion that the maximum is caused by interactions between polysoap molecules. The increase in the thermal energy presumably disrupts these interactions sufficiently to bring about the observed viscosity decrease. At the viscosity minimum, on the other hand, the 20° temperature rise seems to be without effect on the reduced viscosity, thus confirming our conclusion that the minimum reflects a change in the size of the polysoap molecules.

REACTION RATES OF POLYELECTROLYTE DERIVATIVES. I. THE SOLVOLYSIS OF ACRYLIC ACID-*p*-NITROPHENYL METHACRYLATE COPOLYMERS¹

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The solvolysis rate of acrylic acid copolymers containing up to 9 mole % *p*-nitrophenyl methacrylate is independent of the composition of the copolymer. In methanol or water the reaction rate is controlled by the attack of a neighboring carboxylate ion on the ester. In aqueous solution, the rate does not bear the usual relationship to hydrogen and hydroxyl ion concentration but is approximately proportional to the degree of ionization of the copolymer. Between pH 5 and 7 the hydrolysis of the copolymer is 5 to 6 orders of magnitude faster than that of *p*-nitrophenyl trimethylacetate. Addition of dioxane reduces the hydrolysis rate of the unneutralized copolymer sharply and increases the effectiveness of HCl in slowing it down still further. For 9.1% neutralized copolymer, the rate is a maximum in a medium containing 40–50 volume % dioxane.

Introduction

The base-catalyzed hydrolysis of dicarboxylic acids is retarded by the mutual repulsion of the catalyzing hydroxyl ion and the monoester anion. Ingold³ has shown that this effect is related to the ratio of the two ionization constants of the dicarboxylic acid. The comparison of hydrolysis rates of polyelectrolyte derivatives and corresponding rates observed with uncharged analogs would appear, in principle, to provide an attractive approach to the calculation of electrostatic potentials in the neighborhood of the polyions. Katchalsky has recently reported⁴ that potentials calculated from the rate of the alkaline hydrolysis of pectin are in good agreement with those calculated from titration data.

The results of the present investigation show that, instead of this expected retardation, attaching an ester group to a polyelectrolyte chain can produce an acceleration of the reaction by many orders of magnitude. This effect cannot be due to the concentration of hydrogen ions in the neighborhood of the polyanion, since strong mineral acid is found to retard the solvolysis. The available evidence indicates that the peculiar behavior of the ester copolymers is the consequence of a change in the mechanism of the reaction.

Copolymers of acrylic acid with less than 10 mole % *p*-nitrophenyl methacrylate were chosen for this study, since the high optical density of the ester groups and the characteristic shift of the absorption spectrum on solvolysis provide a con-

venient method for following the reaction at high dilution of the copolymer.

Experimental

Monomers.—Glacial acrylic acid (Rohm and Haas) was distilled under nitrogen at 20 mm. and the middle fraction boiling at 50.2° collected. *p*-Nitrophenyl methacrylate was prepared from C.P. *p*-nitrophenol recrystallized twice by cooling a toluene solution from 63° to 5° and methacrylyl chloride made according to directions by Rehberg, Dixon and Fisher.⁵ The esterification was carried out in pyridine at 0°. After warming to 20° for 30 minutes, the ester was extracted with ether, washed with 0.5 *N* HCl, water and 0.5 *N* NaOH, followed by water washing until the aqueous layer was colorless. After evaporating the ether, the crude crystals were washed with ice-water and recrystallized from ether five times. The *p*-nitrophenol content found spectrophotometrically after saponification was 2% above the theoretical value, m.p. 94.5–95.5°.

Polymerizations of acrylic acid homopolymer and copolymers were carried out in benzene at 52° using 30 mg. of azobis-isobutyronitrile (Eastman Kodak Co.) 5 g. of monomer and 25 ml. of benzene. Copolymer conversions were held to below 20%. After dilution with ether the polymer was separated by centrifugation, purified by repeated ether washing and freeze-dried from a benzene suspension. Copolymer compositions were determined by measuring the optical density of their solution in aqueous base at 404 $m\mu$ (ϵ 1.84 \times 10⁴ for *p*-nitrophenate ion). The copolymers contained between 2.2 and 2.4 times as much ester as the mixed monomers.

p-Nitrophenyl trimethylacetate was prepared from trimethylacetyl chloride⁶ (b.p. 30° at 150 mm.) using the same esterification procedure as for the methacrylate, m.p. 94–96°. The *p*-nitrophenol content found after saponification was 2% above the theoretical value.

Solvents.—Anhydrous methanol was prepared from the Fisher certified reagent by the method recommended by Fieser⁷ and its anhydrous condition was checked by titra-

(1) Financial support of this research by the Eli Lilly Co. is gratefully acknowledged.

(2) Part of a dissertation to be submitted by Paula Zimmering to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

(3) C. K. Ingold, *J. Chem. Soc.*, 1375 (1930).

(4) A. Katchalsky, *J. Polymer Sci.*, **12**, 159 (1954).

(5) C. E. Rehberg, M. B. Dixon and C. H. Fisher, *J. Am. Chem. Soc.*, **67**, 209 (1945).

(6) G. H. Stempel, R. P. Cross and R. P. Mariella, *ibid.*, **72**, 2299 (1950).

(7) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 360.

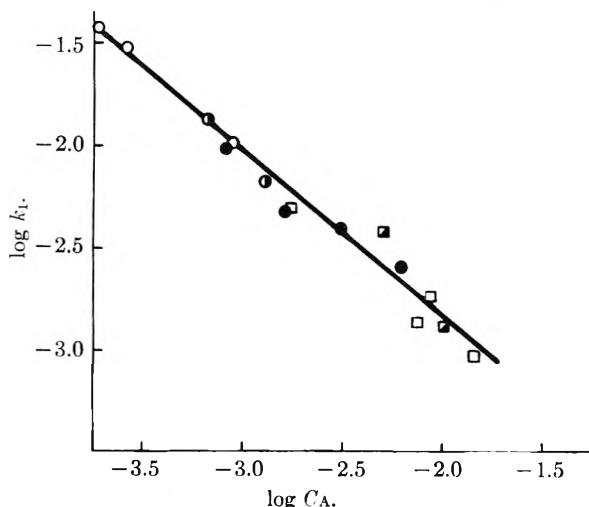


Fig. 1.—Methanolysis of acrylic acid-*p*-nitrophenyl methacrylate copolymer at 20°; mole % ester in copolymer: ○, 8.98; ●, 4.81; ●, 4.18; □, 2.16; ▣, polyacrylic acid with 8.98 mole % copolymer.

where the formation of the cyclic intermediate is the rate-determining step. Transition states of this type have been postulated for the displacement of halogen in *trans* α -acetoxy compounds,⁸ the hydrolysis of γ -bromocaproate ion⁹ and of chlorohydrins in neutral solution.¹⁰ Conclusive evidence also has been presented for a similar mechanism in the hydrolysis of salicyl phosphate¹¹ and α -carboxynaphthyl phosphates.¹²

If the solvolysis rate depends on the presence of an ionized carboxylate group next to the ester group on the polymer chain, and if the formation of the cyclic intermediate is independent of the ionization of the second carboxyl neighbor, the rate should be proportional to the degree of ionization α of the polyelectrolyte. Values of α were calculated as follows:

(a) In solutions containing added HCl, $\alpha = K_a/C_{\text{HCl}}f_{\pm}^2$ where the acid dissociation constant K_a of the polymeric carboxyls was estimated as 1.0×10^{-5} , using the published value for diethylacetic acid¹³ and allowing for the effect of 8.3 volume % dioxane.¹⁴ The ionic activity coefficient f_{\pm} was assumed to be equal to that of a solution containing the HCl without the polymer¹⁵ and C_{HCl} was the normality of HCl.

(b) In solutions containing only polymerized and copolymerized acrylic acid $\alpha = a_{\text{H}^+}/C_A f_{\pm}$. In these solutions only a small fraction of the polymer

(8) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780, 2787 (1942); **65**, 613 (1943); S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2796 (1942); S. Winstein, C. Hanson and E. Grunwald, *ibid.*, **70**, 812 (1948); S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948); S. Winstein, E. Grunwald and L. I. Ingraham, *ibid.*, **70**, 821 (1948); S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).

(9) J. F. Lane and H. W. Heine, *ibid.*, **73**, 1348 (1951).

(10) H. W. Heine, A. D. Miller, W. H. Barton and R. W. Greiner, *ibid.*, **75**, 4778 (1953).

(11) J. D. Chanley, E. M. Gindler and H. Sobotka, *ibid.*, **74**, 4347 (1952).

(12) J. D. Chanley and E. M. Gindler, *ibid.*, **75**, 4035 (1953).

(13) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

(14) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, pp. 547, 548.

(15) Reference 14, p. 514.

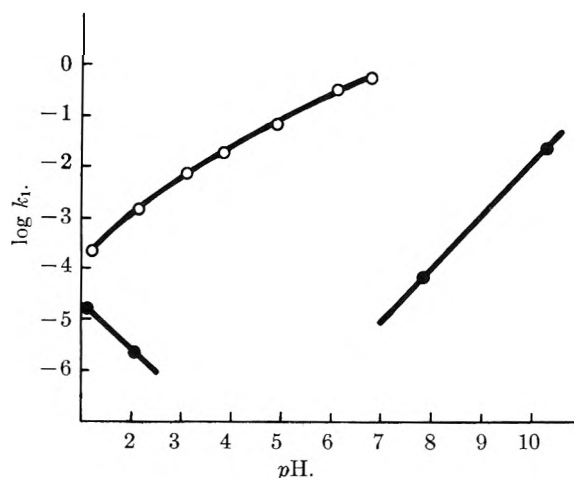


Fig. 2.—Hydrolysis of acrylic acid-*p*-nitrophenyl methacrylate copolymers and *p*-nitrophenyl trimethylacetate in water containing 8.3 volume % dioxane at 20°: ○, copolymer; ●, trimethylacetate.

carboxyls is ionized and for a_{H^+} of the order of 10^{-4} , f_{\pm} is assumed to approach unity.

(c) In solutions of partially neutralized copolymer $\alpha = (C_B + a_{\text{H}^+}/f_{\pm})/C_A$ where C_B is the concentration of added base. Values of the ionic activity coefficients in partially neutralized polymeric acid solutions are uncertain¹⁶ but since $a_{\text{H}^+}/f_{\pm}C_A$ is small compared to C_B/C_A at degrees of neutralization of 0.1 and higher, this term has been neglected.

Values of k_i/α for runs covering a range of acidities from pH 1.16 to 6.82 are listed in Table I and fall within the range 0.6 to 1.3. While this variation indicates the presence of secondary effects (such as the salt effect in passing from 0.001 to 0.1 *N* HCl and carboxylate association with sodium counter-ions in partially neutralized copolymers¹⁷) it should be compared with the 180-fold variation in $k_i a_{\text{H}^+}$, which would be constant (except for salt effects) if hydroxyl ion catalysis were rate determining. Even for methanolysis of the copolymer similar values of the ratio k_i/α were obtained. Thus, on neutralizing 2.54% of the copolymer with sodium methoxide in anhydrous methanol, the rate constant was 0.0557 min.^{-1} corresponding to $k_i/\alpha = 2.2$. Since formation of the transition state involves a dispersion of the anionic charge, the rate would be expected to increase slightly on reducing the dielectric constant of the medium.¹⁸

The interpretation of copolymer hydrolysis data in various mixtures of water and dioxane is more uncertain, since the solvent ratio in the immediate neighborhood of the macromolecule cannot be identified with the bulk average composition of the medium. Hydrolysis rates measured in the presence of varying dioxane concentrations are listed in Table II and plotted in Fig. 3.

(16) Ionic activity coefficients in half-neutralized polyacrylic acid solutions have been calculated from potentiometric data (W. Kern, *Makromol. Chem.*, **2**, 279 (1948)) but little is known about liquid junction potentials in presence of polyelectrolytes. The theoretical and experimental method of A. Katchalsky and S. Lifson (*J. Polymer Sci.*, **11**, 409 (1953)) is only applicable for polyelectrolyte solutions containing some simple electrolyte.

(17) J. R. Huizenga, P. F. Grieger and F. T. Wall, *J. Am. Chem. Soc.*, **72**, 4228 (1950).

(18) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 345-350.

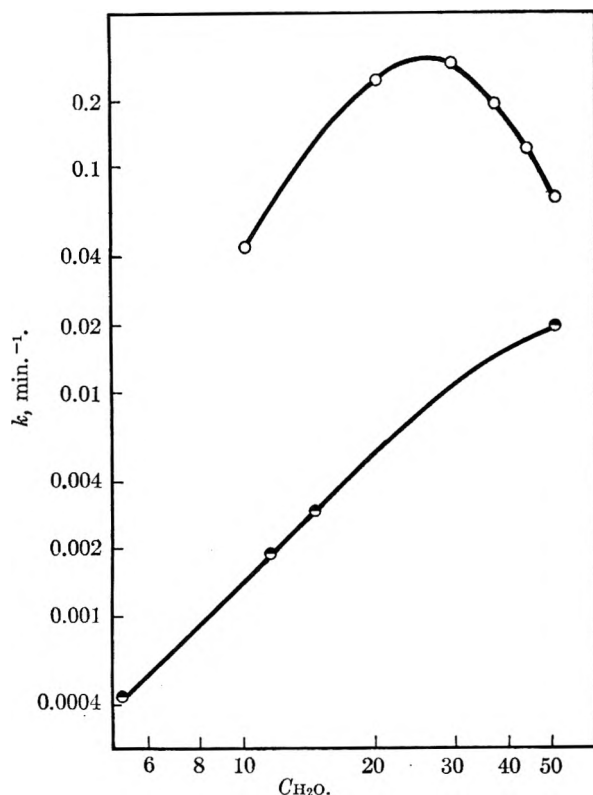


Fig. 3.—Hydrolysis of acrylic acid-*p*-nitrophenyl methacrylate copolymer in dioxane-water mixtures, at 20°: O, un-neutralized copolymer; ● 9.1% neutralized copolymer.

TABLE II
HYDROLYSIS OF ACRYLIC ACID-*p*-NITROPHENYL
METHACRYLATE COPOLYMERS IN DIOXANE-WATER
MIXTURES AT 20°

Vol. % dioxane	10 ³ CA	10 ³ CHCl	C _B /C _A	k _t , min. ⁻¹
8.3	10.05	..	0.091	7.34 × 10 ⁻²
19.0	10.13	..	.091	1.22 × 10 ⁻¹
30.9	10.00	..	.091	1.91 × 10 ⁻¹
45.0	10.07	..	.091	2.93 × 10 ⁻¹
63.3	10.05	..	.091	2.42 × 10 ⁻¹
81.7	10.17	..	.091	4.39 × 10 ⁻²
8.3	6.58	1.92 × 10 ⁻²
73.7	7.86	2.94 × 10 ⁻³
79.2	8.05	1.80 × 10 ⁻³
90.6	7.35	4.17 × 10 ⁻⁴
95.2	8.35	1.34 × 10 ⁻⁴
99.0	7.79	9.5 × 10 ⁻⁶
8.3	6.50	0.91	..	7.50 × 10 ⁻³
74.3	7.08	0.96	..	3.01 × 10 ⁻³

When the degree of ionization of the copolymer was fixed by partial neutralization with NaOH, the

hydrolysis rate was found to be accelerated by addition of up to 40–50 volume % dioxane, and decreased at higher dioxane concentrations. This behavior is similar to that of the hydrolysis of ethyl acetate¹⁹ and valerolactone²⁰ in mixed solvents and has been interpreted²⁰ as being due to the solvation of the transition state in the mixed solvent medium. When the hydrolysis of unneutralized copolymer was studied in mixed solvents, the above effects were overshadowed by the influence of the medium on copolymer ionization, and the rate was found to fall off rapidly with decreasing polarity of the medium. The data corresponded closely to a proportionality of the rate constant to the 5/3 power of the water concentration. Also, the lower the polarity of the medium, the more was the reaction retarded by the addition of strong acid. Whereas the addition of 0.001 *N* HCl slowed the copolymer hydrolysis in the presence of 8.3 volume % dioxane by a factor of 2.6, a hundred-fold retardation was observed in a solution containing 74 volume % dioxane. This observation agrees qualitatively with the mechanism proposed for the reaction, since the degree of ionization in solutions containing only carboxylic acid is proportional to $\sqrt{K_a}$, but becomes proportional to K_a in the presence of added HCl.

DISCUSSION

PAUL DOTY (Harvard University).—Would you agree that a polyacid which kept its ionized protons close to itself would not unduly catalyze a reaction that was first order in H⁺ but may exhibit a substantial effect in reactions of higher order in H⁺?

H. MORAWETZ.—A great deal of experimental evidence supports the view that the rate of hydrogen ion catalyzed reactions depends on the concentration, rather than the activity, of the catalyzing ion. Thus, at any given pH the rate should be inversely proportional to the mean activity coefficient, and since activity coefficients are low in polyelectrolyte solutions, the rate should be appreciably higher than in conventional buffer solutions of the same pH. We have looked for this effect in the hydrolysis of ethyl diazoacetate, but did not find it, although there were some characteristic differences when the reaction was carried out in buffer and partially neutralized polyacrylic acid, respectively.²¹ As Dr. Doty points out, the "polyelectrolyte effect" on reaction velocities should be particularly pronounced for reactions with rates proportional to a higher than first power of hydrogen ion concentration. We have considered in this connection rate studies of the benzidine rearrangement.

(19) J. E. Potts and E. S. J. Amis, *J. Am. Chem. Soc.*, **71**, 2112 (1949).

(20) E. Tommila and M. P. O. Ilamäki, *Acta Chem. Scand.*, **6**, 1249 (1952).

(21) M. Joseph and H. Morawetz, *J. Colloid Science*, **9**, 197 (1954).

LIGHT-SCATTERING BY POLYMETHACRYLIC ACID AND CARBOXYMETHYLCELLULOSE IN VARIOUS SOLVENTS

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A report is given of light-scattering studies on solutions of polymethacrylic acid and carboxymethylcellulose in methanol water, aqueous HCl and aqueous NaCl solutions. The results are well in line with those obtained by other authors. The behavior in methanol and in aqueous solutions of high electrolyte content is much the same as for uncharged polymers. In water and in dilute salt solutions, however, a behavior is found which is typical for polyelectrolytes. Nevertheless, the change of dissymmetry with polymer concentration in water and in dilute salt solutions is almost normal for NaCMC. This is attributed to the low charge density of this polymer. Five series of isoionic mixtures of NaCMC and NaCl have been investigated. The effective radius calculated from the angular intensity distribution is in excellent agreement with that derived from viscosity in previous work. It is shown that the theory of Katchalsky and Lifson does not apply to our data. The second virial coefficients A are compared with values obtained osmotically and with values reported by Doty and Schneider for a sample of NaCMC with twice the charge density of our sample. It is found that A is approximately proportional to the square of this charge density and to the $2/3$ power of the reciprocal ionic strength.

Recent studies on the scattering of light by solutions of charged colloid particles have been published, among others, by Fuoss and Edelson,² Cashin,³ Wall, Drenan, Hatfield and Painter,⁴ Oth and Doty,⁵ Doty and Steiner,⁶ Reichmann, Bunce and Doty.⁷ A review of work on proteins has been given by Edsall and Dandliker.⁸

We will use the customary notations: I_0 is the irradiance of the incident beam, R_θ the reduced intensity: $i_{\theta r^2}/I_0$, $P(\theta)$ the factor which determines the deviation from Thomson's angular distribution $1 + \cos^2 \theta$. In those cases where c/R_θ is a linear function of the polymer concentration c , we use the well-known equation

$$Kc/R_\theta = 1/MP(\theta) + 2Ac \quad (1)$$

where $K = 2\pi^2 n^2 (\partial n / \partial c)^2 / \lambda^4 N_A$, N_A being Avogadro's number, n the refractive index and λ the wave length *in vacuo*. Finally, z_θ is the ratio between i_θ and $i_{\pi-\theta}$ ($0 < \theta < \pi/2$), and $[z_\theta]$ represents the limit of z_θ when c approaches zero.

The formulas concerned can be found in the papers quoted. A short review has been given in a previous article⁹ where also the apparatus used has been described. The absolute values of R_θ were obtained from a comparison with Ludox solutions whose turbidities were determined in transmittance measurements.

1. Treatment of Solvents and Solutes

Polymethacrylic Acid.—A sample of this polyacid was purified and fractionated by precipitation, using dry methanol¹⁰ as solvent and ether as precipitant. Its number average molecular weight was determined osmotically by Benninga¹¹ in solutions of the polysalt in 0.1 *M* aqueous NaCl, the result being $M_n = 1.70 \times 10^6$. The weight average derived from our light-scattering data (see below)

(1) Lab. for Inorganic and Physical Chemistry, University of Leyden.

(2) R. M. Fuoss and D. Edelson, *J. Polymer Sci.*, **6**, 767 (1951).

(3) W. M. Cashin, *J. Colloid Sci.*, **6**, 271 (1951).

(4) F. T. Wall, J. W. Drenan, M. R. Hatfield and C. L. Painter, *J. Chem. Phys.*, **19**, 585 (1951).

(5) A. Oth and P. Doty, *THIS JOURNAL*, **56**, 43 (1952).

(6) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).

(7) M. E. Reichmann, B. H. Bunce and P. Doty, *J. Polymer Sci.*, **10**, 109 (1953).

(8) J. T. Edsall and W. B. Dandliker, *Fortschr. Chem. Forsch.*, **2**, 1 (1951).

(9) H. J. L. Trap and J. J. Hermans, *Rec. trav. chim.*, **73**, 167 (1954).

(10) N. Bjerrum and L. Zechmeister, *Ber.*, **56B**, 894 (1923).

(11) H. Benninga, thesis, Leyden, 1954, p. 98.

was 1.93×10^6 in methanol and 1.96×10^6 in 0.05 *M*, aqueous HCl.

Sodium Carboxymethylcellulose.—Except for slight changes in the procedure we followed a prescription given by Pals¹²: a 1.5% solution in water was centrifuged for one hour to remove gel-like material. After filtering through a glass filter G-2, 0.5 g. of NaCl was added to 1 liter of the solution and the polysalt precipitated by excess alcohol, stirring forcefully. This procedure was repeated twice. The polysalt was washed with 85% alcohol until free from chloride ions, then with 97% alcohol and finally with ether. In Pals' osmotic measurements the number average molecular weight was found to be 0.64×10^6 (NaCMC-72 in reference 12). From our light-scattering results we derived a weight average of 0.86×10^6 . This shows that our rather crude method of fractionation has been fairly successful: it is likely that the fractionation of carboxymethylcellulose proceeds partly with respect to degree of substitution rather than with respect to chain-length alone.

Methanol was purified according to the prescription given by Bjerrum and Zechmeister.¹⁰ **Water** (free from CO₂) was distilled twice. Its specific conductivity was $3 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$. All solvents and solutions were treated in the manner described previously⁹: the water used was filtered through collodion membranes, the solutions were centrifuged, and all glass vessels were made dust-free by Thurmond's method.¹³

2. Polymethacrylic Acid and Carboxymethylcellulose in Various Solvents

The light-scattering by polymethacrylic acid at 25° and a wave length of 546 mμ was measured at 45, 90 and 135° in methanol, water, 0.001 *M* aqueous HCl and 0.05 *M* HCl. The values of $\partial n / \partial c$ at 25° in these solvents were found to be 0.134, 0.142, 0.140 and 0.137 ml./g., respectively. This gives the following values of $10^7 K$: 1.17, 1.33, 1.29 and 1.24. The data are summarized in Figs. 1 and 2. The root mean square end to end distance calculated from $[z_{45}]$ for random coils was 735 Å. in methanol and 780 Å. in 0.05 *M* HCl.

Results similar to Figs. 1 and 2 have been published by other authors; a semi-quantitative explanation has been given by Doty and Steiner.⁶

The data for NaCMC in water, 0.001 *M* NaCl, 0.005 *M* NaCl, 0.01 *M* NaCl and 0.05 *M* NaCl ($\lambda = 436 \text{ m}\mu$) are collected in Figs. 3 and 4. The curves of Fig. 3 are characteristic for polyelectrolytes. The change of dissymmetry with concentration, however, is almost normal. This must probably be attributed to the fact that the charge

(12) D. T. F. Pals, thesis, Groningen, 1951, Ch. I; D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 433 (1952).

(13) C. D. Thurmond, *J. Polymer Sci.*, **8**, 607 (1952).

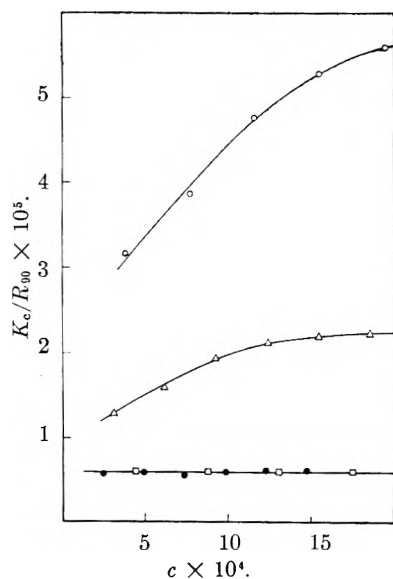


Fig. 1.— Kc/R_{90} versus polymer concentration c for polymethacrylic acid in water, \circ ; aqueous HCl 0.001 N , Δ ; aqueous HCl 0.05 N , \bullet ; and methanol, \square . 25°; $\lambda = 546$ $m\mu$; c in g./ml.

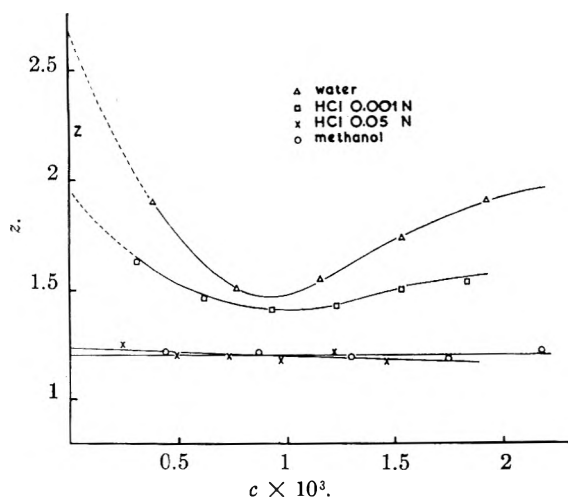


Fig. 2.—Dissymmetry factor z_{45} for solutions of polymethacrylic acid in four solvents, 25°; $\lambda = 546$ $m\mu$.

density along the carboxymethylcellulose chain is much lower than that along the polymethacrylic acid chain.

3. Isoionic Mixtures of NaCMC and NaCl

It has been shown by Pals¹² that straight lines are obtained in the η_{sp}/c versus c diagram if NaCMC is diluted in such a manner that 1 equivalent of the polymer salt is replaced by 1 mole of NaCl. The mixtures in such a series of dilutions are called isoionic. If the concentration c of the polysalt is expressed in g./ml. and the NaCl concentration x in mole/l., the quantities x and c in an isoionic series are related as

$$x + 1000rc = x_0 \quad (2)$$

where r is the number of ionized groups per gram polysalt, which can be determined by titration.

In all NaCl solutions examined the value of $(\partial n/\partial c)_x$ was 0.136 ml./g. at a wave length λ 436 $m\mu$. Light-scattering at $\lambda = 436$ $m\mu$ was measured at various angles ranging from 30 to 135°. These

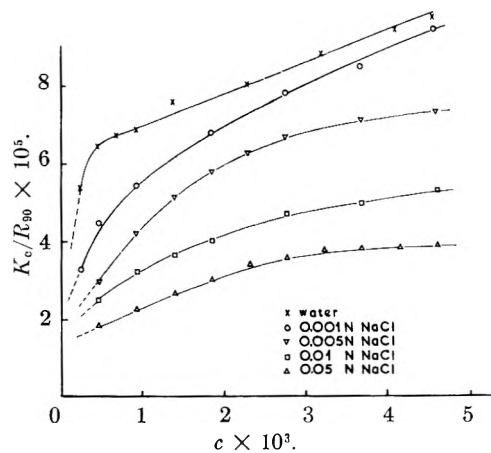


Fig. 3.— Kc/R_{90} as a function of concentration c (g./ml.) for sodium carboxymethylcellulose in five solvents, 25°; $\lambda = 436$ $m\mu$.

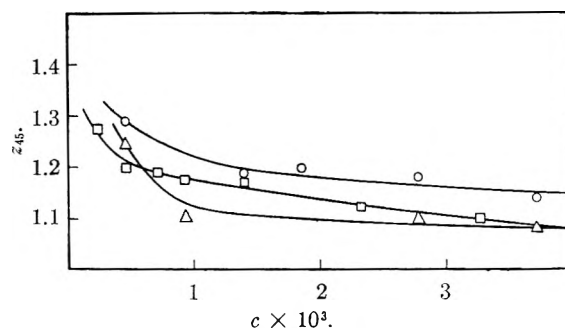


Fig. 4.—Dissymmetry factor z_{45} for NaCMC in water, \square ; aqueous NaCl 10^{-3} N , Δ ; and aqueous NaCl 10^{-2} N , \circ , 25°; $\lambda = 436$ $m\mu$.

measurements were done in five isoionic series, *i.e.*, for five values of x_0 , and for five concentrations of the polysalt in each of these series. The concentrations examined are given in Table I where, for convenience, the series are numbered 1 to 5. For each series a Zimm plot¹⁴ was made, but we will restrict ourselves to giving the extrapolated values of Kc/R_{θ} : for $\theta = 0$ in Fig. 5 and for $c = 0$ in Fig. 6. Moreover, Fig. 7 shows the dissymmetry factor z_{45} as a function of concentration.

TABLE I

Series	x_0 , mole/l.	ISOIONIC SERIES EXAMINED				
		10% c, g./ml.				
1	0.1856	59.4	118.8	178.2	237.6	297.0
2	.0464	74.2	148.5	222.7	297.0	371.2
3	.0116	92.8	185.6	278.4	371.2	464
4	.0029	23.2	46.4	69.6	92.8	116
5	.000725	5.8	11.6	17.4	23.2	29.0

The normal behavior of $(z_{45} - 1)^{-1}$ as a function of concentration confirms the conjecture that the polyelectrolyte molecules are not subject to large changes in size when the polymer is diluted isoionically. The changes in size and therefore in $[z]$ are quite pronounced, however, when going from one value of the ionic strength x_0 to another.

The depolarization was of the order of only 1% and not too well reproducible. It was therefore neglected in the calculation of the molecular weight, which was found to be $M_w = 86000$.

(14) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093, 1099 (1948).

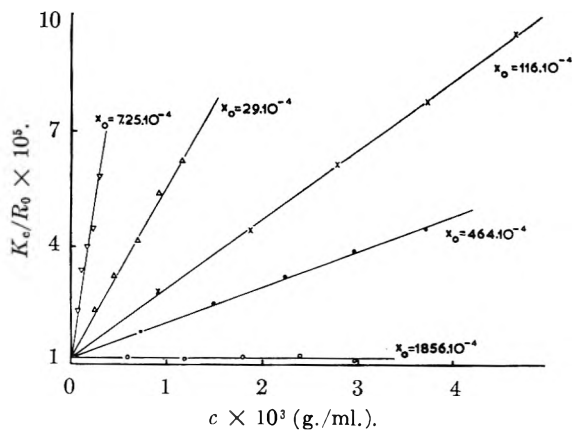


Fig. 5.— $\lim_{\theta=0} Kc/R_0$ for isoionic mixtures of NaCMC and NaCl in water at various ionic strengths x_0 (mole/l.) as a function of polymer concentration c : 25° ; $\lambda = 436 \text{ m}\mu$.

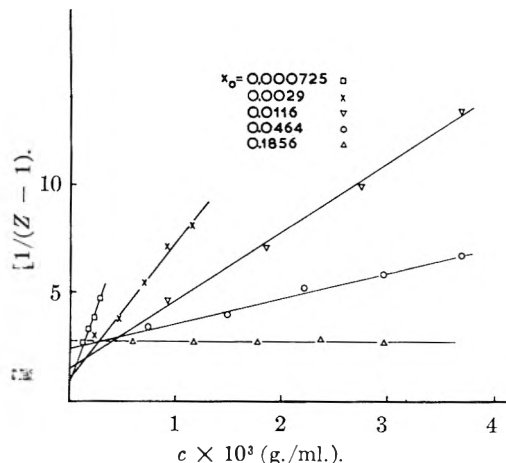


Fig. 7.—Dissymmetry factor z_{45} for isoionic mixtures of NaCMC and NaCl at various ionic strengths x_0 (mole/l.) as a function of polymer concentration c ; 25° ; $\lambda = 436 \text{ m}\mu$.

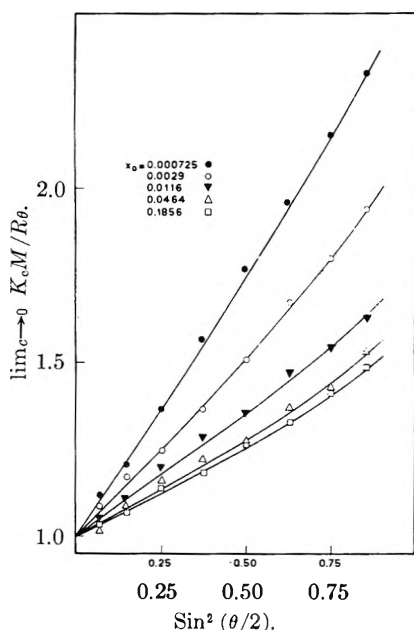


Fig. 6.— $\lim_{c \rightarrow 0} KcM/R_0$ for isoionic mixtures of NaCMC and NaCl as a function of $\sin^2(\theta/2)$. 25° ; $\lambda = 436 \text{ m}\mu$.

4. Discussion

(a) **Molecular Dimensions.**—From the slopes of the curves in Fig. 6 at the limit $\theta = 0$ it is possible to derive¹⁵ the mean square radius $\Sigma_j < R_j^2 > / P$, where P is the degree of polymerization and R_j the distance between the j th monomer group and the center of gravity. For comparison with viscosimetric data Table II gives the “effective radius” defined by¹⁶

$$\rho^2 = (5/3P)\Sigma_j < R_j^2 >$$

Pals¹² has shown that the limiting viscosity number $[\eta]$ of the sample investigated is in good agreement with the theory developed for free-drained coils. Thus $[\eta]$ is proportional to ρ^2 , and the ratio between these quantities can be derived from Table IX in reference 12, where the values of ρ and $[\eta]$ at the limit of infinite ionic strength are given: $\rho_\infty = 400 \text{ \AA}$. and $[\eta]_\infty = 374 \text{ ml./g}$. This enables us at

once to calculate ρ for all other ionic strengths from the $[\eta]$ -values given in Table VIII of reference 12. Pals determined $[\eta]$ for ten values of x_0 , five of which coincide almost exactly with those of our light-scattering measurements. They are given in Table II, where ρ_ξ is the effective radius calculated from ξ , ρ_η that derived from $[\eta]$ and

$$\xi = \lim_{\substack{c \rightarrow 0 \\ \theta = 0}} \frac{KcM/R_\theta - 1}{\sin^2(\theta/2)}$$

TABLE II

COMPARISON BETWEEN EFFECTIVE MOLECULAR RADIUS ρ_ξ DERIVED FROM LIGHT-SCATTERING IN THE PRESENT WORK AND THE SAME RADIUS ρ_η FOUND BY PALS¹² ON THE BASIS OF VISCOSITY DETERMINATIONS

Isoionic mixtures of NaCMC-72 and NaCl in water at 25°

x_0 , mole/l.	ξ	ρ_η , \AA .	$[\eta]$, ml./g.	ρ_ξ , \AA .
0.19	0.52	415	365	396
.048	0.55	440	440	434
.012	0.74	500	588	501
.003	1.03	590	866	608
.00075	1.56	730	1275	732

It is seen that the agreement between ρ_ξ and ρ_η is perfect. In fact, the high degree of agreement must doubtless be considered as to some extent fortuitous.

It is to be remarked, further, that although the viscosity data could be interpreted quantitatively¹² on the basis of the theory for random coils, the extrapolated value of $[\eta]$ at the limit of zero ionic strength could be accounted for almost equally well¹² on the basis of Simha’s viscosity formula¹⁷ for rods. The value found by Pals for the length of the rod was 2300 \AA ., whereas the theoretical fully extended length of the molecule was about 1650 \AA . A similar remark can be made in connection with our light-scattering data. When the ionic strength is 0.00073 mole/l., the dissymmetry factor z_{45} at the limit of zero polymer concentration has the value 2.0. Applying the formula for rods this leads to a length of 2000 \AA .

Finally, we may apply the present data to com-

(15) P. Debye, THIS JOURNAL, 51, 18 (1947).

(16) P. Debye and A. M. Bueche, J. Chem. Phys., 16, 573 (1948).

(17) R. Simha, THIS JOURNAL, 44, 25 (1940).

pare the theory of Hermans and Overbeek¹⁸ with that of Katchalsky and Lifson.¹⁹ It may be remembered that the results obtained by Pals¹² can be quantitatively accounted for by the theory of Hermans and Overbeek if the root mean square end-to-end distance h_0 of the uncharged molecule is properly adjusted. The formula used by these authors to connect the effective radius ρ with the ionic strength of the solution has the form

$$y^3 \frac{y^2 - 2}{y^2 - 1} = \frac{\beta}{3} \frac{1 + 1.2 \kappa \rho + 1.2(\kappa \rho)^2}{[1 + 0.6 \kappa \rho + 0.4(\kappa \rho)^2]}$$

where

$$y = 6\rho/(h_0 5^{1/2}) \text{ and } \beta = (18/5^{3/2})Z^2 e^2 / (\epsilon k T h_0)$$

Here κ is the reciprocal characteristic length defined by Debye and Hückel

$$\kappa^2 = 8\pi e^2 n / \epsilon k T ; n = 10^{-3} x_0 N_A$$

N_A being Avogadro's number. Further e is the elementary charge and Ze the charge of the polyelectrolyte molecule; ϵ is the dielectric constant of the solvent.

On the other hand, Katchalsky and Lifson derived the formula

$$3hkT\lambda/h_0^2 = (Z^2 e^2 / \epsilon h^2) [\ln(1 + m) - m(1 + m)^{-1}] \quad (3)$$

$$m = 6h/\kappa h_0^2$$

Here h is the root mean square end-to-end distance of the charged molecule and is related¹⁸ to the effective radius ρ by the equation

$$\rho^2 = (5/36)(h^2 + h_0^2) \quad (4)$$

λ is a factor which is closely related to the inverse Langevin function of h/L

$$\lambda = (L/3h) L^{-1}(h/L)$$

L being the fully extended length of the molecule. According to Katchalsky, Künzle and Kuhn²⁰ the function λ may be approximated by

$$\lambda = 1 + 0.6 (h/L)^2 [1 - (h/L)^2]^{-1}$$

Our procedure²¹ to check eq. 3 was to calculate λ for each of the x_0 values given in Table II. The value of h_0 is known¹² to be 760 Å., $Z = 140$, $\epsilon = 78$, h is derived from eq. 4. The result of the calculation is given in Table III. It is seen that all λ -

TABLE III

COMPARISON WITH THE FORMULA OF KATCHALSKY AND LIFSON

h_0 , Å.	x_0 , mole/l.	0.192	0.048	0.012	0.003	0.00075
	ρ , Å.	= 396	434	501	608	732
760	h , Å.	= 735	880	1110	1440	1810
	λ	= 0.08	0.21	0.38	0.52	0.59
703	h , Å.	= 785	925	1150	1470	1830
	λ	= 0.06	0.17	0.32	0.42	0.50

The discrepancy observed between the experimental radius and that calculated from the Katchalsky and Lifson theory¹⁹ can be removed if care is taken in the calculation of Katchalsky and Lifson to ensure that h^2 approaches h_0^2 when the ionic strength becomes very large or the molecular charge Ze approaches zero. This can be achieved in the manner indicated by Hermans and Overbeek,¹⁸ and leads to eq. 3 of the present article provided with an extra term $3kT/h$ on the right-hand side. The application of this new formula to the data of Table III leads to λ -values varying from 0.8 to 1.

(18) J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 762 (1948); *Bull. soc. chim. belg.*, **57**, 154 (1948).

(19) A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).

(20) A. Katchalsky, O. Künzle and W. Kuhn, *ibid.*, **5**, 283 (1950).

(21) The calculation was done by F. van Voorst Vader.

values fall appreciably below unity whereas, according to its definition, only values larger than 1 are possible. One might object to the procedure that the h_0 value of 760 Å. has been derived¹² from the curve of $[\eta]$ versus $(x_0)^{-1/2}$ on the assumption that the theory of Hermans and Overbeek gives the correct answer. A straightforward extrapolation¹² of this curve to $(x_0)^{-1/2} = 0$ gives $h_0 = 703$ Å. As can be seen in the second part of Table III, however, this makes the situation worse rather than better. This discrepancy cannot be removed by small changes in h and h_0 ; one would have to assume ρ -values quite different from the experimental ones to obtain λ -values which are larger than unity for all values of x_0 . It appears, therefore, that the theory of Katchalsky and Lifson does not apply to the molecules of carboxymethylcellulose.

(b) **Second Virial Coefficient.**—The mixture of NaCMC and NaCl in water is a three-component system. The light-scattering by solutions consisting of more than two components has been discussed by Zernike,²² Brinkman and Hermans,²³ Kirkwood and Goldberg²⁴ and Stockmayer.²⁵ For three components we have, in Stockmayer's notation

$$R_{90}/K' = (\psi_2^2 a_{33} - 2\psi_2\psi_{32}a_{23} + \psi_3^2 a_{22})(a_{22}a_{33} - a_{23}^2)^{-1} \quad (5)$$

where $K' = 10^3 \cdot 2\pi^2 n^2 / N_A \lambda^4$. The index 2 refers to the polymer salt, the index 3 to NaCl; $\psi_i = \partial n / \partial m_i$ where m_i is the concentration of component i in mole per liter; $a_{ij} = \partial \ln a_i / \partial m_j$ where a_i is the activity of component i .

The application of eq. 5 to serum albumin in NaCl solutions has been discussed by Edsall, Edelhoeh, Lontie and Morrison.²⁶ Taking into account that the molecular weight of our polymer is about 80,000, the value of ψ_2 in our present investigations is about 11. Edsall, *et al.*, mention a value of 13 for their serum albumin, and the concentrations of polymer and NaCl examined by them are of the same order of magnitude as in the present

TABLE IV

SECOND VIRIAL COEFFICIENT A FOR NaCMC IN AQUEOUS NaCl FOR VARIOUS VALUES OF THE IONIC STRENGTH x_0

I, Pals, osmotic pressures; II, present work, light-scattering; III, Doty and Schneider, light-scattering; IV, Doty and Schneider, divided by 4 (see text).

x_0 ($= m_1$), mole/l.	$10^3 A$ from $Z^2/2m_1$ -term	$10^3 A$ experimental	—
		I	II
0.5	7.7		~3
.4	2.9	0.57	
.2	5.7	1.6	
.18	8.5		~0
.05	77		13.8
.046	24		4.6
.04	28	6.4	
.012	135		9.0
.01	385		37.6
.003	540		9.4
.0007	2150		78

(22) F. Zernike, *Arch. Neerl. Sci.*, **III**, **A4**, 74 (1918).

(23) H. C. Brinkman and J. J. Hermans, *J. Chem. Phys.*, **17**, 574 (1949).

(24) J. Kirkwood and R. J. Goldberg, *ibid.*, **18**, 54 (1950).

(25) W. H. Stockmayer, *ibid.*, **18**, 58 (1950).

(26) J. T. Edsall, H. Edelhoeh, R. Lontie and P. R. Morrison, *J. Am. Chem. Soc.*, **72**, 4641 (1950).

work. We need not, therefore, repeat their argument and may merely quote the result obtained.

$$Kc_2/R_{90} = 1/M + (10^3/M^2)c_2[Z^2/2m_3 + \beta_{22} - \beta_{23}m_3(2 + \beta_{33}m_3)^{-1}] \quad (6)$$

Z is the valency of the polymer ion and M its molecular weight; $\beta_{ij} = \partial \ln \gamma_i / \partial m_j$ where γ_i is the activity coefficient a_i/m_i of component i .

From the osmotic measurements of Pals²⁷ it was concluded that the second virial coefficient can be qualitatively accounted for by the first term in the brackets: $Z^2/2m_3$. Quantitatively, however, the agreement was poor, as could be expected: the ratio between the experimental slope of the π/c versus c line and that calculated from the $Z^2/2m_3$ term varied between 2 and 4. As shown in Table IV, a similar result is obtained from an evaluation of our light scattering data while, moreover, it is clear that the ratio between the experimental slope and that derived from the $Z^2/2m_3$ term decreases with decreasing electrolyte content. In Table IV we have added the values of A reported by Doty and Schneider²⁸ for a sample of NaCMC in aqueous sodium chloride. The carboxymethylcellulose investigated by these authors was not fractionated, had a weight average molecular weight of 1.75×10^5 and contained 1.15 carboxymethyl groups per glucose unit. This means that the charge density Z/M of their sample was about twice as large as that of ours. For this reason we have divided their A -values by 4 (sixth column of Table IV). It can be seen in Fig. 8 that all the A -values so obtained

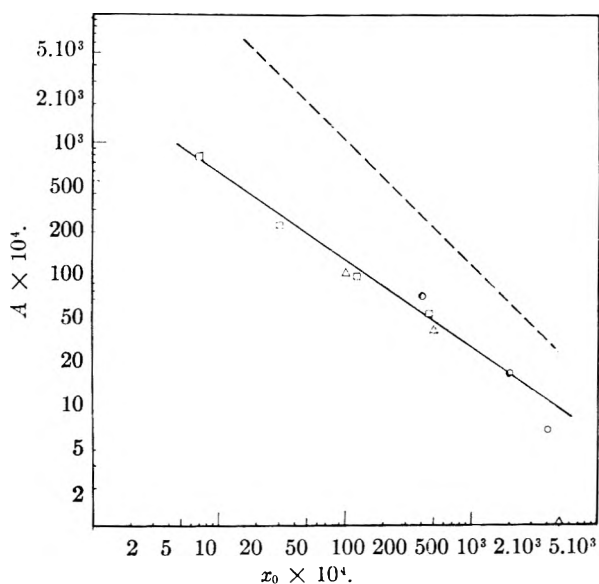


Fig. 8.—Double logarithmic plot of second virial coefficient A versus ionic strength x_0 : dotted line, calculated from $Z^2/2m_3$ -term: (O) Pals, from osmotic pressures; (□) present work, light-scattering; (Δ) Doty and Schneider, divided by 4 (light-scattering).

fall in line with each other. The rather dubious

(27) D. T. F. Pals, thesis, Groningen, 1951, Ch. II; D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 458 (1952).

(28) P. Doty and N. Schneider, ONR report, December 15, 1952.

light-scattering value at $x_0 = 0.18$ mole/l. has been omitted. It is doubtful whether the exceptionally low values of A at ionic strengths 0.4 and 0.5 mole/l. are real: according to our experience²⁷ the NaCMC molecules show some tendency toward association when the NaCl content becomes high.

If in Fig. 8 attention were restricted to the osmotic values, indicated by circles, one might be inclined to draw a line parallel to the dotted one, which would mean that A varies linearly with $1/x_0$ (see Pals, ref. 27). Taken together, however, the data suggest that A is roughly proportional to x_0^{-s} where s is about $2/3$.

A closer comparison with eq. 6 would be possible if activity coefficients were known. A theoretical expression for $\ln \gamma_3$ has recently been given by Katchalsky and Lifson.¹⁹ In the notation of the present paper their equation runs

$$-kT \ln \gamma_3 = \kappa e^2/2\epsilon + (3Z^2e^2/\epsilon)(\kappa h_0^2 + 6h)^{-1}m_2(2m_3 + Zm_2)^{-1} \quad (7)$$

Here κ is the characteristic reciprocal length of the theory of Debye and Hückel. According to Katchalsky and Lifson one must include in κ^2 all the free ions but omit the charges fixed on the polymer chain

$$\kappa^2 = (4\pi e^2/\epsilon kT)(2m_3 + Zm_2) 10^{-3} N_A$$

To calculate β_{23} and β_{33} we must determine the change of $\ln \gamma_3$ with m_2 and m_3 , respectively. In doing so, we must take into account that not only κ but also h undergoes a change when m_2 or m_3 is varied. The change in h should be derived from eq. 3. However, this leads to very complicated formulas, and we know already that eq. 3 does not apply to our sample anyway. For this reason we have neglected changes in h in the calculation of β_{23} and β_{33} , the more so since it can be shown that the inclusion of these changes would not affect the conclusion given below.

Furthermore, eq. 6 is a series expansion in powers of c_2 and eq. 7 was derived by Katchalsky and Lifson on the assumption that all colloid particles are far apart from each other. To be consistent we must therefore use the values of β_{23} and β_{33} at the limit of zero polymer concentration (this is also the reason why m_3 was identified with x_0). The result of the calculation at the limit $m_2 = 0$ is

$$\beta_{23} = -Ze^2\kappa/(4\epsilon kTx_0) - (3Z^2e^2/2\epsilon kTx_0)(\kappa h_0^2 + 6h)^{-1}$$

$$\beta_{33} = -e^2\kappa/(4\epsilon kTx_0)$$

When substituting this in eq. 6 it is found that in all cases examined $\beta_{33}m_3$ is small compared with unity, as was to be expected. Further, $\beta_{23}m_3$ is always less than 3% of $Z^2/2m_3$. Assuming that the theory of Katchalsky and Lifson gives the correct order of magnitude for β_{23} and β_{33} , this result shows that the large difference between the experimental second virial coefficient and that calculated from the $Z^2/2m_3$ term must be attributed to the value of β_{22} . The fact that the A -values of Doty and Schneider were brought into line with ours when multiplied by $1/4$ suggests that β_{22} is approximately proportional to Z^2 .

MACRO-IONS. IV. THE IONIC STRENGTH DEPENDENCE OF THE MOLECULAR PROPERTIES OF SODIUM CARBOXYMETHYLCELLULOSE¹

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Light scattering, titration and viscosity studies have been carried out on a sample of sodium carboxymethylcellulose ($M_w = 440,000$ and degree of substitution 1.15) in the ionic strength range of 0.5 to 0.005. The object of this investigation, beyond that of characterizing the configurational properties of this important polyelectrolyte, was to determine the dependence of the molecular size, pH and second virial coefficient, B , on ionic strength in order thereby to test certain theories and concepts of polyelectrolyte behavior. It was found that the root mean square end-to-end length increased 45% as the ionic strength decreased in the range studied. The increase predicted by the Hermans-Overbeek and Flory theories is considerably greater than this, whereas the Katchalsky-Kuhn theory can provide no predictions for this case. The potentiometry studies show the opposite situation in that the values of $pH - pK_0$ are several hundred per cent. higher than the Hermans-Overbeek theory predicts but agree much better with the Katchalsky theory. These conclusions demonstrate the substantial inadequacy or incorrectness of existing polyelectrolyte theories and have motivated a re-examination of the theoretical problem by Harris and Rice which is presented concurrently. The dependence of B on ionic strength shows little relation to the classical Donnan term. It is, however, correctly predicted from the molecular size alone showing thereby that in this ionic strength range the interaction of the polymeric ion is essentially the same as that of neutral polymer molecules. This indicates that the net charge of the polymeric ion is effectively shielded by its counterion atmosphere so that the excluded volume of the molecular chain and not electrostatic repulsions characterizes the intermolecular interaction.

From the extensive research on polyelectrolytes during the fifteen years that have elapsed since Kern's pioneering investigations, one can conclude that the principal features distinguishing polyelectrolytes from ordinary polymers and ordinary electrolytes are (1) the sensitivity of molecular dimensions to ionic strength and degree of ionization, (2) the titration behavior or the dependence of proton binding on proton concentration, and (3) the binding of oppositely charged counterions which may be of two types, binding at specific charged sites and a non-localized binding due to the potential of the polymeric ion. Although considerable progress has been made, the quantitative exploration of these areas and the subsequent testing of theories by such data has not proceeded very far.

The work described here was undertaken to provide some information on the first two of the features listed above. In particular, our interest focused on two questions: first, how do the dimensions of the polymeric ions depend on ionic strength and is this dependence adequately accounted for by any of the current polyelectrolyte theories? Second, how does the interaction of the polymeric ions in solution as characterized by the second virial coefficient depend on ionic strength and what is the role of the classical Donnan term?

For this investigation sodium carboxymethylcellulose (NaCMC) seemed well suited for several reasons. First, because of the relatively expanded mean configuration of the cellulose chain, the densities of charged groups are at a minimum. Since the Debye-Hückel approximation is used in most theories, the lower density of charged groups within the domain of the polymer chain will lead to lower potentials which may lie within the requirements of this approximation. Secondly, it was of interest to see how an ionized derivative of cellulose compared in molecular properties with its more orthodox counterpart, cellulose nitrate, which was undergoing a re-examination in this Laboratory

at the same time.² A further argument for the choice of this polymer lay in the fact that, although it is a very important cellulose derivative, its behavior in solution had not been studied by the usual physical methods. However, since this work was initiated, such an investigation of NaCMC has been reported.³ There has been little overlap with this work because osmotic pressure determinations rather than light scattering ones were employed. Some relationships between these investigations are taken up in the last section.

Experimental Measurements

Sample.—The sodium carboxymethylcellulose (NaCMC) used in this investigation was kindly furnished by the Hercules Powder Co. It had been prepared from cotton linters on a laboratory scale under conditions which yield a product of greatest homogeneity with respect to substitution (U. S. Patent 2,517,577). The Hercules number for this sample was CMC 120 High, X7520-52.

Titration.—A sample of the polymer in 0.5 *N* NaCl was first adjusted to pH 11 and then titrated with standardized HCl. Corresponding data were taken for the solvent and after adjustment for the greater volume of the NaCMC solution at each pH the values for the solvent were subtracted. For a 10-cc. sample containing 0.350 g./dl. of NaCMC 5.39 cc. of 0.0294 *N* HCl was required. This corresponds to a degree of substitution of 1.15 carboxymethyl groups per glucose unit in good agreement with the value of 1.2 which had been aimed at in the etherification reaction. Most of the measurements recorded below were carried out at a degree of neutralization, α , of 0.96.

Approximate measurements were made of the pH at several degrees of neutralization for the four ionic strengths at which light scattering and viscosity measurements were made. These are listed in Table I. Except for the lowest ionic strength solution, these results extrapolate to a value of 3.40 for pK_0 , the pH at which α becomes zero. This is in agreement with Pals and Hermans.³

Viscosity.—Viscosity measurements were carried out in a three-bulb modified Ubbelohde viscometer with a large reservoir, which made it possible to measure viscosities at three gradients with dilutions made directly in the instrument. The gradients lay within the range of 50 to 250 sec.⁻¹. For NaCMC in 0.5 to 0.005 *M* NaCl, the gradient dependence was within probable experimental error and therefore the measurements may be accepted as free from gradient

(1) This work was supported in part by the Office of Naval Research (Contract No. N5ori-07654) and was reported in part at the Los Angeles Meeting of the American Chemical Society, March 20, 1953.

(2) A. Holtzer, H. Benoit and P. Doty, *THIS JOURNAL*, **58**, 624 (1954).

(3) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 433, 458, 513 (1952).

TABLE I

THE VALUE OF $\text{pH} + \log(1 - \alpha)/\alpha$ FOR NaCMC SOLUTIONS AS A FUNCTION OF IONIC STRENGTH AND DEGREE OF NEUTRALIZATION

Degree of neutralization	0.500	Normality of NaCl 0.050	0.010	0.005
0.40	3.56	3.77	4.40	4.95
0.60	3.62	4.02	4.69	5.34
0.80	3.71	4.14	4.80	5.55

dependence. The results in NaCl are shown in Fig. 1 and in other electrolyte solutions in Fig. 2.

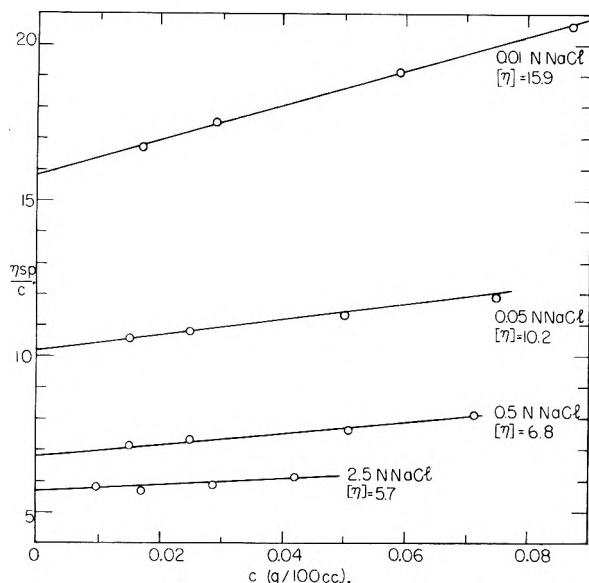


Fig. 1.—Reduced specific viscosity of NaCMC in various NaCl solutions.

Light Scattering.—The light scattering measurements were carried out in a modified Brice-Speiser Photometer⁴ using an Erlenmeyer-flask-shaped scattering cell and light of 4360 Å. wave length. The specific refractive index increment, dn/dc , for NaCMC was determined in both a differential refractometer and a Zeiss interferometric refractometer. In 0.5 M NaCl the value of dn/dc was found to be 0.154 for a wave length of 4360 Å. This gives for the constant K in the light scattering equation a value of 3.93×10^{-7} . At the lower ionic strengths the Gladstone-Dale mixing law, which has been found to serve adequately in similar cases, gave for dn/dc 0.158 and correspondingly the value of K becomes 4.13×10^{-7} .

The solutions were clarified by centrifuging at least 90 minutes at 44,000 g in a Spinco preparative ultracentrifuge. Two-ounce Polythene bottles with bakelite caps were adapted to serve for centrifuge tubes as described elsewhere.² The solvent was measured first and then successive amounts of solution were added from the pipet in which the centrifuged solution was stored.

The circular uniformity of the cell was demonstrated by the fact that the scatterings from fluorescein solutions were constant to within $\pm 1\%$ in the angular range of 30–135°. The cell constant, used to convert measurements for this type of cell to those for the square type with which the instruments had been calibrated, was determined by comparing the scattering from Ludox (SiO_2) suspensions in both cells.

The results of a typical measurement are shown as a Zimm plot in Fig. 3. In this and the other measurements it was found that the reciprocal envelopes (Kc/Re versus $\sin^2 \theta/2$) are curved and this causes some reduction in the accuracy of the extrapolation over that obtained with the usual linear envelopes.

(4) (a) B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950); (b) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

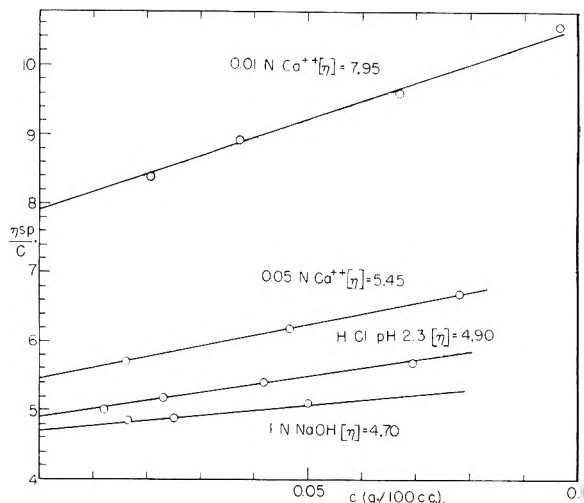


Fig. 2.—Reduced specific viscosity of NaCMC in various aqueous solvents.

The type of curvature observed here could conceivably arise from three causes: (1) polydispersity substantially exceeding that corresponding to a weight to number molecular weight average of 2, (2) the non-Gaussian character of the chains in the sense that the mean end-to-end dimension was less than about three times the contour length, and (3) the non-Gaussian character of the chains in the sense that the mean segment density about the center of gravity was more concentrated near the center than in the usual case. A similar situation has arisen in the study of cellulose nitrate^{2,5} and there it was fairly definitely shown that this type of curvature in this molecular weight range is due solely to polydispersity. Accepting this as the case, a new method of evaluating such data becomes possible.^{5,6}

Evaluation of Light Scattering Data.—As shown in detail in the references cited, two limiting conditions apply to the reciprocal envelopes such as shown in Fig. 3. At sufficient low values of the parameter

$$u = \left[\frac{4\pi}{\lambda'} \sin \frac{\theta}{2} \right]^2 \frac{\bar{r}^2}{6} \quad (1)$$

(λ' is the wave length of light in the medium, θ the scattering angle, and \bar{r}^2 the mean square end-to-end dimension), that is, at sufficiently low angles or polymer chain dimension, we have the well known limiting case

$$K \frac{c}{R_{\theta \rightarrow 0}} = \frac{1}{M_w} \left[1 + N_z \frac{u}{3} + \dots \right] \quad (2)$$

showing that the size determined is that of molecules having the z -average molecular weight. However, since it is the weight average molecular weight that is determined by the intercept, the comparison of dimension and molecular weight or the evaluation of the effective bond length, $(\bar{r}^2/N)^{1/2}$ (N is the degree of polymerization) requires an assumption or an estimate concerning the molecular weight distribution. The other limiting condition is that occurring at sufficiently high values of the parameter u where we have

$$K \frac{c}{R_{\theta \rightarrow 0}} = \frac{1}{M_n} \left[\frac{1}{2} + N_n \frac{u}{2} + \dots \right] \quad (3)$$

This defines an asymptote, the slope and intercept of which give the number average molecular weight and the dimension thereof independent of the molecular weight distribution. Relying again on the experience with cellulose nitrate^{2,5} we can conclude that in the sample under consideration the low angle measurements do lie on the limiting slope and the high angle points are at least close to the asymptote. Assuming this to be the case, the data at the four ionic strengths investigated can be evaluated. The results are assembled in Table II.

(5) H. Benoit, A. H. Holtzer and P. Doty, *THIS JOURNAL*, **58**, 635 (1954).

(6) H. Benoit, *J. Polymer Sci.*, **11**, 507 (1953).

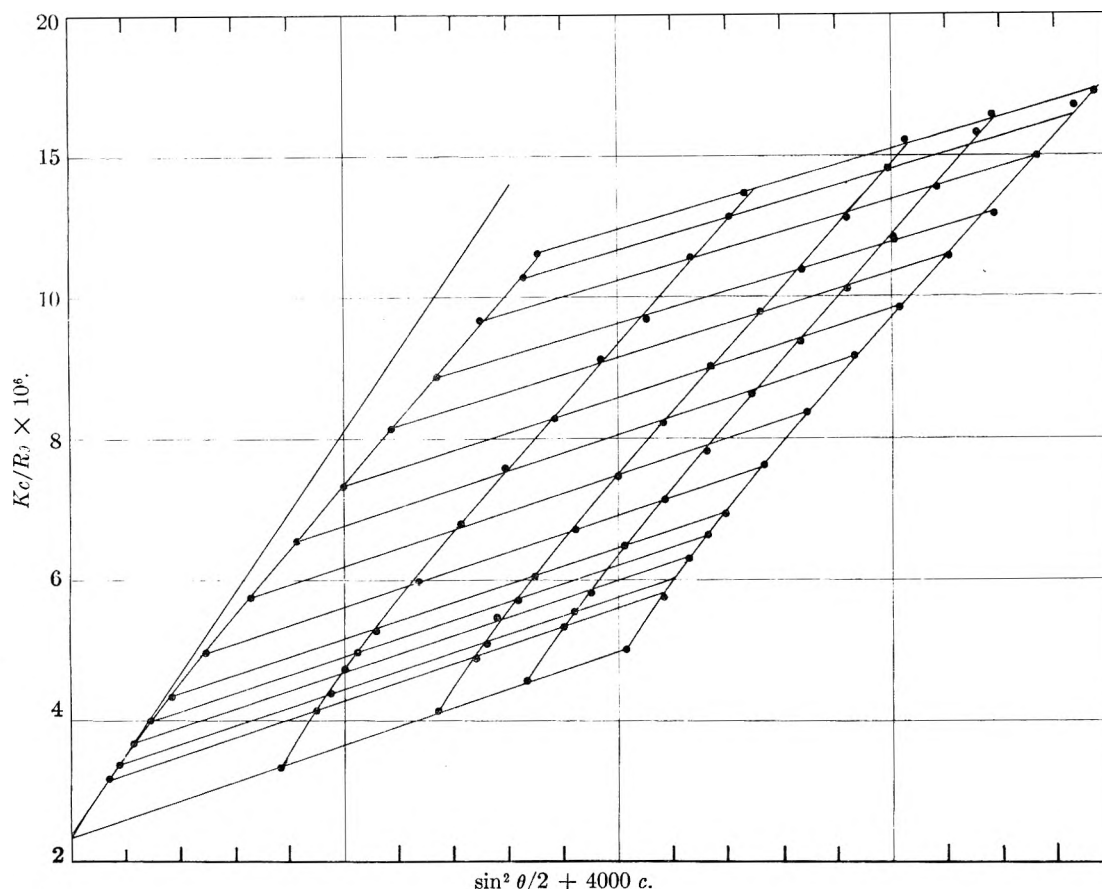
Fig. 3.—Light scattering plot for NaCMC in 0.05 *M* NaCl.

TABLE II

DATA ON NaCMC COMPUTED DIRECTLY FROM LIGHT SCATTERING PLOTS

Ionic strength	$B \times 10^3$	M_w	M_n	$\overline{r_z^2}, \text{\AA}$	$\overline{r_n^2}, \text{\AA}$
0.500	1.35	365,000	121,000	2140	825
	1.67	480,000	208,000	2420	1220
.050	5.70	410,000	170,000	2440	1140
	5.70	410,000	170,000	2440	1140
.010	14.9	443,000	152,000	3170	1300
	16.6	488,000	170,000	3030	1170
.005	26.0	475,000	(94,000)	3660	(960)
Av.		440,000	165,000		

The values of the dimensions listed in Table II were obtained by multiplying the square root of the ratio of slope to intercept by appropriate constants (see reference 5). Some improvement may be expected if the reciprocal of the average molecular weights above is used instead of the intercepts obtained for each individual experiment. The results of this procedure are shown and averaged in Table III. The high angle data at 0.005 ionic strength clearly led to unacceptable results. This may be due either to increased experimental errors due to diminished scattering or to the onset of downward curvature due to chain stiffness.⁷ As a consequence the value of $\sqrt{\overline{r_n^2}}$ in this case is computed by multiplying the $\sqrt{\overline{r_z^2}}$ value by the average of the ratio $(\overline{r_n^2}/\overline{r_z^2})^{1/2} = 2.27$, for the other three sets of measurements. In addition the intrinsic viscosity data are listed in Table III.

Inasmuch as the experimental data from which these results were derived were obtained before the importance of high angle data was appreciated and since computations involving such data require the additional assumption that the

TABLE III

SUMMARY OF MOLECULAR PROPERTIES OF SODIUM CARBOXYMETHYLCELLULOSE AS A FUNCTION OF IONIC STRENGTH

Ionic strength	$B \times 10^3$	Individual values $[\eta]$	Individual values		Av. values	
			$\sqrt{\overline{r_z^2}}$	$\sqrt{\overline{r_n^2}}$	$\sqrt{\overline{r_z^2}}$	$\sqrt{\overline{r_n^2}}$
0.500	1.51	6.8	2370	970	2300	1030
			2230	1095		
.050	5.70	10.2	2450	1110	2450	1110
.010	15.7	15.9	3010	1265	2935	1235
			2860	1205		
.005	26.0	20.5	3350	1475	3350	1475

data lie on the asymptote, the larger scattering of number average results is to be expected. It is interesting to note that if $\overline{r^2}$ is proportional to M as it was found to be in cellulose nitrate² the ratio, $\overline{r_z^2}/\overline{r_n^2}$, can be used in conjunction with the molecular weight measurements to estimate M_z . The value obtained is 850,000 and the proportion $M_z:M_w:M_n$ is 1:2.65:5.15. This result is considerably larger than that corresponding to the most probable distribution of molecular sizes but is very similar to the estimates made on cellulose nitrate samples.^{1,6} The z and number average degrees of polymerization are 3320 and 645 and the corresponding contour lengths are 17,100 and 3320 \AA . Upon comparing these with the dimensions in the last two columns of Table III, it is seen that the ratio of the contour length to the mean dimension in most cases exceeds a value of three to four which is usually taken as the criterion of chains whose mean configurations are Gaussian.⁸ The exceptions are number average values at the lower ionic strengths but since the lowest ionic strength value was obtained from the z -average dimension it is not likely that the results listed are significantly affected by the contribution of non-Gaus-

(7) A. Peterlin, *Makromolek. Chem.*, **9**, 244 (1953).(8) H. Benoit and P. Doty, *This Journal*, **57**, 958 (1953).

sian chains to the character of the reciprocal scattering envelope.

The Ionic Strength Dependence of the Molecular Dimensions

Since both number and z average sizes are available from Table III, we can utilize both by computing the effective bond length, $b = (\bar{r}^2/N)^{1/2}$, employing the appropriately averaged degree of polymerization, N . In Table IV the values of the effective bond lengths computed in this way are listed. The differences between the values obtained using the number and z average is of the order of probable experimental error: consequently they are averaged to obtain the values to be used in the following discussions. The last entry (0.005 M NaCl) is the least accurate for the reasons already mentioned. The values of $(\bar{r}^2/N)^{1/2}$ extrapolate to 37.4 Å. at infinite ionic strength. This is to be compared with 35.0 for cellulose trinitrate in acetone.²

TABLE IV

THE EFFECTIVE BOND LENGTHS AND DIMENSIONS OF SODIUM CARBOXYMETHYLCELLULOSE AS A FUNCTION OF IONIC STRENGTH

Ionic strength	$(\bar{r}_n^2/N_n)^{1/2}$, Å.	$(\bar{r}_z^2/N_z)^{1/2}$, Å.	$(\bar{r}^2/N)_{av.}^{1/2}$, Å.	$(\bar{r}_w^2)^{1/2}$, Å.	α	α^2
0.500	39.8	40.6	40.2	1670	1.078	1.161
.050	42.5	43.8	43.1	1790	1.156	1.336
.010	50.9	48.6	49.8	2070	1.335	1.780
.005	58.1	58.1	58.1	2410	1.55	2.41

We now wish to compare these values with the theories due to Hermans and Overbeek,⁹ Kuhn, Katchalsky and others,¹⁰ and Flory.¹¹ In the Hermans-Overbeek theory the polyion is considered as a sphere in which the separate charges are replaced by a continuous charge distribution and the small ions are assumed to be governed by the Poisson-Boltzmann equation. Using the Debye-Hückel linearization approximation, the latter is solved and the electrical free energy of the polyion as a function of its size is thereby derived. Adding this to the customary entropy term in the exponent of the normal distribution function for molecular extensions, and averaging leads to the following expression relating size and ionic strength for the conditions under which our experiments have been made. The result is expressed in terms of quantity y^2 which is equal to $(1 + \bar{r}^2/\bar{r}_0^2)$ where \bar{r}_0^2 represents the mean square end-to-end length for the uncharged polymer chain. Then

$$y^5 \frac{y^2 - 2}{y^2 - 1} = \frac{\alpha^2}{\kappa^2} \quad (4)$$

where $\alpha^2 = (36/5r_0^2)^{1/2}(3Z^2e^2/2\epsilon kT)$, Z representing the number of charges per polyion and ϵ the dielectric constant. κ is the reciprocal Debye radius. This relation can be approximated by a much simpler one in the range of interest⁹

$$y^2 = 1 + \alpha^2 = 1.55 + 0.53 \frac{\alpha^2}{\kappa} \quad (5)$$

(9) J. J. Hermans and J. T. G. Overbeek, *Rec. trav. chim.*, **67**, 762 (1948); *Bull. soc. chim. Belg.*, **57**, 154 (1948).

(10) A. Katchalsky, O. Kuzle and W. Kuhn, *J. Polymer Sci.*, **5**, 283 (1950); A. Katchalsky and S. Lifson, *ibid.*, **11**, 409 (1953).

(11) P. J. Flory, *J. Chem. Phys.*, **21**, 162 (1953).

where α^2 has replaced \bar{r}^2/r_0^2 . Thus it is seen that α^2 should vary linearly with $1/\kappa$, that is, with the reciprocal of the square root of the ionic strength.

Since there is considerable evidence that cellulose derivatives are free-draining chains (see, for example, reference 2), the intrinsic viscosity should be proportional to \bar{r}^2 and α^2 . Hence equation 5 predicts that $[\eta]$ should be proportional to $1/\kappa$. Behavior of this type has already been demonstrated by Pals and Hermans³ and our results plotted in Fig. 4 provide further confirmation. Similar results would be expected when \bar{r}^2 or α^2 is plotted. Values of \bar{r}_w^2 are obtained by multiplying the averaged values of the effective bond length by $\sqrt{N_w}$. If these are plotted against $1/\kappa$, the extrapolation back to zero yields a value of 1550 ± 70 Å. for $\sqrt{\bar{r}_w^2}$. With this value the expansion factor, α , can be evaluated: the results are listed in Table IV and plotted in Fig. 4.

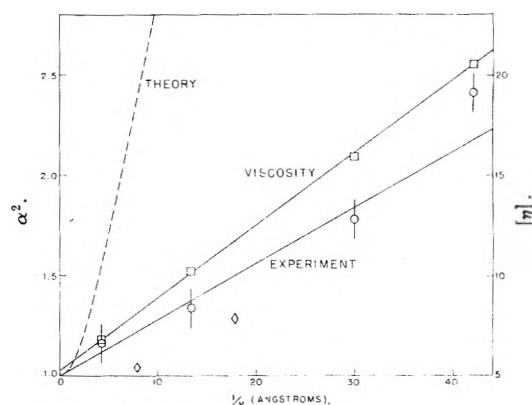


Fig. 4.—Dependence of molecular expansion of NaCMC on ionic strength. Abscissa is Debye radius. Ordinate is intrinsic viscosity and α^2 . The dashed line represents the variation of α^2 predicted by the Hermans-Overbeek theory. Values denoted by \diamond correspond to $[\eta]$ in calcium nitrate solutions.

Having seen that the functional relationship of Hermans and Overbeek is supported, it is of interest to see whether our data are in quantitative agreement with equation 4. Hence a must be evaluated. Using the weight average charge per molecule, Z , we find $a = 0.44$, giving rise to the dashed line in Fig. 4. The slope of this dashed line in its nearly linear region is about 8-fold greater than the one drawn through the experimental points. This means that the Hermans-Overbeek theory predicts about a three times greater rate of expansion with increasing Debye radius ($1/\kappa$) than is found experimentally for NaCMC.

Turning next to the Flory theory, we find again the spherical model employed and the method used is an extension of his basic calculation of the expansion of non-electrolyte polymers by long range interactions. The use of the Donnan equilibrium theory to calculate the osmotic contribution of the mobile ions to the free energy of expansion of the polymer molecule leads to the relation

$$\alpha^5 - \alpha^3 = 2C_{M1} \left(1 - \frac{\theta}{T}\right) M^{1/2} + 2C_{11}^2 M^{1/2}/S \quad (6)$$

where

$$C_1 = 3.56 \times 10^{-22} \left(\frac{\bar{r}_0^2}{M} \right)^{-3/2} M_0^{-2}$$

M_0 being the monomer weight, i the degree of charge, and S the ionic strength. The first term is the non-ionic contribution and the second is the first of a series of terms making up the ionic contribution. For univalent ions higher ionic terms may be neglected. The value of \bar{r}_0^2 in terms of which C_1 is defined has here the clear meaning of the mean end-to-end length exhibited by the molecule when the second virial coefficient is zero. This is a somewhat different definition than that adopted by Hermans and Overbeek. In this case, however, it appears that the difference is small numerically. If the second virial coefficients in Table III are plotted against the reciprocal ionic strength or the square root thereof, it can be seen that either extrapolation leads to essentially zero values of B at infinite ionic strength. We shall therefore continue to use the same values of \bar{r}_0^2 and α as before.

The comparison between equation 6 and the data is made in Fig. 5, where $\alpha^5 - \alpha^3$ derived from values given in Table IV is plotted against reciprocal ionic strength. Excluding the least reliable point a linear relation is observed. The small finite value of the intercept corresponds to $\alpha = 1.06$. This is within probable experimental error of unity. However, if it were accepted as real and new \bar{r}_0^2 and α values computed, the slope of the new plot would be only 30% greater. This difference is negligible when we turn to the value of the slope predicted by equation 6. This is plotted as the dashed line in Fig. 5 and the slope is seen to be about 30 times that of the experimentally determined line. In terms of α this difference is comparable to that found for the Hermans-Overbeek theory. For example, in the 0.01 M NaCl case, it is found that the Flory theory predicts $\alpha = 2.0$ and the Hermans-Overbeek 2.7 in comparison with the experimental value of about 1.4.

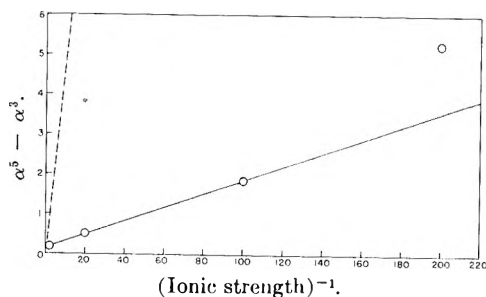


Fig. 5.—Plot of $\alpha^5 - \alpha^3$ against reciprocal ionic strength: O, light scattering values; —, plot of equation 6.

The Kuhn-Katchalsky theories are the only ones which preserve in the model the essential chain-like character of the polyelectrolyte. In this theory it is assumed that the probability of the various possible configurations of the chain depends only on its mean end-to-end length. The electrical free energy is then computed in terms of the electrostatic interaction among the different chain charges as a function of the end-to-end length. The relation

between α and the ionic strength as represented by the Debye-Hückel κ contains the mean end-to-end length $\sqrt{\bar{r}^2}$ and a factor λ defined in terms of the ratio of $\sqrt{\bar{r}^2}$ to the contour length (length at maximum extension), L . The result may be written

$$\alpha^2 = \frac{Z^2 e^2}{3\epsilon k T \sqrt{\bar{r}^2 \lambda}} \left[\ln \left(1 + \frac{6\alpha^2}{\kappa \sqrt{\bar{r}^2}} - \frac{6\alpha^2/\kappa \sqrt{\bar{r}^2}}{1 + 6\alpha^2/\kappa \sqrt{\bar{r}^2}} \right) \right]$$

$$\lambda \cong 1 + \frac{3}{5} \frac{\bar{r}^2}{L^2 - \bar{r}^2} \quad (7)$$

It is somewhat surprising to find that this equation has no solution for the values of ionic strength used in this investigation and hence no comparison is possible. The nature of this failure can be seen if λ is set equal to unity since solutions then exist for all ionic strengths. These solutions, however, correspond to impossibly large values of \bar{r}^2 , that is to values which would require the end-to-end length to exceed the contour length. Therefore, it appears that serious errors having the effect of vastly overestimating the expansion due to intrachain electrostatic repulsions have been made. Thus we conclude that this theory, while employing the most realistic model, offers the least adequate representation of the data. A thorough theoretical investigation of this situation has been undertaken by Harris and Rice¹² and they are reporting their results concurrently.

Returning to the relatively moderate overestimation of the expansion made by the Hermans-Overbeek and Flory theories, the observation may be made that a correction in the required direction and order of magnitude could be introduced if the neglect of counter-ion binding were taken into account. If one uses as an estimate the measurements on sodium polyacrylate¹³ and sodium polymethacrylate,¹⁴ the charge Z should be reduced by a factor of about 2. Introducing this change into the expression for α , equation 5 is then brought into good agreement with the experimental points.

The Interrelation of pH and Molecular Expansion

In the dissociation of weak monobasic acids, the sum of the pH and $\log(1 - \alpha)/\alpha$ is equal to pK_0 where K_0 is the intrinsic dissociation constant. For polybasic acids the electrical free energy of the polyion opposes the dissociation. Overbeek¹⁵ proposed that this effect on the pH of polybasic acids could be represented by

$$pH + \log(1 - \alpha)/\alpha = pK_0 + \frac{0.434}{kT} \left(\frac{\partial F_e}{\partial Z} \right) \quad (8)$$

where F_e is the free energy of electrical origin per polyion and Z is the number of elementary charges per polyion. The expressions for $(\partial F_e/\partial Z)$ obtained by Hermans and Overbeek and by Katchalsky are, respectively

$$\left(\frac{\partial F_e}{\partial Z} \right) = \frac{648Z e^2}{5^{3/2} \epsilon \kappa^2 (\bar{r}_0^2 + \bar{r}^2)} \quad (9)$$

$$\left(\frac{\partial F_e}{\partial Z} \right) = \frac{2Z e^2}{\epsilon (\bar{r}^2)^{1/2}} \ln \left(1 + \frac{6(\bar{r}^2)^{1/2}}{\kappa \bar{r}_0^2} \right) \quad (10)$$

(12) F. E. Harris and S. A. Rice, *J. Polymer Sci.*, in press (1954); *THIS JOURNAL*, **58**, 725 (1954).

(13) J. R. Huizenga, P. F. Grieger and F. T. Wall, *J. Am. Chem. Soc.*, **72**, 2636 (1950).

(14) A. Oth and P. Doty, *THIS JOURNAL*, **56**, 43 (1952).

(15) J. T. G. Overbeek, *Bull. soc. chim. Belg.*, **57**, 252 (1948).

Using these to compute the last term in equation 8, one obtains the results listed in Table V. These are to be compared with the values of $pH + \log(1 - \alpha)/\alpha - pK_0$ which are tabulated in the last column. These values are obtained by extrapolating the data in Table I to $\alpha = 0.96$ and subtracting pK_0 (3.40).

TABLE V
COMPARISON OF $pH + \log(1 - \alpha)/\alpha - pK_0$ WITH EXPERIMENT

Ionic strength	Equation 9	Equation 10	Experiment
0.500	0.0005	0.123	0.3
.050	.0044	.371	0.9
.010	.0174	.795	1.4
.005	.0256	1.07	2.2

It is seen that the Hermans-Overbeek equation underestimates this quantity by a factor of 100 to 800 whereas the Katchalsky equation differs only by about a factor of 2. Since the use of the bulk dielectric constant can easily be in error by a factor of 2, we conclude that equation 10 adequately represents the experimental data.

It is paradoxical that the Hermans-Overbeek theory which serves rather well for the expansion of the polyion cannot predict the pH , whereas the Katchalsky theory which requires an impossible extent of expansion yields an accurate estimate of the pH . In other words, it appears that the Katchalsky theory adequately accounts for the potential close to the chain against which ionization occurs but fails badly in dealing with the effects of this potential on longer range interactions on which the expansion depends. The reverse situation seems to hold for the Hermans-Overbeek theory. These same conclusions can be derived from the earlier investigation of polymethacrylic acid.¹⁴

Despite the fact that a reasonable modification of the charge of the polyion to take account of counter-ion binding brings the Hermans-Overbeek theory into excellent agreement with chain expansion, two reservations must be made. One is the increasing inadequacy of the approximation of spherical symmetry with increasing expansion. The general success of the Flory molecular configuration theory for non-electrolyte polymers indicates that this approximation is a useful one when only short range forces are involved. However, this approximation is surely put to a more severe test with longer range electrostatic forces. The other reservation lies in the use of the Debye-Hückel linearization approximation which assumes that $e\psi/kT$ is less than 1.

Now it has been proposed¹⁶ that $e\psi$ can be identified with $(\partial F_e/\partial Z)$ and could therefore be determined from titration data. Using this procedure on the data in Table I, one finds that $e\psi/kT$ is less than 0.5 for the NaCMC investigated here only when the degree of dissociation is less than 0.5 and the ionic strength greater than 0.5. Under the conditions employed in this study, the

value of $e\psi/kT$ ranges from 1 to 8.¹⁷ Consequently the requirements for the use of the Debye-Hückel approximation do not exist in this system and the approximate agreement that has been obtained with the polyion expansion is probably fortuitous.

The Second Virial Coefficient in Polyelectrolyte Solutions

We pass now to a brief consideration of the effect of electrostatic forces on intermolecular interactions in dilute solution. These interactions are most clearly assessed in terms of the second virial coefficient, that is, the quantity B in the light scattering equation $Kc/R_0 = 1/M + 2Bc$, and the osmotic pressure equation $\pi/cRT = 1/M + Bc$. The values of B listed in Table III show that it increases sharply as the ionic strength is decreased. Our principal interest lies in the origin of this variation.

Two extreme situations may be visualized. In the first the polyions exhibit a net charge whose shielding decreases with lowering ionic strength thereby increasing the mutual repulsion among the polyions. If the potential is so low ($e\psi/kT < 1$) that the counterions can distribute themselves between the atmosphere and the solution, this case approaches that of the classical Donnan membrane equilibrium and the dominant term in the expression for B should be $1000Z^2/2M^2m_3$ where m_3 is the molality of the third component, in this case NaCl. This has been shown to be the case in solutions of charged protein molecules at ionic strengths below about 0.02.¹⁸ Mysels¹⁹ has recently examined in some detail the consequences to be expected in light scattering for the idealized case of Donnan equilibrium with all activity coefficients unity.

In the second case, representing the opposite extreme, the potential is quite high: $e\psi/kT > 1$. Under this circumstance the counterions are held close to the polymer chain. Since they are not lost to the body of the solution, the polyion is completely shielded and does not exhibit a net charge at average distances of approach to other similarly shielded polyions. In this case the charge Z does not manifest itself in intermolecular interactions directly and the dominant term in B would be that due to the interactions of chains characterized by the sizes which can be determined independently. Provided that the expansion is great enough for the value of B to be determined principally by the molecular size, the non-electrostatic interaction energy being negligible, several ways exist for estimating the value of B for a chain molecule of given mass and end-to-end length. Perhaps the best of these is the relation based upon the Flory theory of molecular configurations which can be written in the following manner

$$B = \left(\frac{2\pi}{9}\right)^{3/2} \frac{N}{M^{1/2}} \left(\frac{r_0^2}{M}\right)^{3/2} (\alpha^5 - \alpha^3) F(X) \quad (11)$$

(17) Harris and Rice (ref. 12) show that this identification of $e\psi$ with $(\partial F_e/\partial Z)$ implies a random filling of charge sites with protons or bound counter-ions. If account is taken of this non-random filling, the value of $e\psi$ is reduced. Calculations similar to those made in their paper show that for the present case, however, the reduction would be quite small. Hence this estimate of $e\psi$ remains valid.

(18) J. T. Edsall, H. Edelhoeh, R. Lontie and P. R. Morrison, *J. Am. Chem. Soc.*, **72**, 4641 (1950).

(19) K. J. Mysels, *This Journal*, **58**, 303 (1954).

(16) G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.*, **36**, 101 (1940). See also A. Katchalsky, N. Shavit and H. Eisenberg, *J. Polymer Sci.*, **13**, 69 (1954).

where N is Avogadro's number and $F(X)$ is a slowly varying function which takes on values in the range 0.98 to 0.76 for conditions employed here.

We can now see whether either of these extremes are satisfied by the data from Table III. The weight average of M and Z is employed throughout. It can be shown that the average required is considerably higher than the number average but some uncertainty is attached to the use of the weight average. The values of B calculated on the assumption that it arises only from the Donnan term or only from equation 11 are listed in Table VI together with the observed values. It is seen that Donnan term greatly overestimates B , becoming worse with decreasing ionic strength, whereas equation 11 offers agreement that is so good as to be at least partly fortuitous. Thus it appears that the second case described above is the one that applies to highly charged polyelectrolytes such as NaCMC.

TABLE VI

THE COMPARISON BETWEEN CALCULATED AND OBSERVED SECOND VIRIAL COEFFICIENTS

Ionic strength	$B \times 10^3$		Eq. 11
	Experimental	Donnan	
0.500	1.45	1.01	1.25
.050	5.70	10.1	3.00
.010	15.6	51.0	9.25
.005	26.0	101.0	25.0

This behavior is that which would be expected in view of the finding of the previous section that the value of $e\psi/kT$ is much greater than unity. As a consequence of these two observations, we view the polyion as a randomly-kinked chain enclosed by a sheath of counterions which essentially neutralize its charge with respect to other polyions. The sheath of counterions is probably thinner than the Debye-Hückel radius (4.2 to 42 Å. in the present case) but large enough to permit substantial repulsion of adjacent monomeric elements due to incomplete local shielding. This local repulsion causes expansion with lowering ionic strength.

The Intrinsic Viscosity of Sodium Carboxymethylcellulose and Its Relation to Molecular Dimensions

In this final section we discuss briefly the dependence of $[\eta]$ on the composition of the aqueous solution serving as solvent, the relation of $[\eta]$ to \bar{r}^2 and the related work of Pals and Hermans previously mentioned.³

The viscosity behavior in some other aqueous solutions is shown in Fig. 2. In dilute HCl and in 1 molar NaOH $[\eta]$ is found to be somewhat lower than in NaCl solutions of comparable molarity. Of course, in HCl the acid groups are almost completely discharged and some difference is expected. The replacement of NaCl by NaOH, which changes $[\eta]$ from 6.5 to 4.7, is hardly predictable but is presumably the result of the strong interactions possible between NaOH and the hydroxyl groups. It is interesting to note that cellulose trinitrate of the same chain length in acetone would exhibit very nearly the same intrinsic viscosity as found here for NaCMC in 1 M NaOH.

The two measurements in $\text{Ca}(\text{NO}_3)_2$ solutions serve to show the extent to which the ionic strength principle fails in polyelectrolyte solutions. If the Debye-Hückel theory were applicable, it would be expected that no change would be brought about upon replacing Na^- by Ca^{++} at the same ionic strength. It is seen from Fig. 4, where these two points are plotted as diamonds, that very substantial reductions $[\eta]$ occur. This may be due to more effective shielding of polyion charges by bivalent ions or to the contracting effects of chelation.

We turn now to the relations of the intrinsic viscosity to the sizes determined from light scattering (Table IV). If it is assumed that the polymer is at all ionic strengths behaving as a free draining coil, the Kirkwood-Riseman equation can be employed to calculate the frictional constant of the monomeric unit, ζ . This relation is

$$\zeta = 2400\eta_0 M_0 [\eta] / (\bar{r}_w^2 N)$$

and upon substitution it is found that ζ equals 2.70, 3.26, 3.78 and 3.70×10^{-10} for 0.5, 0.05, 0.01, and 0.005 ionic strength, respectively. Recalling the greater uncertainty for the lowest ionic strength, there is some evidence here that the value of ζ is increasing with expansion of the polymer chain but further work would be required to prove this point. The value of ζ for the 0.5 M NaCl solution is the same as that found for the best fit of the more extensive data on cellulose nitrate in acetone.² Consequently it appears that at high ionic strength chain dimensions and mean configurations are the same for NaCMC as for cellulose nitrate of equal degree of polymerization. Since Staudinger law behavior was found in the latter case it is likely that the Staudinger constant found for the cellulose nitrate-acetone system would provide a good estimate of degree of polymerization for NaCMC when measurements are made in 0.5 M NaCl.

Finally, we take up a quantitative comparison of this work with that of Pals and Hermans.³ Their principal conclusion is that the dependence of size computed from viscosity measurements is in excellent agreement with the predictions of the Hermans-Overbeek theory. However, our results show a pronounced difference and moreover indicate that the model employed for the theory is not representative of NaCMC.

Pals and Hermans determine what we have called α by use of the relation: $[\eta]/[\eta]_0 = \bar{r}^2/\bar{r}_0^2 = \alpha^2$ where the subscript zero refers to the values extrapolated to infinite ionic strength. When this is applied to our data, it is found that the fractional expansion ($\alpha - 1$) is about double that deduced from \bar{r}^2/\bar{r}_0^2 . For example, in 0.01 M NaCl the value of α from viscosity is 1.73 in comparison with 1.335 from light scattering. This disagreement is equivalent to the finding, noted above, that the frictional constant depends on the state of expansion because the use of the equality of the viscosity and \bar{r}^2 ratios implies that the frictional constant remains constant. Because of the uncertainties in assigning values to $[\eta]_0$ and \bar{r}_0^2 and the probable error in \bar{r}^2 , it does not appear that a choice can now be made as to which procedure yields the more nearly correct values of α . However, even if the viscosity esti-

mates were taken as correct the gap between our earlier results and the Hermans-Overbeek theory would only be narrowed about one third of the way. The remainder, and really the major difference, lies in the evaluation of the quantity a in equation 5. For this we have used weight average values of the charge, Z , and the unperturbed length, $\overline{r_0^2}$. Pals and Hermans, on the other hand, have used a number average for Z and have evaluated r_0^2 in an indirect fashion involving the use of the theory itself. Had we followed their procedure on this point, we would have obtained a value of $\overline{r_0^2}$ that is 2.7 times that which we have employed. The sensitivity of this procedure to the molecular weight distribution and its dependence upon the theory which is being tested are sufficient causes for using a more direct evaluation of $\overline{r_0^2}$. Having done this, it is our conclusion that the difference between the value of a computed by using measured values of $\overline{r_0^2}$ and Z and determined experimentally, substantially exceed probable experimental error.

It is a pleasure to acknowledge helpful discussions of this work with Drs. H. Benoit, S. A. Rice and W. H. Stockmayer and to express appreciation for financial aid to part of this work from the Mallinckrodt Fund.

DISCUSSION

J. J. HERMANS (University of Leiden).—Part of the discrepancies between Doty's results and ours probably can be explained by the larger charge density on the polymer chains investigated by him. The Debye-Hückel approximation will accordingly be less adequate to describe his results. In fact, if one calculates the electric potential from the theory, it turns out that $e\psi/kT$ is less than $1/2$, in all cases examined by Trap. This is *not* true for the quantity $(6F/6e)/kT$ as derived from the titration data, where F is the free energy. I should like to point out in this connection that the results of titration experiments are of dubious value for several reasons. (1) To calculate the degree of dissociation of the polymer, one has to take into account that the concentration of hydrogen ions inside the coil is different from the average concentration, and this cannot be done with great accuracy. (2) A considerable uncertainty is introduced by the unknown activity coefficients of the ions present. Arnold and Overbeek, who carried out titration experiments in the presence of potassium chloride, could not obtain agreement with theoretical predictions unless they replaced the activity coefficient of potassium chloride by that of hydrogen chloride at the relevant concentration. (3) There is also the so-called suspension effect.

It is possible that a correction for these factors would considerably reduce the discrepancy between the data derived from the expansion and those derived from titration experiments.

A point of great interest which is clearly brought out by Doty's work is the great sensitivity of calculated molecular dimensions to the value of the molecular charge Ze . This is due to the fact that the electrical free energy contains the square of Z . In Doty's sample the ratio between average Z and number average Z is about 2.5 and this introduces, therefore, data a very large uncertainty in the dimensions calculated from theory. Both this *and* the dubious value of titration data do, of course, reflect also upon the comparison between the theory of Harris and Rice and experiment.

G. EHRLICH (General Electric Company).—The emphasis on the Donnan term shown in the preceding papers²⁰ appears to warrant a more careful examination of the proper formulation of the light scattering from polyelectrolytes. The Donnan term arises in the usual discussions of the scattering from such systems solely because of the requirement of electrical neutrality which we impose on the volume element

for which fluctuations are calculated, in recognition of the long range forces between the various charged species in solution. A formalism (such as that proposed by Mysels,¹⁹ for example) which does not account for these interactions by including both the Donnan term and activity coefficients to correct for the non-ideality of the solute species as well is obviously inconsistent. The more significant the Donnan term, the more important the deviations from ideality, so that a quantitative agreement with experimental results cannot be hoped for without a theory for the activity corrections (β_{22} , etc.). Inasmuch as such a detailed theory is still lacking, emphasis on the Donnan term is understandable though unfortunate.

It is, however, possible to present a formalism, as rigorous as that of Edsall, *et al.*, without *explicit* consideration of the counter-ions. This is most readily accomplished by circumventing fluctuation theory and considering instead the optical problem of the scattering from an array of molecules whose arrangement in space is specified by the radial distribution function $g(R)$. For a polyelectrolyte we neglect as usual scattering due to small ions and density fluctuations and thus obtain the familiar relation

$$R_\sigma = KcMP(\sigma) \left[1 + \frac{N}{v} \int [g(R) - 1] \frac{\sin hR}{hR} dv \right]$$

in which K takes proper account of the optical constants of the scattering centers. For dilute solutions in the limit of zero scattering angle, $h \rightarrow 0$, and

$$\frac{Kc}{R_\sigma} = \frac{1}{M} \left[1 - \frac{N}{v} \int [g(R) - 1] dv \right] = \frac{1}{M} + 2Bc$$

B being the second virial coefficient. The problem of the scattering from polyelectrolytes is thus equivalent to that of ordinary polymer solutions, namely, that of evaluating the distribution in space of the scattering centers; the fact that we are dealing with electrolytes enters of course in the specification of the forces which dictate the configuration peculiar to such systems. The results presented by Professor Doty indicate, however, that these are very satisfactorily approximated by segment-segment interactions typical of non-polar polymer molecules.

The fact that in this interference treatment the presence of counter-ions need not be explicitly recognized should be apparent from thermodynamic reasons as well. As already shown by Stockmayer,²¹ the fluctuations in the concentration of the macrocomponent are determined by $(\partial\mu_2/\partial N_2)_{T,P,\mu}$, that is, by the concentration dependence of the chemical potential μ_2 of the macrocomponent, with all other chemical potentials being held constant.

Finally, it should be noted that the relations presented by Edsall, *et al.*, are formally incorrect, due to an error in transforming the concentrations originally employed by Stockmayer. Thus, for a simple two component system, the scattering intensity is properly given by

$$R_\sigma = KM\varphi_1RT/(\partial\mu_2/\partial c)_{T,P}$$

where φ_1 is the volume fraction of solvent. This term, previously omitted, will not affect molecular weights determined by extrapolation to $c \rightarrow 0$; its neglect in expressing the concentration dependence of scattering must be justified for each particular system under consideration.

GEORGE SCATCHARD (Massachusetts Institute of Technology).—The net charge of colloid particle and bound gegenions can be determined, at least approximately, by measuring electrophoresis. The β_{22} term can always be eliminated by assuming the binding of additional ions of both species. It is often convenient to define the colloid component so that each formula weight of component contains one mole of particles. If the colloid particle in sodium chloride is pictured as containing n sodium ions, c chloride ions and a net valence of z , which will be negative (or zero) for an acid, the component would be pictured as $\text{Na}^+_{(n-z/2)}\text{P}^z\text{Cl}^-_{(c+z/2)}$.

(20) J. T. Edsall, H. Edelhoeck, R. Lontie and P. R. Morrison, *J. Am. Chem. Soc.*, **72**, 4641 (1950).

(21) W. H. Stockmayer, *J. Chem. Phys.*, **18**, 58 (1950).

TEMPERATURE DEPENDENCE OF DIFFUSION IN AQUEOUS SOLUTIONS

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The diffusion coefficients, in dilute aqueous solution, of some representative materials whose molecular weights range from 19 to 68,000 have been determined at several temperatures. The results indicate that the temperature coefficient for diffusion increases only slightly with increasing particle size and is less than that predicted by the Stokes-Einstein relation (assuming the diffusion radius to be independent of the temperature) only for solute molecules so small that the solvent, water, cannot be considered a continuum.

Within the last few years methods have been developed¹⁻³ that permit the determination of diffusion in liquids with a precision of about 0.1%. Since the older data were often uncertain by several per cent. or more, this development has not only made possible the study of many interesting problems such as the concentration dependence of the diffusion coefficient and the variation in the diffusion behavior of isomers but has also necessitated a re-examination of some of the prevalent ideas based on the older results. One of these is that the temperature coefficient of diffusion increases with the size of the diffusing particle. This conclusion is based on a table published by Oholm⁴ in 1913 and cited by Taylor.⁵ After conversion of Oholm's data to cm.²/sec. they are as follows

$D_{20} \times 10^6$	28	23-21	18-16	14-13	9-8	5-3	2-1
D_{20}/D_{10}	1.18	1.20	1.22	1.25	1.29	1.35	1.40
E_D	2730	3010	3280	3680	4200	4950	5550

and predict that if a substance has a diffusion coefficient at 20° in the range given in the first row the ratio of this to the value at 10° will be approximately as given in the second row. Reference to the activation energies, E_D , in the third row will be made later in this report.

Since there are reasons to think that the dimensions of a particle are nearly independent of the temperature the variation of the ratio D_{20}/D_{10} with D represents a contradiction of the Stokes-Einstein relation and will be discussed below. The purpose of this report is to present the results of diffusion measurements of selected solutes at a sufficient number of temperatures to establish not only the value of the temperature coefficient but also the manner in which this changes with the temperature. The materials selected have a molecular weight range of 19 to 68,000 and include those that previous work⁶ has shown to have extreme values for the temperature coefficient.

Experimental.—The method employed in the present research was that of free diffusion from an initially sharp boundary between solution and solvent, the spreading of the boundary with time being followed optically with the aid of Rayleigh interference fringes. The Tiselius electrophoresis cell, modified to facilitate the formation of the Rayleigh fringes, has served as the diffusion cell. Except for the use of a platinum resistance thermometer to measure the thermostat temperature the experimental procedure was

the same as in previous work by the author and has been adequately described.^{3,6}

Measurements have been made at 1, 13, 25 and 37°. At 37° two sources of difficulty were encountered only one of which has been overcome. Solutions prepared at room temperature are frequently supersaturated at 37° with respect to dissolved air and this is likely to appear as bubbles on the walls of the diffusion channel. The use of freshly boiled water in preparing the solutions and storing them under reduced pressure effectively prevented bubble formation. The more serious difficulty arises from the relatively high temperature coefficient, dn/dt , of the refractive index of water at 37°. In the case of a thermostat regulating near room temperature little energy enters or leaves the system. This is not true, however, at other thermostat settings and appreciable thermal gradients are then present in the bath water. At settings near 0° dn/dt is quite small and the thermal gradients are not accompanied by schlieren. At 37° on the other hand dn/dt is relatively large and the resulting schlieren in the path of the light through the bath produce "quivering" of the Rayleigh fringes at the photographic plate. Although this fringe movement is largely averaged out over the 3- to 4-second interval required for an exposure it impairs the fringe definition. At 37° the diffusion coefficients computed from successive exposures show larger deviations from the mean value for the experiment than at the lower temperatures. Partial immobilization, with the aid of a metal trough immersed in the bath, of the water in the light path appeared to reduce the schlieren somewhat. The thermoregulator used in the present research was a Rudolph Graves instrument (Stockholm, Sweden) with a sensitivity of 0.01 to 0.02°. In future work it is hoped that the use of a more sensitive regulator, together with immobilization of the bath water in the light path, will minimize the schlieren. It should be noted that at 1° and 37° gradients of as much as 0.03° existed between the hottest and coldest regions of the bath. More vigorous circulation is not contemplated, however, owing to the possibility of disturbing the diffusion process thereby.

Materials.—The deuterium oxide used in this work was the material recovered from a previous investigation.⁸ Dr. Dexter French generously supplied the cycloheptaamylose.⁹ The bovine plasma albumin was a crystalline product, Armour lot number G4502, and was found, on electrophoretic analysis by Dr. Gertrude Perlmann of these Laboratories, to be free of globulins. A second crystalline sample, Armour lot number 128-175, was also examined at 13° and gave a diffusion coefficient of 0.4672×10^{-6} , a value 1% higher than that of the first sample. These results, together with those of Akeley and Gosting¹⁰ for this protein, suggest that a recrystallization immediately prior to use may be essential if the values obtained are to be independent of the sample. However, the results for the three samples are in sufficiently close agreement to warrant the conclusion that the effect of temperature on the diffusion of a "pure" sample would not differ significantly from the values reported below. All other materials were of reagent grade and were used without further purification.

In the diffusion of D₂O high concentrations were required to give a reasonable number of fringes and the concentration dependence of D made it desirable to extrapolate to infinite dilution. The extrapolations are shown in Fig. 1. Except

(1) G. Kegeles and L. J. Gosting, *J. Am. Chem. Soc.*, **69**, 2516 (1947).

(2) L. J. Gosting and M. S. Morris, *ibid.*, **71**, 1998 (1949).

(3) L. G. Longworth, *ibid.*, **74**, 4155 (1952).

(4) L. W. Oholm, *Medd. Vetenskapsakad. Nobelinstit.*, **2**, 1 (1913).

(5) H. S. Taylor, *J. Chem. Phys.*, **6**, 331 (1938).

(6) L. G. Longworth, *J. Am. Chem. Soc.*, **75**, 5705 (1953).

(7) L. W. Tilton and J. K. Taylor, *J. Research Natl. Bur. Standards*, **20**, 419 (1938).

(8) L. G. Longworth, *J. Am. Chem. Soc.*, **59**, 1483 (1937).

(9) D. French and R. E. Rundle, *ibid.*, **64**, 1651 (1942).

(10) D. F. Akeley and L. J. Gosting, *ibid.*, **75**, 5685 (1953).

TABLE I
DIFFUSION COEFFICIENTS, $D \times 10^6$, AND THE STOKES RADII, $r \times 10^8$, OF SOME SOLUTES IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES

1	2	3	4	5	6	7	8	9	10	11
Solute	c , wt. %	D_{13} , cm. ² /sec.	D_{13}	D_{25}	D_{27}	r_1	r_{13}	r_{25}	r_{27}	r_V
$(kT/6\pi\eta) \times 10^{13}$						1.1512	1.7255	2.4230	3.2573	
H ₂ O	0.00	11.28		22.61		1.021		1.072		1.93
Urea	0.38	6.885	10.043	13.781	18.08	1.672	1.718	1.758	1.802	2.59
Glycine	.30	5.151	7.606	10.554	13.97	2.235	2.269	2.296	2.332	2.58
Alanine	.32	4.317	6.484	9.097	12.17	2.667	2.661	2.664	2.676	2.88
Dextrose	.38	3.137	4.736	6.728	9.088	3.670	3.643	3.601	3.584	3.53
Cycloheptaamylose	.38	1.492	2.274	3.224	4.362	7.716	7.588	7.516	7.467	6.56
Bovine plasma albumin	.25	.3066	.4626	.6577		37.55	37.30	36.84		27.0

for the protein all other solutes were used at such a concentration as to give about fifty fringes. The values of D for the albumin refer to a 44 fringe pattern and a solvent of pH 4.6 that was 0.01 molal in both sodium acetate and acetic acid and 0.15 molal in sodium chloride. Prior to the diffusion measurement the protein solution was dialyzed overnight against the buffer at 4–6° and then at the temperature of the experiment for 1–2 hours. The dialyze was used to form the boundary with the protein solution.

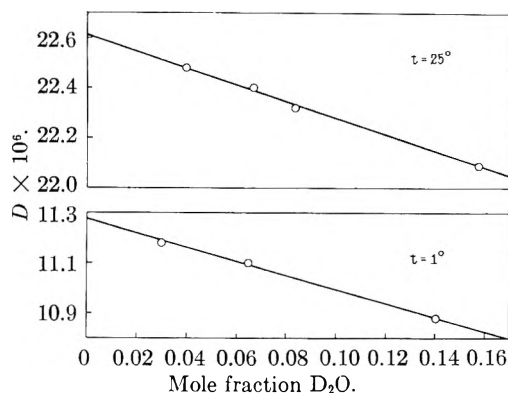


Fig. 1.—Variation of the diffusion coefficient of H₂O with the mean concentration in the boundary.

Results.—In Table I the solute is listed in the first column and then the mean concentration to which the diffusion coefficients correspond. Subsequent columns of the table contain the observed values of these coefficients at the temperature denoted by the subscript. These are followed by values of the radius r at each temperature as computed from the Stokes–Einstein relation $r = kT/6\pi\eta D$ where k is the gas constant, T the absolute temperature and η the viscosity of water. The values for $kT/6\pi\eta$ used in the computation of r at each temperature are given at the head of the appropriate column. In the final column of Table I are values of the radius r_V computed from the molal volume V of the solute at zero concentration, i.e., $V = 4/3\pi N r_V^3$ where N is Avogadro's number.

In Fig. 2 the Stokes radius r_t for a given solute at the temperature t has been divided by the value at 1° and plotted as ordinate against the temperature as abscissa.

Discussion.—From the data of Table I it will be seen that the variation of the Stokes radius with temperature is generally small in comparison with the discrepancy between this radius and that computed from the molal volume. In the case of the larger molecules $r > r_V$ and the difference is adequately accounted for by hydration, or asymmetry, or such a combination of the two as to satisfy not

only Perrin's extension of the Stokes–Einstein relation but also Simha's for viscous flow. Since the assumption of the fluid as a continuum in the derivation of the Stokes relation implies that the dimensions of the diffusing particles are large in comparison with those of the solvent molecules it is not surprising that $r < r_V$ for small molecules. The reaction rate theory¹¹ suggests that for such solutes the numerical factor in the denominator of the Stokes relation is less than 6π . In the case of the most rapidly diffusing material of Table I, H₂O, a factor of 3π would still allow for some asymmetry and interaction with the solvent.

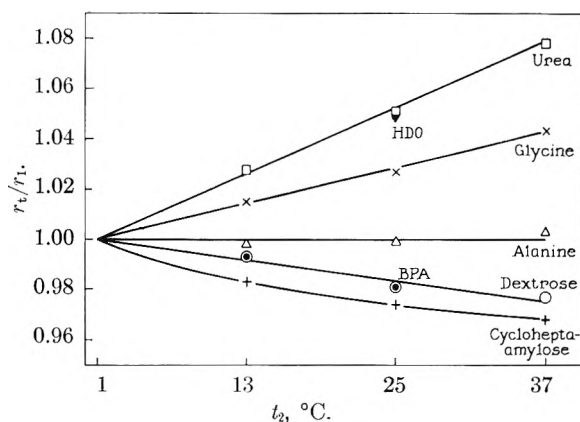


Fig. 2.—The variation of the Stokes' radius, relative to its value at 1°, with the temperature for different solutes.

In the case of large molecules the decreasing Stokes radius with increasing temperature is usually ascribed to decreasing hydration, a reasonable explanation since most solutions become more nearly ideal at high temperatures. An explanation for the fact that the radius of small molecules increases with the temperature must await further development of the theory of the liquid state. However, the data of Table I suggest the generalization that if the solute is large enough for the solvent to be considered a continuum the temperature coefficient of its diffusion will not be less than that predicted by the Stokes–Einstein relation.

Most of the twofold increase in D on raising the temperature from 1 to 25° is due to a decrease in the viscosity of the solvent, less than 10% being due to the increase in the kinetic energy, kT , of the diffusing particles. Although the Stokes–Einstein

(11) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 521.

relation predicts a relation between T and the $D\eta$ product it does not indicate the temperature dependence of either factor. The reaction rate theory is more useful in this regard, as may be illustrated with the aid of the data of Table I for alanine. In Table II the coefficients given in the second column

TABLE II
TEMPERATURE COEFFICIENTS FOR THE DIFFUSION OF
ALANINE

1 t	2 $D_2 \times 10^6$	3 E_D , cal.	4 100α
1	4.317		
13	6.484	5283	3.34
25	9.097	4783	2.80
37	12.171	4457	2.41

are those for alanine at the temperatures of column 1. Subsequent columns of Table II contain derived quantities that are useful in considering the temperature dependence of the diffusion coefficient. Thus the activation energy, E_D —column 3, defined by the relation

$$E_D = \frac{2.303RT_1T_2}{T_2 - T_1} \log \frac{D_2}{D_1} \quad (1)$$

varies by 17% over the 36° interval of the table whereas the conventional temperature coefficient

$$\alpha = \frac{2}{D_2 + D_1} \frac{D_2 - D_1}{t_2 - t_1}$$

changes by some 33%—column 4. Since E_D is more nearly independent of t than α it provides a better index of the temperature dependence of the diffusion coefficient for the comparison of data obtained over different temperature intervals.

Values of the activation energy for diffusion have been computed from the data of Table I for the 13–25° interval and are given in Table III.

TABLE III
ACTIVATION ENERGIES FOR DIFFUSION OVER THE INTERVAL
FROM 13 TO 25°

Solute	$D_{25} \times 10^6$	E_D , cal. 19°
Urea	13.78	4470
Glycine	10.55	4627
Alanine	9.097	4783
Dextrose	6.728	4959
Cycloheptaamylose	3.224	4931
Bovine plasma albumin	0.6577	4969

Ohlm appears to have been correct in his conclusion that the temperature coefficient tends to increase with the size of the diffusing particle. In order to compare his results with those of Table III activation energies have been computed with the aid of equation 1 and are given in the third row of the table in the opening paragraph. Although Table III covers much the same range of particle size as Ohlm's the new results show a variation in E_D of only some 11% whereas in the case of the older data the variation is about 100%. Apparently HCl was the most rapidly diffusing solute that Ohlm studied. This accounts, in part, for the low value of E_D derived from his results since the low temperature coefficient for the electric

mobility of the hydrogen ion is one of the arguments for its "non-Stokesian" conductance.¹²

At infinite dilution the diffusion and electric mobilities of ions are identical, the relation being $D = RT\lambda/F^2$ for univalent ions, where λ is limiting ionic conductance, F faraday equivalent and D ion diffusion coefficient as measured, for example, with the aid of tracers.^{13–16} Thus from the extensive conductance and transference data on electrolytes inferences may be drawn as to the diffusion behavior of ions. Some typical data are given in Table IV. The ion diffusion coefficients in

TABLE IV
ACTIVATION ENERGIES FOR ION DIFFUSION

Ion	$D_{25} \times 10^6$	E_D , cal. 18°
H	93.11	3230
OH	52.7	3610
Cl	20.32	4220
K	19.57	4230
NO ₃	19.01	4030
Na	13.34	4690
Acetate	10.89	4590
Li	10.30	5040

column 2 were computed from the conductances at 25°¹⁷ and are thus comparable with the values of Table III for non-electrolytes. This is also true of the activation energies since those of Table IV were computed from the values of $a = (1/\lambda)(d\lambda/dt)$ at 18° as given in the I.C.T.¹⁸ The relation is $E_D = RT(1 + aT)$. If the hydrogen and hydroxyl ions be excluded from consideration, owing to their abnormal transport in water, it is clear that the activation energies for ionic diffusion are similar to those for non-electrolytes and also tend to increase slightly, though irregularly, with increasing size until the particles are large enough to conform to Stokes relation. In no instance, however, are activation energies encountered as low as those derivable from Ohlm's data.

Since the variation in the radius r for a given temperature interval is less than that in E_D the Stokes-Einstein relation is a better interpolation formula than equation 1. However, in using this relation, for example, to correct the diffusion coefficient of a protein to the temperature at which its sedimentation constant has been determined, in the evaluation of its molecular weight, account should be taken of the variation in r .

Acknowledgment.—As mentioned above Dr. Dexter French of Iowa State College supplied the cycloheptaamylose used in this research. I am grateful to him for this interesting material and to Dr. D. A. MacInnes of these Laboratories for his criticism of this manuscript.

(12) J. D. Bernal and R. H. Fowler *J. Chem. Phys.*, **1**, 515 (1933).

(13) A. W. Adamson, *ibid.*, **15**, 760 (1947).

(14) J. H. Wang and J. W. Kennedy, *J. Am. Chem. Soc.*, **72**, 2080 (1950).

(15) J. H. Wang, *ibid.*, **73**, 510 (1951).

(16) R. Mills and J. W. Kennedy, *ibid.*, **75**, 5696 (1953).

(17) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 342.

(18) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926, Vol. VI, p. 230.

DISCUSSION

D. A. MACINNES (Rockefeller Institute).—How does the hydronium ion fit into your system?

L. G. LONGSWORTH.—If one prepares a plot of the limiting diffusion coefficient as abscissa with the temperature coefficient, *e.g.*, the activation energy for diffusion, as ordinate, the points are scattered about a line with a negative slope. With such a plot there is no clear segregation of the points for the few non-electrolytes for which the data are available from those for ions, *i.e.*, a rapidly diffusing particle tends to have a low activation energy whether it is charged or uncharged. Although isolated from any neighbors, owing to its very high mobility, the point for the hydronium ion is not markedly out of line with those for other solutes. Thus it is only in conjunction with other properties of the hydronium ion that its high mobility and low temperature coefficient can

be taken as evidence for the abnormal transport mechanism of this species.

Cox and Wolfenden (*Proc. Roy. Soc. (London)*, **A145**, 475 (1934)) have discussed the correlation between the ion mobility, its variation with temperature, and the *B* coefficient in the Debye-Falkenhagen viscosity equation. Small and negative *B* values are generally associated with high mobilities and low temperature coefficients. It would be of interest to see whether sufficiently mobile non-electrolytes would reduce the viscosity of water, *i.e.*, have negative *B* values.

R. M. FUOSS (Yale University).—The correlation between the constant *B* of the Debye-Falkenhagen viscosity equation and the diffusion constant suggests that the diffusion coefficient of bi-bolaform electrolytes would be quite small, because their *B*-values are very much larger than those of simple electrolytes (P. Goldberg and R. M. Fuoss, *Proc. Natl. Acad. Sci. U. S.*, **38**, 758 (1952)).

SIZE DISTRIBUTION ANALYSIS IN PLASMA EXTENDER SYSTEMS.

I. GELATIN¹

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Sedimentation analyses provide means for the determination of solute molecular weight and of distribution of molecular weights in systems of polyelectrolytes in proper solutions. The equilibrium method gives absolute molecular weights, while the velocity studies give valuable data about the actual form of the distribution curve. The combination of the two approaches, in effect a calibration of sedimentation constant in terms of molecular weight, serves several useful purposes. The application of such analyses to gelatin solutions establishes the fact that for the large molecules the sedimentation constant is closely proportional to the square root of the molecular weight. This fact and the intrinsic viscosity-molecular weight behavior lead one to assert that the gelatin molecules in saline solution exist in the form of random coils, with the solvent being entrapped to a considerable extent.

I. Introduction

a. The Nature of Gelatin.—For all the scientific work which has been done with gelatin systems there remains a substantial body of incompletely defined properties. There is much evidence of differences in behavior from gelatin to gelatin, perhaps not unexpected when one considers the various sources of the material and the several modes of manufacture.

Gelatin is obtained from the naturally occurring protein collagen. It can be expected that the amino acid compositions of parent and product will be the same, at least on the average. Also it seems quite probable that there will be some differences in amino acid composition between the various collagens, depending upon the particular tissue, the species, the age of the mammal or fish, etc., which is used. The respective gelatins will be correspondingly variant.

In general, gelatin has high glycine and high proline and hydroxyproline contents, and is lacking in cystine and tryptophan. The basic substances, lysine, hydroxylysine, histidine and arginine; and the acidic units, glutamic and aspartic acids; are present. In gelatin which has been prepared by an acid process some of the acidic residues will be present as amides. Such gelatins will have more basic groups than acidic ones, and thus have isoelectric points at about *pH* 9. On the other hand, lime process gelatins will have more acidic than basic groups and the isoelectric point will occur at *pH* 5 or below. The amide groups will have been lost through an hydrolytic reaction which liberates ammonia.

Thus, gelatin in solution answers the description of a polyelectrolyte. From the viscosity and sedimentation experiments of Kraemer² the solute molecular weights were found to be in the region 15,000 to 150,000. The systems were characterized by a high degree of polydispersity, so that such properties as viscosity and rigidity were described in terms of an average molecular weight. Little was determined by way of a description of the polydispersity and its (possible) effects on the physical properties of the systems.

In the meantime much work has been done on

(1) This investigation has been carried out under contract between the Office of the Surgeon General, Department of the Army, and The University of Wisconsin (DA-49-007-MD-114). Released for publication on March 14, 1952.

(2) E. O. Kraemer, *THIS JOURNAL*, **45**, 660 (1941).

the fractionation of gelatin, and the methods of characterization have been extended to include light scattering and osmotic pressure. It was hoped that by fractionation reasonably homogeneous molecular weight fractions of gelatin could be obtained and progress could be made in relating properties and structure. In general these hopes have not been realized, perhaps because fractionation does not give the desired homogeneity. At any rate, we have considered it to be important to develop more effective and more exact methods by which the heterogeneity can be described.

Problems such as the ones suggested above have become more pressing since gelatin systems have been under serious consideration for use as "plasma extender" materials. Such solutions meet many of the requirements, but there is a serious objection, manipulative in character, to its emergency infusion. At or somewhat below ordinary room temperatures the gelatin system sets to a solid or gel, and while it is perfectly fluid at body temperatures it must be melted before application. When gelatin systems are autoclaved to form "degraded" gelatin, the melting point of the system is indeed lowered, but at the same time the molecular size is so diminished that its retention time in the circulatory system, and therefore its value as an oncotic agent, is greatly reduced.

There have been several approaches in the attempt to reduce the tendency of the gelatin system to set to a gel, at the same time maintaining a practical molecular size and osmotic pressure. Several chemical treatments have been suggested and attempted, and the effects of the addition of gel point depressor substances such as urea and sodium acetyltryptophan have been studied. In the formation of the gels it has been supposed that the individual gelatin molecular chains are bound together by secondary attractive forces which are localized at widely separated points. Thus, among the molecules of various lengths which are present, it might be assumed that only the longer ones participate in the gel formation, with the shorter ones being unable to do so. The effects of chemical treatments and of the addition of highly polarizable anions are assumed to be such that the attractive forces between molecular chains are diminished. The marked effects on the melting point which are produced are evidently the result of some specific interaction at the points where the attractive forces are normally operative.

For this phase of the problem the important physical property of the gel is its rigidity. It is a well-defined property which may be measured in several basically different ways with concordant results. The modulus of rigidity is defined as the ratio of shearing stress (force per unit area) to shearing strain (angular deformation), thus it has the dimensions of force divided by area. The change in resistance to deformation when the gelatin solution sets to a gel is due to an abrupt appearance of rigidity. It has been quite generally accepted that this gel point (or melting point) is quite sensitive to molecular weight, although even this point is now in some dispute. It must be noted, however, that where changes in physical properties (such as rigidity) which accompany gelation have been studied it has not been possible to use gelatin solutions in which the molecules have been predominately of one size or even where the several average molecular weights of the solute have been known.

With these ideas prevalent, retention time and gel point as functions of molecular weight, it will be understood that much of our effort has gone into the development of methods for the determination of molecular weight and molecular weight distribution in gelatin systems and into the study of methods whereby the material could be fractionated. In this report we present methods to describe the size distribution by using sedimentation analysis and we make some remarks about the molecular form in solution. The results of some selected and typical experiments with representative gelatin plasma extender systems serve to illustrate the approaches, sedimentation equilibrium and sedimentation velocity, and their combination, to these ends.

b. Descriptions of Molecular Weight Heterogeneity.—Perhaps the simplest procedure for expressing molecular heterogeneity is to make use of the several average molecular weights. If the system is homogeneous all these averages will have the same value, and as a qualitative statement, the greater the spread of the successive average molecular weights, the greater is the heterogeneity. The most common averages are M_n and M_w , the number average and the weight average molecular weights, respectively. In the definitions which follow it is assumed that the distribution is known as a continuous function, so that definitions based upon integrations can be set up. However, if the size distribution data are available in tabular form, summations may be used in the definitions. Spe-

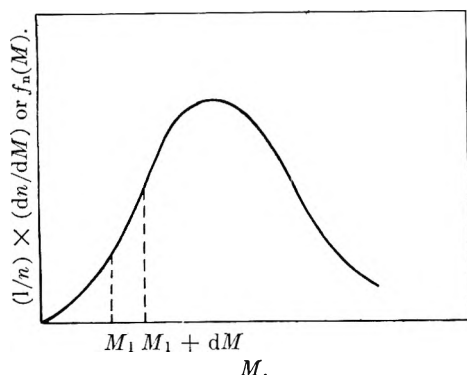


Fig. a.—Number distribution curve.

cifically we consider the cases of number distribution and weight distribution.

1. Number Distribution.—Fig. a

$$\text{Total no. of molecules} = \int_0^\infty f_n(M) dM = \int_0^\infty \frac{dn}{dM} \times dM$$

where f_n is the mathematical function descriptive of the number distribution. If it is desired to describe the number of molecules in the sample which have molecular weights between M_1 and $M_1 + dM$ we write

$$\text{No. of molecules} = \int_{M_1}^{M_1+dM} f_n(M) dM$$

where f_n is the number distribution function. Making the approximations that

$$\sum_i n_i = \int_0^\infty f_n(M) dM$$

and

$$\sum_i n_i M_i = \int_0^\infty M f_n(M) dM$$

we then have

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\text{first moment of no. distribution curve}}{\text{area}}$$

The number distribution curve may be given in integral form by plotting F_n as a function of M , where

$$F_n = \int_0^M f_n(M) dM$$

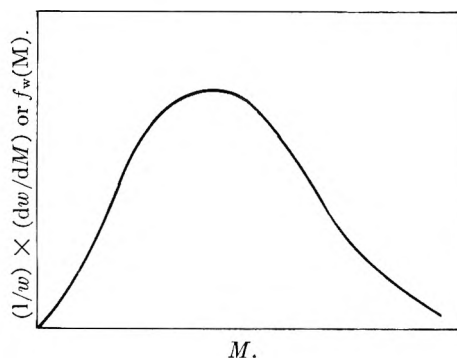


Fig. b.—Weight distribution curve.

2. Weight Distribution.—Fig. b

Total wt. of the sample on the mol. wt. scale =

$$\sum_i n_i M_i = \int_0^\infty f_w(M) dM$$

where f_w is the mathematical function descriptive of the weight distribution. Hence

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i c_i M_i}{\sum_i c_i}$$

or

$$M_w = \frac{\int_0^\infty M f_w(M) dM}{\int_0^\infty f_w(M) dM} = \frac{\int_0^\infty M^2 f_n(M) dM}{\int_0^\infty M f_n(M) dM}$$

The first fraction (in terms of the integrals) represents the first moment of the weight distribution of molecular weight curve relative to the frequency axis, otherwise known as the centroidal ordinate of the curve. From the second fraction, it appears that the first moment of the weight curve is equal to the second moment of the number curve.

The weight distribution curve may be also expressed in integral form by plotting the function F_w as a function of M , where

$$F_w = \int_0^{\infty} f_w(M) dM$$

These relationships readily can be generalized. The independent variable may be any quantity which is descriptive of molecular size or shape, or it may be any function of one of these quantities that is descriptive of the size and shape, such as sedimentation constant, diffusion constant and electrophoretic mobility. The dependent variable must sum up the total amount of one of these descriptive properties associated with one class of molecules with respect to the property which determines the magnitude of the dependent variable per molecule.

The unique evaluation of a molecular size distribution is an extremely complicated problem. In the case of the plasma extenders no real purpose would be served to perform such an intricate analysis. In practice it is convenient to fit an assumed parametric function to the observed average molecular weights. In a well-known example Lansing and Kraemer³ have used this approach to study the molecular weight distribution in some gelatin systems by using sedimentation equilibrium experiments, and the significance of the results in connection with the description of polydispersity in other macromolecular systems such as organic high polymers is at once evident. The distribution function selected, the logarithmic number distribution curve, has a single maximum, furthermore it was chosen so as to have a substantially zero number of molecules at low molecular weights. It is

$$dn = \frac{N}{\sqrt{\pi}} e^{-y^2} dy$$

in which

$$y = (\ln M/M_0)/\beta$$

N = total no. of molecules

dn = no. of molecules corresponding to the interval between y and $y + dy$

β = "non-uniformity" coefficient = zero for a homogeneous material

On a weight basis the equation becomes

$$\frac{1}{w} \frac{dw}{dM} = \frac{1}{M_n \beta \sqrt{\pi}} e^{-y^2} = f_w(M)$$

where

dw = wt. of material with mol. wt. between M and $M + dM$

M_0 = mol. wt. at the maximum in the wt. distribution curve

M_n = no. av. mol. wt., obtained in the experiment

The logarithmic number distribution curve, with two parameters, is not the only possible distribution function which fits a given set of average molecular weights. Actually accuracy may be gained

by using equations with three and four parameters, again average molecular weights, but the problem then becomes more than correspondingly difficult without too much assurance that after all there may have been minor details of the distribution which have failed to make their appearance. Even though sedimentation *velocity* constant is a function both of molecular size and shape, the distribution of sedimentation constants is much more useful to show up such minor details of molecular weight distribution.

II. Sedimentation Equilibrium.—At least in principle, the most satisfactory method so far developed for the determination of the molecular weights in polydisperse macromolecular systems is by means of the sedimentation equilibrium in an ultracentrifuge. The equations which are descriptive of the equilibrium can be derived from purely thermodynamic considerations. Such a derivation leaves out all reference to the shape of the molecule and requires either that the solution be sufficiently dilute so that it behaves like an ideal solution (usually not a practical situation) or that proper correction for the non-ideality be made. Since the theory has been described in several other places⁴⁻⁶ there is no need to present more than an outline of it in this report. We shall simply describe in brief some of the points in connection with the performance of the experiments and with the computations as they pertain to the particular gelatin systems which have been under study for their suitability as plasma extender fluids.

The experiments themselves were performed at 25°. From what is known about the reversible sol-gel transformation, 40° would have been a much more desirable temperature, but the rate of thermal degradation is now so great that in the time required for the establishment of the sedimentation equilibrium, eight to twelve days, an appreciable change in molecular weight would have resulted. At 25°, gelatin is probably aggregated in aqueous solution, so it was necessary to select a solvent system in which this effect would be depressed. The earlier experiments of Kraemer² had indicated that gelatin is molecularly dispersed in 2 *M* KSCN solution at this temperature. The question at once arises as to whether this effect is caused by binding of KSCN by the gelatin, and if so, would there be introduced a considerable error in the molecular weights as determined. Boedtker and Doty⁷ have shown by light scattering measurements that there may be involved a 10 to 12% reduction in the weight average molecular weight in the presence of the salt. In order further to answer the question, a series of equilibrium dialysis experiments was performed. Pre-dialyzed gelatin was equilibrated for three days across a cellulose membrane with KSCN solution, and the resulting "outside" solution titrated with standard silver nitrate to determine the CNS⁻ concentration. The equilibrium was approached from both sides. The observed concentrations agreed with those calculated from

(4) R. J. Goldberg, *THIS JOURNAL*, **57**, 194 (1953).

(5) J. W. Williams, *J. Polymer Sci.*, **12**, 351 (1954).

(6) M. Wales, *THIS JOURNAL*, **52**, 235 (1948).

(7) H. Boedtker and P. M. Doty, O. N. R. Technical Report No. 1, Contract N5 ori-07654., Dec. 15, 1952.

(3) W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).

simple dilution to within about 1%, on the average.

The gelatins studied were received in the form of transfusion samples of approximately 6% w./v. concentration. For our measurements it was necessary to determine the concentrations more accurately; this was done by drying a 10-cc. weighed sample for about 3 days at 105°. This result had to be corrected for the sodium chloride contained in the samples; this was assumed to be 0.9 g./100 cc., as stated. To correct from weight to volume concentrations, the density of two samples was determined pycnometrically.

Gelatin $c = 5.98$ g./100 cc. $d_{25}^{25} 1.022$
 Oxypolygelatin $c = 4.90$ g./100 cc. $d_{25}^{25} 1.019$

These data are in good agreement with values which may be calculated from the partial specific volume, 1.021 and 1.018, respectively.

All samples were opened in sterile manner. Afterward all samples were injected with 1 cc. of 10% merthiolate solution (yielding a final merthiolate concentration of 2:10,000).

In addition to the concentration, the sedimentation equilibrium calculations require knowledge of the quantities \bar{V} , the partial specific volume of the solute; $\alpha = dn/dc$, the refractive index increment; and B , the correction for non-ideality in the system. These will be briefly discussed in order.

1. For the partial specific volume, the value of 0.680 given by Kraemer was used for both gelatin and oxypolygelatin. Kraemer also gives values for the density of KCNS solutions, used with the gelatin. Experiments with samples of oxypolygelatin were performed in 0.15 M sodium chloride.

2. The refractive index increment was determined for both gelatin and oxypolygelatin, in the appropriate solvents at 25.0°. For gelatin in 2 M KCNS, a Pulfrich refractometer was used, using the Hg green line. The best straight line gives $\alpha = 0.00168$ in good agreement with the value 0.00163 calculated from a previous determination in water, assuming the volume mixing law. For oxypolygelatin a value of 0.00179 is obtained, using an immersion refractometer.

3. The constant B , the non-ideality correction, may be determined from the several sedimentation equilibrium experiments at various concentrations. Wales⁸ gives the expression

$$\frac{1}{M_{wi}} = \frac{1}{M_w} + Bc_0$$

in which

M_w = weight av. mol. wt.

M_{wi} = weight av. mol. wt. calcd. by assuming $B = 0$ (ideal)

c_0 = initial concn.

This equation is an approximation, valid for a small separation of molecular components. We have been able to show that, more exactly

$$\frac{1}{M_{wi}} = \frac{1}{M_w} + Bc'$$

where

$$c' = c_0 \frac{\int_a^b M_{wxi}^2 c_x^2 (x + \delta) dx \int_a^b (x + \delta) dx}{\left[\int_a^b M_{wxi} c_x (x + \delta) dx \right]^2}$$

(8) M. Wales, et al., THIS JOURNAL, 55, 145 (1951).

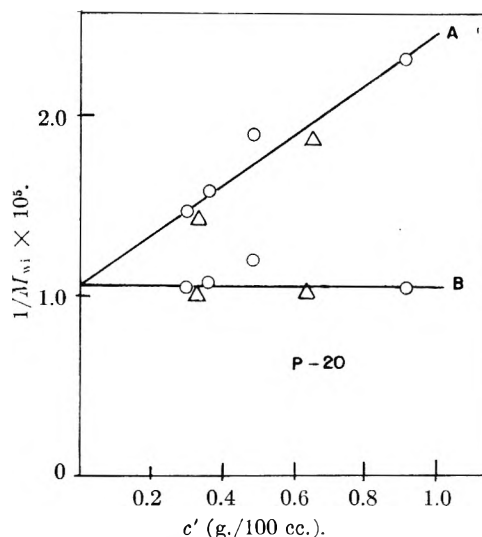


Fig. 1.—Non-ideality correction, gelatin P-20: Δ , 0.15 M NaCl; O , 2 M KSCN; A, $1/M_{wi}$ vs. c ; B, $1/M_w$ vs. c' .

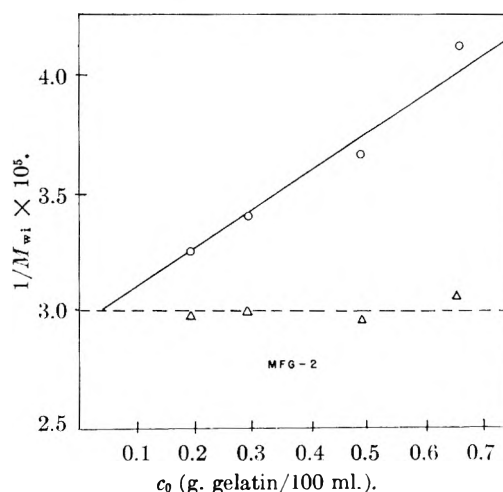


Fig. 2.—Non-ideality correction, gelatin MFG.

- x = distance from center of rotation
- M_{wxi} = ideal wt. av. mol. wt. at point x in the cell.
- c_x = concn. at point x
- δ = cor. for convergence of cell walls
- a, b = ends of the solution column

As typical of the kind of results which are obtained in the evaluation of the constant "B" we present data for two types of Knox gelatin; the standard P-20 material and a chemically modified gelatin, MFG, in Figs. 1 and 2. Both sets of experiments give a value of $B = 1.34 \times 10^{-5}$, which is quite large for a protein.⁹

It was observed that within the limits of the accuracy of the sedimentation equilibrium experiments the same non-ideality coefficient is obtained irrespective of whether the substances urea and potassium thiocyanate are present. An important constituent of the system is the sodium chloride which is used to repress the Donnan effects during the establishment of the sedimentation equilibrium.

For the oxypolygelatins a much smaller non-ideal-

(9) The data of J. Pouradier and A. M. Venet, *J. chim. phys.*, 47, 391 (1950), for osmotic pressure determinations in 4 M urea solution, a comparable gelatin-suppressing medium, give $B = 1.4 \times 10^{-5}$.

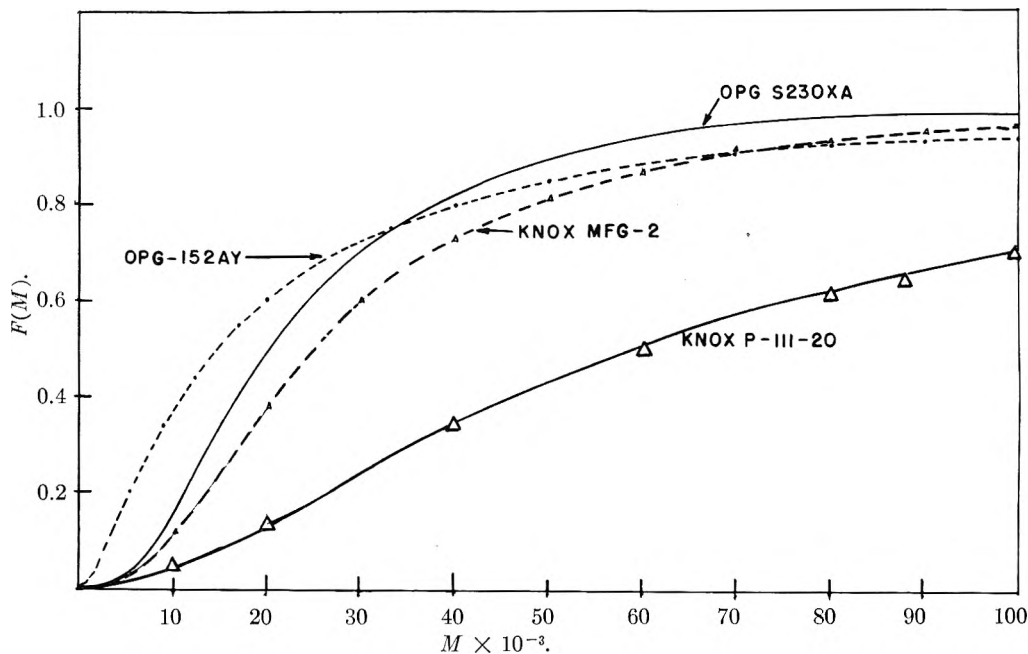


Fig. 3.—Integral distribution curves for several gelatins.

ity coefficient is obtained. Campbell, *et al.*,¹⁰ have measured the osmotic pressure of representative OPG systems as a function of protein concentration and have observed that the non-ideality coefficient is now substantially reduced. The osmotic pressure as a function of concentration may be represented by the formula

$$\frac{\pi}{c} = \frac{RT}{M_n} + bc$$

where the sedimentation equilibrium coefficient B is related to the new osmotic pressure coefficient b , by the formula

$$B = 2b/RT$$

From the article of Campbell, *et al.*

At $c = 0$, $\pi/c = 82$ mm. Hg./g./100 cc. = 0.793 atm./g.

At $c = 0.04$ g./cc., $\pi/c = 115$ mm. Hg./g./100 cc. = 1.113 atm./g.

Therefore

$$\frac{d(\pi/c)}{dc} = b = 8.0 \text{ (cc.)}^2 \text{ atm./g.}^2$$

and

$$B = \frac{2 \times 8.0}{82.05 \times 310} = 0.6 \times 10^{-5} \frac{\text{mole/g.}}{\text{g./100 cc.}} \text{ (at } 37^\circ \text{, the temp. of the osmotic pressure experiments)}$$

While this value of the coefficient B is lower than that found for the Knox gelatins of the series P-20 and MFG, the two different figures are entirely consistent with the osmotic pressure data of Campbell, *et al.*, for gelatins which have and have not been treated with glyoxal and hydrogen peroxide and with our own sedimentation equilibrium experiments.

Sedimentation equilibrium studies were carried out with a number of gelatin samples. The results of the experiments are presented in two ways: 1, as average molecular weights, obtained after cor-

rection for non-ideality (Table I); 2, in the form of integral distribution curves (Fig. 3). The average molecular weight data, M_n , M_w and M_z , have been computed directly from the scale line displacement-distance curves which were obtained in the experiment. The averages M_n and M_w have been already defined. The average M_z , the next higher moment of the distribution curve, may be defined by the expression

$$M_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i}$$

where, as before, n_i is the number of molecules of molecular weight M_i while w_i is the total weight of that species. Values of M_z are subject to a considerably higher degree of uncertainty as compared to those for M_w simply because they represent a higher moment of a distribution curve.

TABLE I
AVERAGE MOLECULAR WEIGHT DATA FOR SOME GELATIN SYSTEMS

Gelatin	$[\eta]$	M_n	M_w	M_z	$B \times 10^6$
Knox P-20	0.35	37,600	95,000	237,000	1.3
Knox P-111-20	.36	38,000	95,000	250,000	1.3
Knox P-180	.175	17,900	24,000	61,000	1.3
Knox MFG-2	.195	19,300	34,000	60,000	1.3
Knox MFG-7	.189	23,000	34,000	55,000	1.3
OPG-152AY	.140	10,000	33,000	150,000	0.65
OPG-153AY	.157	15,000	35,000	160,000	.65
OPG-S230XA	.137	15,950	26,100	42,700	.65

Representative experimental data for the several average molecular weights which characterize some of the more common gelatin materials are here tabulated. The several intrinsic viscosities, $[\eta]$, are included for reference.

It will be noted from the table that the gelatins studied fall roughly into two classes, gelatins of the descriptions P-20 and P-180. Furthermore, the intrinsic viscosities and number average molecular

(10) D. H. Campbell, J. B. Koepfli, L. Pauling, N. Abrahamsen, W. Dandliker, G. A. Feigen, F. Lanni and A. Le Rosen, *Texas Reports Biol. and Med.*, **9**, 235 (1951).

TABLE II
COMPUTATION OF DISTRIBUTIONS OF MOLECULAR SIZE GELATIN OPG-S230XA

$$M_w = 26,100; M_z = 42,700; M_z/M_w = 1.636$$

$$\frac{M_z}{M_n} = e^{0.5\beta^2} = 1.636; 0.5\beta^2 = 0.492; \beta = 0.992$$

$$M_p = \frac{M_w}{e^{1.25\beta^2}} = \frac{26,100}{e^{1.23}} = \frac{26,100}{3.4212} = 7,630$$

$$M_0 = M_p e^{0.5\beta^2} = 7.63 \times 10^3 \times 1.636 = 12,500$$

$$M_n = M_p e^{0.75\beta^2} = 7.63 \times 10^3 \times e^{0.738} = 7.63 \times 10^3 \times 2.09 = 15,950$$

M	M/M ₀	ln M/M ₀	y = $\frac{\ln M/M_0}{\beta}$	y ²	e ^{-y²}	$\frac{W}{M_0\beta\sqrt{\pi}} \times e^{-y^2}$	$\int_0^M f(M)$
2,000	0.16	-1.833	-1.848	3.415	0.033	0.118 × 10 ⁻⁶	0.0012
4,000	.32	-1.139	-1.148	1.318	.267	0.952	.0095
6,000	.48	-0.734	-0.740	0.548	.578	2.061	.0411
8,000	.64	-.416	-.419	.176	.839	2.992	.0908
10,000	.80	-.223	-.225	.051	.950	3.387	.1572
12,000	.96	-.041	-.041	.002	.998	3.559	.2248
13,000	1.04	+.0392	+.039	.002	.998	3.559	.2604
14,000	1.12	.1133	+.114	.013	.987	3.518	.2958
15,000	1.20	.1823	.184	.034	.966	3.444	.3306
16,000	1.28	.2469	.249	.062	.940	3.352	.3646
17,000	1.36	.3075	.310	.096	.908	3.238	.3976
18,000	1.44	.3646	.368	.135	.877	3.127	.4294
19,000	1.52	.4187	.422	.178	.837	2.984	.4600
20,000	1.60	.4700	.474	.225	.798	2.845	.4891
30,000	2.40	.8920	.899	.808	.445	1.587	.7023
40,000	3.20	1.1632	1.173	1.376	.253	0.902	.8255
50,000	4.00	1.3863	1.397	1.952	.142	.506	.8923
60,000	4.80	1.4061	1.417	2.008	.135	.481	.9390
70,000	5.60	1.7228	1.737	3.017	.049	.175	.9791
80,000	6.40	1.8563	1.871	3.501	.030	.107	.9819
100,000	8.00	2.0794	2.096	4.393	.012	.043	.9960

weights of the P-20 and P-180 gelatins correspond closely with those of the preparations B and D of Scatchard, *et al.*,¹¹ as they should. The figures indicate the time in minutes in an autoclave at 205°. The materials P-180, MFG-2 and MFG-7 are substantially alike in all three average molecular weights. The OPG samples have similar weight average molecular weights, but there is a much greater spread over the several averages, indicative of a broader size distribution. At least one of the chemicals used, perhaps the hydrogen peroxide, has caused the modification in the distribution of molecular size.

In the Boedtker and Doty⁷ studies of light scattering from dilute solutions of the Gelatin Knox P-111-20, the *M_w* values fell into two classes, those equal to 100,000, and those equal to 113,000. The lower value is that of the non-aggregated gelatin in KCNS solvent and is to be compared with our value of 95,000. When one realizes that a sedimentation equilibrium experiment must always give a value which approaches the true one from the low side, and the opposite represents the situation for light scattering, it is seen at once that the results obtained from the two methods are in excellent agreement.

In the construction of the distribution curves it was arbitrarily assumed that all of the distributions were of the Lansing-Kraemer form, that is

$$f(M)dM = \frac{1}{\beta M_n \sqrt{\pi}} e^{-(1/\beta \ln M/M_0)^2} dM$$

where *M₀* and β are adjustable parameters which

(11) G. Scatchard, J. L. Oncley, J. W. Williams and A. Brown, *J. Am. Chem. Soc.*, **66**, 1980 (1944).

are obtained from *M_w* and *M_z*.¹² In order that the procedure may be most simply understood we include an outline and the record of the actual computations of the differential and integral distribution curves for the gelatin OPG-S230AX. It appears as Table II.

The integral distribution curves for the representative gelatins are given in Fig. 3. It will be at once evident that the several curves make possible the computation of the weight per cent. of the material in each size class. We present some such data in Table III.

TABLE III
MOLECULAR WEIGHT DISTRIBUTIONS % IN EACH SIZE CLASS

Size Class	Knox P-111-20	OPG S152AY	Knox MFG-2
Less than 10,000	6	37	10
10,000-20,000	11	23	27
20,000-40,000	23	20	37
40,000-60,000	13	8	13
60,000-80,000	9	4	6
80,000-100,000	6	3	4
100,000-140,000	10	2	2
140,000-170,000	6	2	1
Over 180,000	16	1	..

III. Sedimentation Velocity.—The usual sedimentation velocity criterion for the homogeneity

(12) Actually, it might have been better to make use of the idea of Scatchard, *et al.*,¹¹ in setting up a distribution function based still upon the original Kuhn and Flory equations but with more suitable modification. The exact form used in the earlier communication is now inconsistent with the weight and "Z" average molecular weights. While the latter are still subject to a considerable uncertainty the weight average figures now seem to be well established.

of a protein is that a peak in the scale line displacement-distance curves moves in the centrifugal field as a single, apparently symmetrical boundary when the protein is dissolved in buffers of various hydrogen ion concentrations and ionic strengths. Actually, this is judgment based largely upon diffusion and, to be more precise, the investigation should be made to determine whether the boundary has been broadened solely by diffusion. This may be accomplished by comparing the diffusion curves obtained in the ultracentrifuge experiments (corrected for the sector shape of the cell) with the theoretical curves calculated from the values of the diffusion coefficient, D , found by independent diffusion experiments.

A method has been developed to sort out the contributions of heterogeneity and diffusion to the spreading of the sedimentation boundary.¹³ In a combined distribution composed of independent distributions the second moments of the individual distributions are additive to give the second moment of the combined distribution. Thus the second moment of the gradient curve, σ^2 , (the square of the standard deviation) is equal to the second moment which would have been observed had all the boundary spreading been due to diffusion plus the second moment which would have been found from the spreading due to the distribution of sedimentation constants alone.

(1) The second moment due to diffusion is $2Dt/(1 - \omega^2 s_m t)$ where s_m is the mean sedimentation coefficient and D is a weight average diffusion coefficient.

(2) The second moment due to the distribution of sedimentation coefficient is

$$\bar{x}^2 \left[\rho\omega^2 t + \frac{(\rho\omega^2 t)^3}{3!} + \frac{(\rho\omega^2 t)^5}{5!} + \dots \right]^2$$

where

ρ = std. dev. of the sedimentation constant distribution
 x = distance in the cell
 ω = the angular velocity of the rotor
 t = the time

Adding the second moments, and we have

$$\sigma^2 = \sigma_0^2 + \frac{2Dt}{1 - \omega^2 s t} + \bar{x}^2 \left[\rho\omega^2 t + \frac{(\rho\omega^2 t)^3}{3!} + \frac{(\rho\omega^2 t)^5}{5!} \right]$$

To a good approximation we may write

$$(1 - \omega^2 s t) \frac{\sigma^2 - \sigma_0^2}{2t} = D^* = D + \frac{\rho^2 \omega^4}{2} \bar{x}^2 t$$

where D^* is the apparent diffusion coefficient as indicated from the standard deviations of the sedimentation gradient curves.

The general distribution function, $g(s)$, which gives the relative amount of the molecular species with sedimentation constant of s , is given by

$$g(s) = \frac{dn}{dx} \times \frac{\omega^2 x t}{n_1 - n_0}$$

when diffusion is negligible. When diffusion is not negligible, an "apparent distribution" defined in this manner may be extrapolated to infinite time to give the actual distribution of sedimentation constants, since the spreading of the boundary due to differences in s is proportional to $\bar{x}t$, while the

spreading due to diffusion is proportional to $t^{1/2}$, as is shown by the general equation.

The sedimentation velocity experiments with the several gelatin solutions were performed in a Svedberg high-velocity oil-turbine ultracentrifuge. The gelatin was diluted to approximately 1% concentration in 2 *M* KCNS. The ultracentrifuge was operated at 50,400 r.p.m. A schlieren optical system was used to record the position and shape of the sedimentation boundaries as a function of time at this rotor speed.

The apparent distribution of sedimentation coefficient was calculated by using the formula

$$g^*(s_e) = e^{2s_e \omega^2 t} \times x' \times \frac{dn}{dx} \times \frac{\omega^2 t}{(A)_{t \rightarrow 0}}$$

where

s_e = experimentally detd. sedimentation coefficient
 x' = position in cell from reference bar for material of s_e at time t
 dn/dx = height of gradient curve at x'
 A = area = limiting area obtained by plotting the area of various pictures vs. time and extrapolating to zero time

Viscosity corrections have not been indicated in the interest of simplicity.

By plotting $g^*(s)$ vs. $1/\bar{x}t$ and extrapolating to infinite time, the desired distribution, $g(s)$, of the sedimentation coefficient was obtained.

To this point it has been assumed that the sedimentation coefficient, s , is independent of the concentration of the gelatin solution. To obtain the true distribution of sedimentation constants with such concentration effects eliminated we can perform a reliable extrapolation to infinite dilution of several sedimentation velocity distribution diagrams at several finite concentrations. This true distribution curve, $g(s_0)$ vs. s_0 , is still a function of the parameters of size and shape of the sedimenting molecules, but the quantities, s_0 , are now sedimentation constants.

This is a laborious procedure and Baldwin¹⁴ has demonstrated that it is possible to use the distribution of sedimentation coefficient curve at a single finite concentration, plus a knowledge of a function which describes the dependence of sedimentation coefficient with concentration for that particular macromolecular system to obtain the desired $g(s_0)$ vs. s_0 curve. The end result is the same; the two procedures may be defined by the terms graphical and analytical.

The results of a typical series of such sedimentation velocity experiments with the gelatin P-111-20 are shown below in tabular and graphical form. The $g(s_0)$ vs. s_0 curve, Fig. 4, has been obtained by the graphical procedure in which the points defining it are obtained by the extrapolation of $g(s)$ values for a number of arbitrary sedimentation coefficients, s , each to zero concentration. The actual data are given by Table IV.

It is unfortunate that the ultracentrifuges of the present day have insufficient resolving power to analyze the more highly degraded gelatins of the several P-180 types, chemically treated or not. In principle, at least, the sedimentation velocity method has its advantages, because minor details

(13) R. L. Baldwin and J. W. Williams, *J. Am. Chem. Soc.*, **72**, 4325 (1950); J. W. Williams, et al., *ibid.*, **74**, 1542 (1952).

(14) R. L. Baldwin, *ibid.*, **76**, 402 (1954).

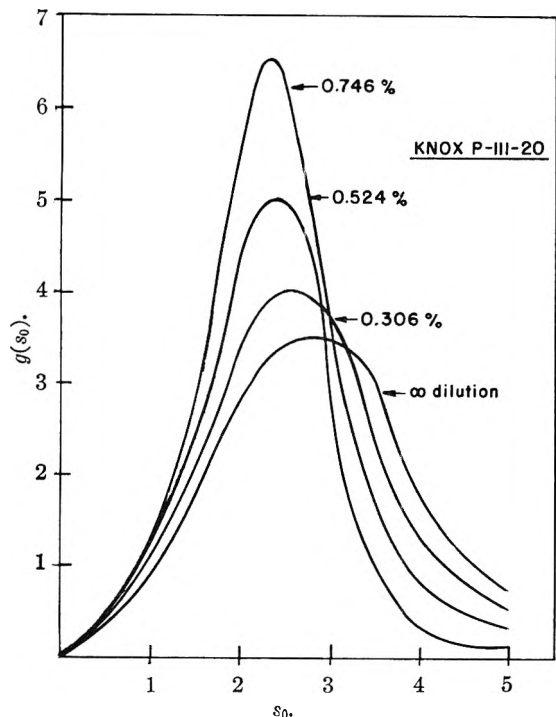


Fig. 4.— $g(s_0)$ vs. s_0 curves at several concentrations and at infinite dilution for gelatin P-111-20.

of the distribution make their appearance and any arbitrary distribution of velocities can be treated in the manner we have described.

TABLE IV

NORMALIZED DATA, $g(s)$, AS A FUNCTION OF CONCENTRATION GELATIN P-111-20

s	$c = 0.746$	$c = 0.524$	$c = 0.304$	$c = 0$	$G(s)$
0.5	0.55	0.50	0.39	0.37	0.009
1.0	1.05	1.22	1.18	0.87	.039
1.5	2.24	2.25	2.25	1.81	.103
2.0	5.61	4.25	3.30	2.85	.222
2.4	6.52	5.04	4.00	3.47	.381
2.8	4.55	4.14	3.88	3.50	.538
3.0	2.57	3.46	3.71	3.43	.558
3.5	1.00	1.74	2.43	2.94	.716
4.0	0.31	0.83	1.31	1.75	.841
5.0	0.13	0.37	0.55	0.71	.956

IV. Relationship between Sedimentation Constant and Molecular Weight.—In an article which describes the determination of molecular mass distribution in some dextran samples¹⁵ it was shown that the results of sedimentation velocity and sedimentation equilibrium experiments could be combined in such a way that one can gain advantage by a combination of both methods of analysis. It has been shown how $f(M)$, the distribution of molecular weights and $g(s_0)$, the distribution of sedimentation constants, can be obtained by experiment. Then, if to each molecular species there corresponds one sedimentation constant and molecular weight, we may write

$$g(s_0)ds_0 = f(M)dM$$

and

$$G(s_0') = F(M')$$

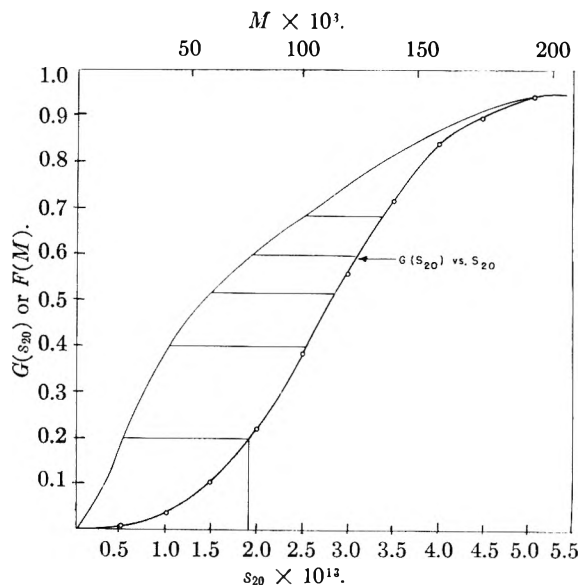


Fig. 5.—Double plot of integral distribution curves of molecular weight, $F(M)$, and of sedimentation constant, $G(s)$, to give relationship between s and M for gelatin P-111-20.

In the second expression $G(s_0')$ is the weight fraction of the solute molecules with $s \leq s'$, $F(M')$ is the weight fraction with $M \leq M'$, and s' corresponds to M' .

From the double plot, $G(s')$ vs. s' and $F(M')$ vs. M' for the gelatin P-111-20, shown in Fig. 5, we may determine the s' value which corresponds to a given M' by taking values of the two abscissas at equal ordinates. The curves have been plotted in such a way that the ordinates run from zero to unity, in other words they have been normalized. Further details of the mathematical analysis and the justification of the procedure have been given in another place.⁵ The interesting result is that the sedimentation constant is a linear function of the square root of the molecular weight, Fig. 6. The significance of this result will be discussed in an article devoted to a discussion of the form of the gelatin molecule in solution. In this place we make rather general remarks.

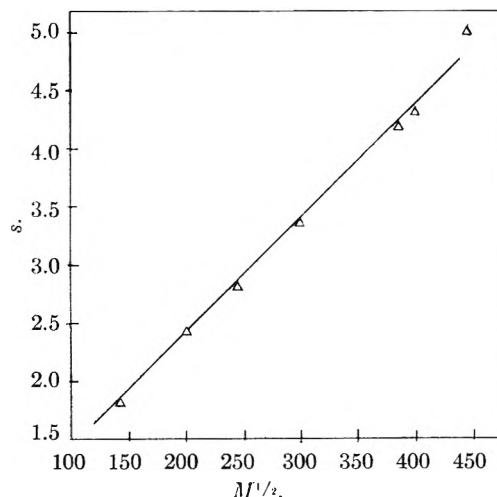


Fig. 6.—Plot of sedimentation constant vs. square root of molecular weight for gelatin P-111-20.

(15) J. W. Williams and W. M. Saunders, THIS JOURNAL 58, Nov. (1954).

V. The Molecular Form of Gelatin Molecules in Solution.—It has been established that for protein molecules in solution true sedimentation velocity constant is very nearly proportional to the square root of the absolute molecular weight. As a consequence of this relationship one is led to assert that the gelatin molecules in solution exist in the form of a random coil, inside of which there will be some solvent molecules as well as the segments of the polymer chains. The solvent within the coil is entrapped to an extent which depends on the number of segments within the coil. For a swollen molecule with complete immobilization of solvent such a square root relationship between sedimentation constant and molecular weight is to be expected. On the other hand, for a free-draining linear molecule, the sedimentation constant is almost independent of molecular weight—a true “sedimentation by segments” behavior.

Viscosity measurements, carried out under iso-electric condition and in the presence of salt, provide another means for the structural characterization of the gelatin molecule in solution. The earlier interpretation of enhanced viscosity of a solution in terms solely of solvation and swelling of the solute molecules has given way to the notion that it is a combination of swelling and molecular length (form) which is responsible. Thus, for situations in which there is a swelling (immobilization of solvent) the solute molecules will act in part like Einstein spheres in their effect on increasing the viscosity of the solution. The intrinsic viscosity $[\eta]$, might be expressed as $[\eta] = 0.025 S\bar{V}$, where

S is a swelling factor, \bar{V} is the partial specific volume, and 0.025 is the Einstein factor. For the random coil with entrapped liquid the swelling factor S is proportional to the square root of the molecular weight. On the other hand, for the free-draining molecule the intrinsic viscosity would be directly proportional to the molecular weight. Thus, in the modified Staudinger equation, $[\eta] = KM^a$, the combination of (a) the free-draining linear molecule, and (b) the swollen molecule with immobilization of solvent, frequently leads to values of the exponent a which are between 0.6 and 0.9.

For the gelatin solutions in question it is found by experiment that

$$[\eta] = 2.9 \times 10^{-4} [M_w]^{0.62}$$

The value of the exponent a , is seen to be well within the range of that found for many high polymers and polyelectrolytes.

Therefore, from the sedimentation and viscosity data which have been presented it seems reasonable to remark that in the presence of added simple electrolytes the gelatin molecules in solution assume the form of a random coil, with the solvent being entrapped to a considerable extent. It can be said with little fear of contradiction that we do not now have a globular molecule for which an ellipsoidal model can be assumed.

Acknowledgment.—We wish to record our thanks for the invaluable assistance of Messrs. A. Fuhlbrigge, A. Haltner, Jr., K. E. van Holde and M. Wales in the performance of many tasks, including the interpretation of the data.

PHYSICAL CHEMISTRY OF PROTEIN SOLUTIONS. VI. THE OSMOTIC PRESSURES OF MIXTURES OF HUMAN SERUM ALBUMIN AND γ -GLOBULINS IN AQUEOUS SODIUM CHLORIDE¹

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The osmotic pressure of solutions of human serum albumin, γ -globulins and their mixtures in aqueous salt solutions of various concentrations at various hydrogen-ion concentrations and temperatures are measured in a modified Hepp osmometer. Although each protein molecule has a charge of plus or minus twelve in an equimolar isoionic mixture of albumin and γ -pseudoglobulin, the electrostatic attraction is swamped out by 0.03 *M* sodium chloride, and the osmotic coefficients are greater than unity in more concentrated salt solutions. The results are correlated empirically and are compared qualitatively with electrostatic theory.

Introduction.—We expect the interaction of two proteins to be most important in the pH range between their isoelectric points. We have studied human serum albumin and γ -globulin because they have the extreme isoelectric points of the major plasma proteins. The method is the comparison of the osmotic pressure of mixed solutions with those of the single proteins in aqueous salt, usually sodium chloride, solutions. In the four component system we designate the water by 1, salt by 3, albumin by 2 and globulin by 4. We let $w = w_2 + w_4$ and $m = m_2 + m_4$ stand for the concentration in grams and in moles per kilogram of water, \bar{W}_2 and \bar{W}_4 stand for the molecular weights, and let $x_2 = m_2/m$, $x_4 = m_4/m$; R and T have their usual meaning and V^0 is the volume of outside, protein-free, solution containing one kilogram of water. Then we define the osmotic second virial coefficients B and B' , and the quantities J_0 and J by the relations

$$PV^0/RT = gm = m(1 + Bm + \dots) = 10^{-6}Jw = 10^{-6}J^0w(1 + B'w + \dots) \quad (1)$$

J^0 is obviously $10^6/(x_2\bar{W}_2 + x_4\bar{W}_4)$. To determine the molecular weight, it is customary to plot J against w , and the intercept at $w = 0$ is J^0 . In many cases J is a linear function of w over a large range, and the interactions can be determined from B . The first sign of insufficiency in the linear expression is usually not curvature, but variation of J^0 with temperature or salt concentration. Then a less quantitative analysis may be made from $g = J/J^0$. If the second virial coefficient is sufficient, equations 35 and 38 of Scatchard² may be combined to give

$$2B = \frac{(z_2x_2 + z_4x_4)^2}{2m_3} + (\beta_{22}x_2^2 + 2\beta_{24}x_2x_4 + \beta_{44}x_4^2) - \frac{(\beta_{23}x_2 + \beta_{43}x_4)^2 m_3'}{2 + \beta_{33}m_3'} \quad (2)$$

in which $\beta_{ij} = \partial \ln \gamma_i / \partial m_j$. We may define the protein components so as to include bound ions and make β_{23} and β_{43} each zero. In this case m_3' should be kept constant in a dilution series. However, the difference between constant m_3' and constant m_3 is very small. Since $x_4 = 1 - x_2$, each term on the right in equation 2 is a quadratic in x_2 , and therefore B itself is a quadratic. We will express it as

$$B = B_2x_2 + B_4x_4 + \delta_{24}x_2x_4 \quad (3)$$

(1) Adapted from the Ph.D. Thesis, M.I.T., 1950, of Allen Gee, National Bureau of Standards, Washington, D. C.

(2) G. Scatchard, *J. Am. Chem. Soc.*, **68**, 2315 (1946).

NOTE ADDED AT THE SYMPOSIUM.—It should be noted that β_{22} , β_{24} and β_{44} in equation 2 need not be independent of the composition of the protein since the reaction $x_2A + x_4G = x_2A^{z_2} + x_4G^{z_4}$, $x_2z_2 = -x_4z_4$ is independent of the total protein concentration. Experimentally, however, B is a quadratic within the precision of our measurements, indicating that $d(2\beta_{24} - \beta_{22} - \beta_{44})/dx_2 = d\delta_{24}/dx_2 = 0$ at all values of x_2 .

Materials.—Ordinary dialysis was carried out at 2° in Visking sausage tubing containing a glass bead. The filled tubing was placed in a larger cylinder containing solvent and was inverted about twice each minute. The dialyzate was changed once or twice a day.

Electrodialysis was carried out at 2° through cellophane membranes in the apparatus of Scheinberg and Hollies.³

Centrifugation was at 5°, or occasionally at -5°, and at about 5000 times gravity.

All protein solutions were sterilized before the osmotic pressure measurements by filtering through ultrafine fritted glass filters under one atmosphere pressure.

The albumin was from lots 24, 25 and 29 prepared by the Massachusetts State Biological Laboratories by cold alcohol method 6.⁴ It showed no globulins by electrophoresis. Solutions A₂ and A₃ were merely dissolved in salt solutions, A₄ was dialyzed against 0.03 *M* NaCl solution, A₅ and A₆ were treated to remove bound fatty acids. A₃ was brought to pH 8 with solid NaHCO₃ and then electro-dialyzed, A₅ was brought to pH 7.3 with 0.07 *M* NaOH and then electro-dialyzed.

The starting materials for the γ -globulin solutions were received from the University Laboratory of Physical Chemistry related to Medicine and Public Health of Harvard University. They were fractionated⁵ from fraction II of method 6.⁴ Solutions G₁, G₇, G₁₁ and G₁₂ were prepared from 172-2, II-1, 2, and the other globulin solutions were prepared from L 428-434, II-R. The differences between solutions from different starting materials were no larger than those between two from the same material. Neither showed any heterogeneity in the standard electrophoretic diagram, but they would doubtless have done so by the "reversible boundary spreading" method.⁶ The γ -globulins did not dissolve completely, particularly in dilute salt solution. G₁ was dissolved in 0.15 *M* NaCl and decanted from the residue; G₂, G₃ and G₄ were prepared similarly with 0.03 *M* NaCl. G₅, G₆, G₇ and G₈ were dissolved in 0.15 *M* NaCl and cleared by centrifugation for 4 hours. G₉ was dissolved in 0.15 *M* NaCl, dialyzed against 0.15 *M* NaCl and then centrifuged for 20 hours. G₁₀ was G₉ kept frozen at -5° for three months, then thawed out, supercooled to -5°, and separated from the resulting precipitate. G₁₁ was dissolved in 0.07 *M* NaCl, dialyzed against 0.03 *M* NaCl, centrifuged for 15 hours, supercooled to -5° and separated from the resulting precipitate. G₁₂ was the euglo-

(3) I. H. Scheinberg and N. R. S. Hollies, "Mimeographed Notes," Harvard Medical School (1950).

(4) E. J. Cohn, L. E. Strong, W. L. Hughes, D. W. Mulford, J. N. Ashworth, M. Melin and H. L. Taylor, *J. Am. Chem. Soc.*, **68**, 409 (1946).

(5) J. L. Oncley, M. Melin, D. A. Richert, J. W. Cameron and P. M. Gross, *ibid.*, **71**, 541 (1949).

(6) E. A. Anderson and R. A. Alberty, *THIS JOURNAL*, **52**, 1345 (1948).

bulin precipitate from the preparation of G₁₁, washed with 0.03 *M* NaCl and then dissolved in 0.15 *M* NaCl. For the preparation of G₁₃, 7.5 g. of γ -globulin and 70 ml. of water were stirred slowly at 2° overnight. The supernatant was separated by centrifugation, added to another 7.5 g. of γ -globulin and again stirred slowly at 2° overnight. This γ -globulin dissolved completely. Dialysis against water gave no precipitation, but dilution with water gave an abundant precipitate, which appeared complete when the volume reached 120 ml. After centrifuging, the solution was supercooled to -5° for three days and the resultant precipitate removed by centrifugation. It was then electro-dialyzed for 3 hours, supercooled to -5° again and centrifuged. Since the concentration was now only 4%, a portion was "freeze dried," and redissolved in the remaining solution to give 45 ml. of a 10% solution.

Measurements.—The osmotic pressures were measured in the Hepp osmometer⁷ as modified by Brown, Bridgforth⁸ and the authors, which is shown in Fig. 1. The time to attain equilibrium in our measurements is essentially the time necessary to attain the equilibrium distribution of small ions. The advantage of the Hepp osmometer is that the ratio of the volume of the outer, protein-free, solution to the area of the membrane is extremely small. That part of the solution which attains equilibrium is that which is held in the pores of the filter paper directly beneath the membrane after as much as possible has been pressed out.

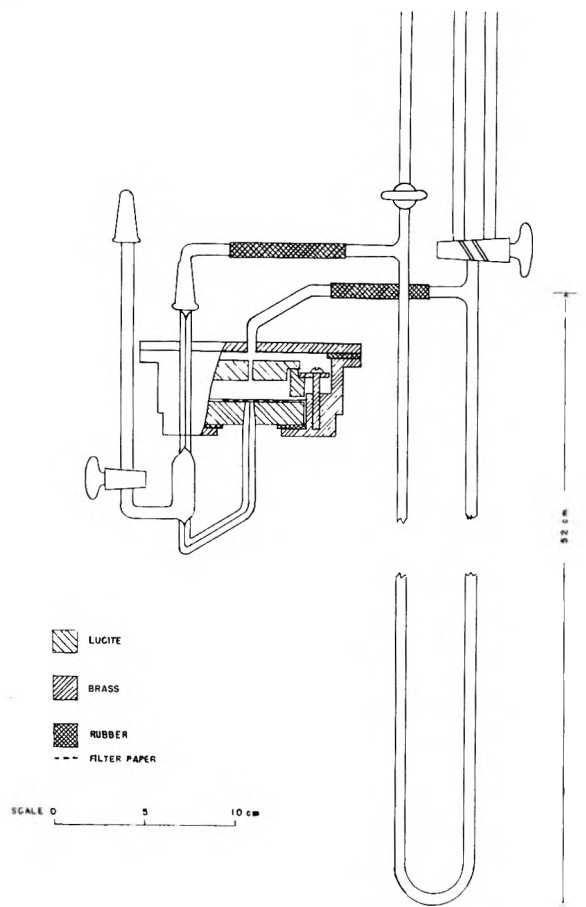


Fig. 1.—Osmometer.

The osmometer as pictured requires 1 ml. of protein for rinsing, 2 ml. for the measurement. With a smaller collar the volume may be reduced at least a half without loss of precision. The whole system, osmometer and manometer, is set in a thermostated water-bath to avoid pressure changes from changes of temperature in the gas spaces.

(7) O. Hepp, *Z. ges. exp. Med.*, **99**, 709 (1936).

(8) R. M. Bridgforth, M. S. Thesis, Department of Chemistry, M.I.T., 1949. Detailed drawings and mimeographed instructions are available on request.

The salt solution fills the capillary below the membrane and the lower half of the side bulb. The upper half of this bulb and the rate-reading capillary are filled with *n*-decane.

The membranes were collodion, prepared from an anhydrous solution of 8 g. of nitrocellulose (viscosity 40) in 32 ml. of ethylene glycol, 50 ml. of ethyl ether and 150 ml. of ethyl alcohol. The permeability and the speed of the membranes may be varied by changing the fraction of glycol. The membranes should be conditioned to the approximate pH of the solutions to be used, but they must not be left long with alkali since oxidation produces charges which retard the diffusion of small ions.

With good membranes equilibrium is reached in 1 to 2 hours. The osmotic pressure is determined statically when the meniscus in the rate-reading capillary becomes stationary, and, more accurately, dynamically by determining the rates of motion as the pressure is varied by 1 or 2 cm. of decane, and interpolating to zero rate. The precision is about 1 mm. of decane at 25° for a moderate pressure. It is 2-3 mm. when the pressure is very small or the temperature very different from 25°. Several measurements on each parent solution were usually made over a dilution range from 10 to 100 g. protein per kilogram of water. Details of the measurements are given in Gee's thesis.¹

Albumin Solutions.—The measurements with albumin solutions are all expressed satisfactorily with the osmotic coefficient linear in the concentration. All but A₆ have a J_0 value of 14.60, which corresponds to a molecular weight of 68,500. The A₆ showed this same molecular weight when alkaline, but after electro-dialysis, J_0 fell to 14.20, or a molecular weight of 70,400. The linear term appeared to be the same as that of A₅, which is considerably larger than those for the untreated albumins. The values of B for isoionic solutions are given in Table I, which also shows the values of the Donnan term, $z^2/4m_3$, determined from the equations of Scatchard, Scheinberg and Armstrong⁹ for the binding of chloride ion to isoionic human serum albumin.

TABLE I
SECOND VIRIAL COEFFICIENTS OF ISOIONIC ALBUMIN SOLUTIONS

m_3	$t, ^\circ\text{C.}$	B		$z^2/4m_3^9$
		Untreated	Treated	
0.15	37	180 A ₃		160
.15	25	190 A ₃	320 A ₅	160
.15	25		290 A ₆	160
.03	37	95 A ₂		200
.03	25	105 A ₄	220 A ₆	200
.005	25		85 A ₆	133
.005	1.5		125 A ₆	133

These results indicate that the major part of the second virial coefficient for isoionic albumin solutions is the Donnan effect due to the bound chloride ions. If the bound ions account for all of the observed values of B , neutralization followed by electro-dialysis must increase the binding, probably by removing competing fatty acids which are not ionized at this pH, the binding probably increases slightly with decreasing temperature, and the binding must be somewhat different for our albumins and those studied previously.

The variation of B with pH in 0.15 *M* and 0.03 *M* NaCl is shown in Figs. 4 and 5, and discussed later.

γ -Globulins.—The measurements with γ -globulins were more difficult than those with albumins, because of the smaller osmotic pressure-concentra-

(9) G. Scatchard, I. H. Scheinberg and S. H. Armstrong, Jr., *J. Am. Chem. Soc.*, **72**, 535 (1950).

tion ratios, and also because of an unexplained lack of reproducibility, and a slight instability of the protein. In 0.15 M NaCl, G₁ showed a molecular weight of 185,000, but the other unfractionated globulins gave a molecular weight of 238,000, and B values which varied from preparation to preparation. The 172-2, II-1,2 had been studied about four years earlier,¹⁰ soon after its preparation, and its molecular weight from osmotic pressures determined as 140,000. This may be slightly low, but the measurements surely indicate a value not greater than 160,000. The fractionated euglobulin, G₁₂, showed a molecular weight of about 350,000. The pseudoglobulin, G₁₃, showed a molecular weight of 187,000 when freshly prepared. A portion which had been kept salt free at 2° for about two months showed a molecular weight about 196,000. In the sedimentation ultracentrifuge a 1% solution of G₁₃ in 0.15 M NaCl at 25° gave the following estimated molecular weights.

Molecular weight	Weight Percentage	
	Fresh	After two months
300,000	19	22
156,000	78	78
100,000	3	0

The corresponding number average molecular weights are 182,000 and 187,000, in rather good agreement with the osmotic pressures, though both somewhat smaller. An electrophoretic diagram after the two months standing showed 99% with the normal γ -globulin mobility. Sometimes at $m_3 = 0.03$, and always at lower salt concentrations there are indications of association as shown by the osmotic coefficients in Fig. 2 and in Table II for G₁₃ ($J_0^0 = 5.35$).

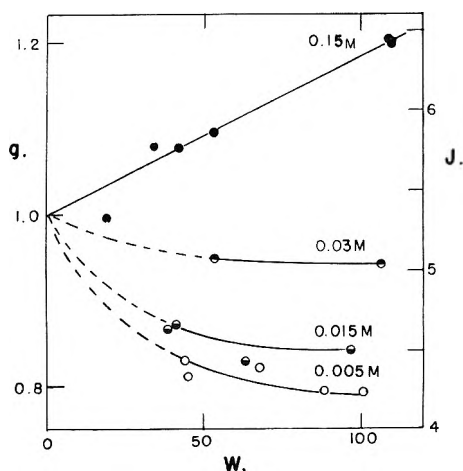


Fig. 2.—Osmotic coefficients of isoionic γ -globulin (G₁₃) in NaCl at 25°.

The pseudoglobulin G₁₃ was studied in 0.15 M LiCl at 25 and 15° as well as in 0.15 M NaCl at 37, 25 and 1.5°. These results are also shown in Table II. Association is indicated if $2g$ when $w = 50$ is less than 1 plus g when $w = 100$.

Measurements of the effect of pH on B in 0.15 and in 0.03 M NaCl are shown in Figs. 4 and 5 and discussed later.

Albumin- γ -Globulin Mixtures.—We have studied several isoionic mixtures in 0.15 and 0.03 M

(10) J. L. Oneley, G. Scatchard and A. Brown, THIS JOURNAL, 51, 184 (1947).

TABLE II
OSMOTIC COEFFICIENTS, g , OF PSEUDOGLOBULIN G₁₃

t°	m_3	$w_4 = 50$		$w_4 = 100$	
		NaCl	LiCl	NaCl	LiCl
37	0.15	1.09	..	1.18	..
25	.15	1.10	1.01	1.20	1.03
1.5	.15	0.98	0.85	1.06	0.76
25	.03	.95	..	0.95	..
25	.015	.87	..	.84	..
25	.003	.82	..	.79	..

NaCl. At the higher concentration, and sometimes at the lower, the quadratic expression is sufficient at each composition, and B is a quadratic function of x . For these systems, B_2 , B_4 and B_{24} of equation 3 are listed in Table III.

TABLE III
SECOND VIRIAL COEFFICIENTS FOR ISOIONIC MIXTURES

Components	$t, ^\circ\text{C.}$	m_3	B_2	B_4	$\delta_{24}/4$
A ₁ -G ₁	37	0.15	220	120	140
A ₃ -G ₃	37	.15	180	320	240
A ₃ -G ₁₀	25	.15	190	330	190
A ₇ -G ₁₃	25	.15	300	350	30
A ₂ -G ₂	37	.03	95	60	40
A ₄ -G ₁₁	25	.03	105	-130	0

Some mixtures in 0.03 M NaCl and all those studied in more dilute solutions showed the association which we expected to find also at higher salt concentrations. The values of g for an equimolal mixture of A₆ and G₁₃ are shown in Fig. 3.

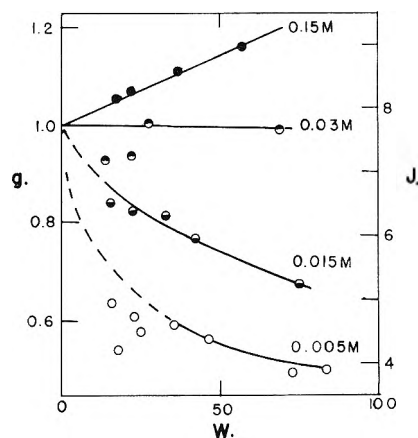


Fig. 3.—Osmotic coefficients of isoionic, equimolal albumin (A₆)- γ -globulin (G₁₃) in NaCl at 25°.

The effects of pH on B in 0.15 and 0.03 M NaCl for two equimolal mixtures are shown in Figs. 4 and 5 and discussed later.

Discussion.—The pH of the equimolal mixtures of albumin and γ -globulin is about 6.3, which corresponds to the addition of about 12 equivalents of acid to the γ -globulin and 12 equivalents of base to the albumin. The negative charge of the albumin molecules is further increased by the bound chloride ions, which vary in number with the chloride ion concentration. We should expect very large electrostatic attraction between oppositely charged ions with such large charges. This is doubtless the effect shown in Fig. 3 at low salt concentrations. It is not surprising that it appears to stop with the

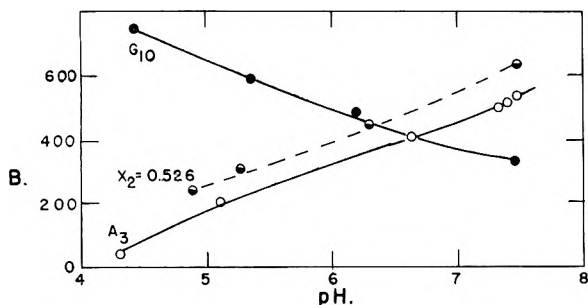


Fig. 4.—Second virial coefficients of albumin, γ -globulin, and their equimolar mixture in 0.15 M NaCl at 25°.

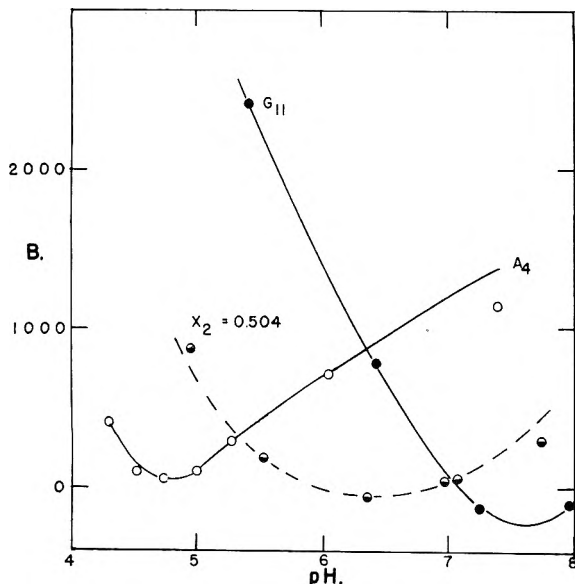


Fig. 5.—Second virial coefficients of albumin, γ -globulin and their equimolar mixture in 0.03 M NaCl at 25°.

association to double molecules, for this is sufficient to neutralize the charge except that due to bound chloride ions. The γ -globulin itself seems to show in Fig. 2 evidence of the same sort of heterogeneity, which is in accord with the fact that γ -globulin is a mixture of several components with different isoionic points.¹¹ The surprising result is that a concentration of small ions as low as 0.03 molal is sufficient to swamp out the electrostatic attraction, and that in 0.15 M solutions the interaction is strongly positive, as shown by B_{24} of Table III. The fractionation to produce G_{13} has reduced greatly the value of this interaction. A possible explanation of this effect would be that γ -globulin at low pH also binds chloride ions, and that the total bound by half a mole of albumin and half a mole of globulin at pH 6.3 is greater than the amount bound by a mole of albumin at its isoionic point. There is no other evidence for this assumption, but it should be tested. The difference between the pseudoglobulin and the unfractionated samples might lie in the larger molecules of the latter. Our measurements confirm the accepted belief that there is no binding by isoionic γ -globulin, for neither NaCl nor LiCl changes the

(11) J. R. Cann, R. A. Brown and J. G. Kirkwood, *J. Biol. Chem.*, **181**, 161 (1949).

isoionic pH. The great difference in their effects on the osmotic coefficient, like the increase of these effects at low temperatures shown in Table II, must be attributed to other causes.

The variation of B with pH for albumin solutions is similar to that already observed from osmotic pressures¹² and from light scattering.¹³ In 0.15 M NaCl our measurements show only one nearly linear wing, which extends beyond the isoionic point because of the bound chloride ions. Figure 4 shows the same behavior for the mixture of albumin and γ -globulin. The curve for γ -globulin itself does not extend beyond the isoionic point. At 0.03 M all the curves show minima, and are much more nearly hyperbolic than parabolic. This depression of the wings must be attributed to deviations from ideality, which may be expected with ions of large charge. We have found that this may be accounted for empirically by replacing the valence in equation 2 by an effective valence, $z^* = (\sqrt{1 + 0.16|z|} - 1)/0.08$, which is equal to $z - 0.04z^2$ when z is small. The curves of Fig. 5 are $z^{*2}/4m_3$ plus a term independent of pH, which is +40 for the albumin, -230 for the γ -globulin and -30 for the mixture. We note that this expression fits the very flat minimum for the mixture as well as the depression of the wings for all the curves.

We were able to find a more quantitative treatment by using the equations of Scatchard¹⁴ for ions of different sizes, but the "higher terms" are certainly not negligible, and we could have done better with the equations of Mayer¹⁵⁻¹⁷ which were not then available. It should be noted that the osmotic pressure discussed by Mayer is the pressure difference across a membrane permeable only to the solvent, not to small ions. The equations should be used to determine the differential coefficients β_{22} , β_{23} , etc. In the terms used by Scatchard,¹⁷ Mayer's theory gives

$$\beta_{tk} = \frac{d \ln \gamma_t}{dm_k} = \frac{z_t z_k}{\sum_{i=1}^{\sigma} m_i z_i^2} \sum_{\nu=0}^{\infty} b_{tk}^{\nu} - 1 f_{\nu}(x_{tk}) - \frac{2z_t z_k^2}{\left(\sum_{i=1}^{\sigma} m_i z_i^2\right)^2} \sum_{s=1}^{\sigma} m_s z_s \sum_{\nu=0}^{\infty} b_{ts}^{\nu} - 1 g_{\nu}(x_{ts}) - \frac{2z_t^2 z_k}{\left(\sum_{i=1}^{\sigma} m_i z_i^2\right)^2} \sum_{s=1}^{\sigma} m_s z_s \sum_{\nu=0}^{\infty} b_{ks}^{\nu} - 1 g_{\nu}(x_{ks}) + z_t^2 z_k^2 \sum_{s=1}^{\sigma} \sum_{r=1}^{\sigma} \frac{m_s z_s m_r z_r}{\left(\sum_{i=1}^{\sigma} m_i z_i^2\right)^3} \sum_{\nu=0}^{\infty} b_{sr}^{\nu} - 1 [g_{\nu}(x_{sr}) + h_{\nu}(x_{sr})] \quad (4)$$

in which σ is the total number of ion species, of which t , s , r , k and i are examples

$$b_{ts} = -\epsilon^2 z_t z_s / DkT a_{ts} \quad (5)$$

(12) G. Scatchard, A. C. Batchelder and A. Brown, *J. Am. Chem. Soc.*, **68**, 2320 (1946).

(13) J. T. Edsall, H. Edelhoek, R. Lontie and F. R. Morrison, *ibid.*, **72**, 4641 (1950).

(14) G. Scatchard, *Physik. Z.*, **33**, 22 (1932).

(15) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

(16) J. C. Poirier, *ibid.*, **21**, 965, 972 (1953).

(17) G. Scatchard, National Bureau of Standards Circular **524**, 185 (1953).

if ϵ is the protonic charge, z the valence of an ion, D the dielectric constant, k Boltzmann's constant, T the absolute temperature, and a_{ts} the sum of the radii of the ions t and s ; $x_{ts} = \kappa a_{ts}$, with κ the Debye function, $(4\pi\epsilon^2 N \sum_i c_i z_i^2 / 1000 D k T)^{1/2}$. The values of the Mayer coefficients are given by Poirier¹⁶ as $b_\nu = f_\nu - g_\nu$, g_ν and h_ν for ν from 0 to 16 except for $\nu = 1$, which is important in mixtures of ions of very different sizes, but is not hard to compute. Scatchard¹⁷ gives an approximate method of extension to all values of ν by using Kirkwood's expression^{18,19} for the sum from $\nu = 4$ to ∞ for the leading term in $f(\nu)$, proportional to κ^2 . For large charges the series does not converge rapidly enough for 16 terms to be sufficient.

We shall confine ourselves here to a qualitative discussion. Since a_{22} is less than twice a_{23} , b_{22} will be much larger than b_{23} if z_2 is much greater than 2. For β_{22} then, the "higher terms" come from the first term in equation 4, which is proportional to $\Sigma f_\nu(x_{22}) / (x_{22})^2$, which decreases very rapidly as κ increases; $\Sigma g_\nu(x) / x^2$ and $[\Sigma g_\nu(x) + \Sigma h_\nu(x)] / x^2$ each start at zero. The first shows a maximum and the second, which is negative, a minimum at somewhat less than 0.1, and $[\Sigma g_\nu(x) + \Sigma h_\nu(x)]$ becomes positive for larger values of x . The values of $f_\nu(x)$ and of $g_\nu(x)$ vs. x are shown in Fig. 19.1 of Scatchard.¹⁷

Mayer's theory accounts qualitatively for the shape of the B vs. pH curves, including the straightening of the wings and the flattening of the mini-

um for mixtures, and for the damping of electrostatic protein-protein interaction by rather low concentrations of small ions. We have not tested it to determine whether the same reasonable sizes will account quantitatively for each of these effects.

We take this opportunity to express our gratitude to the University Laboratory of Physical Chemistry Related to Medicine and Public Health of Harvard University, to the Massachusetts State Biological Laboratories, and particularly to Drs. J. L. Oncley and D. W. Mulford for the materials and for the ultracentrifuge and electrophoresis measurements.

DISCUSSION

GEORGE PHILLIPS (National Bureau of Standards).—I would like to ask regarding the lowest concentrations used in the osmotic pressure measurements, for example, for bovine serum albumin.

Investigators at the National Bureau of Standards, in unpublished work with the modified Hepp osmometer, have found that measurements at high concentrations permitted extrapolation to agreeing molecular weights. The measurements at concentrations below 1%, however, resulted in values of the osmotic coefficient higher than would be predicted from the high concentration extrapolation. This trend is noticeable also in the 1946 paper. Similar measurements in the Zimm-Myerson osmometer did not give the above anomalous results.

GEORGE SCATCHARD.—The lower limit of protein concentration was about one per cent, because we found that the absolute precision decreases for very low pressures. We did not find, however, that the pressures tend to be higher than expected more often than lower. I can find no indications of such a trend in our 1946 papers.

(18) J. G. Kirkwood, *Chem. Revs.*, **19**, 275 (1936).

(19) G. Scatchard and L. F. Epstein, *ibid.*, **30**, 211 (1942).

EFFECT OF TEMPERATURE ON THE INTERACTION OF HUMAN SERUM MERCAPTALBUMIN WITH ZINC IONS¹

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The interaction of human serum mercaptalbumin with zinc ions at 0° is indistinguishable from that of the total human serum albumin studied previously. Raising the temperature from 0 to 25° had little effect on the binding of zinc ions by the protein, but the protein was less soluble. At 37° the binding was distinctly increased and at the same time irreversible changes were noted in the solubility properties of the protein. The addition of urea at 0° increased the binding somewhat, but not to the same degree as exposure to zinc ions at 37° in the absence of urea.

In an earlier study² it was shown that human serum albumin interacts reversibly with zinc ions at 0°. The interaction was interpreted in terms of competition between zinc and hydrogen ions for imidazole groups in the protein. The zinc-albumin complexes are soluble at 0° (ionic strength >0.04) and are nearly completely precipitated by mole fraction 0.066 ethanol at -5°.³ It was observed, however, that if the temperature is allowed to rise above 5-10° precipitation occurs very rapidly even in the absence of ethanol. The present study was undertaken to determine whether or not the marked effects of temperature on the solubility of the zinc-albumin complexes could be correlated with any changes in the binding of zinc ions by the protein.

Materials and Methods

Human Serum Mercaptalbumin.—The two different lots of mercaptalbumin used in this study were from the same preparations as were used in a study of the interaction of mercaptalbumin with plumbous ions.⁴ The protein solutions were kept frozen at -18° until immediately before use. The concentration of protein was determined as before.^{2,4} The molecular weight of both protein preparations was taken to be 69,000.

Determination of Zinc.—In the earlier measurements the dithizone procedure was used as described,² except that glass-stoppered test-tubes were used for equilibrating the aqueous layer with CCl₄. Later the somewhat more convenient ethylenediaminetetraacetate (EDTA) method (method A) of Schwarzenbach, *et al.*,⁵ was used. It was not necessary to remove the protein before titration of the zinc.⁶ The preparation of standard reagents has been described.^{2,4}

Measurement of pH.—Either a Cambridge Instrument Company pH Meter modified for use at 0°² or a Beckman Model G pH Meter⁴ was used. For the experiments in which the protein was equilibrated with zinc ions at 37°, the pH determinations were made after cooling the mixture to room temperature, about 25°.

Equilibration Procedure.—The dialysis equilibrium technique was followed exactly as before.² The solvent consisted of 0.15 M NaNO₃, and zinc was introduced as the nitrate. Equilibrations were carried out in baths maintained at 0.0 ± 0.1°, 25.0 ± 0.01° and 37.0 ± 0.01°.

(1) This work was supported by the Eugene Higgins Trust, by grants from the Rockefeller Foundation, the National Institutes of Health, by contributions from industry, and by funds of Harvard University.

(2) F. R. N. Gurd and D. S. Goodman, *J. Am. Chem. Soc.*, **74**, 670 (1952).

(3) E. J. Cohn, F. R. N. Gurd, D. M. Surgenor, B. A. Barnes, R. K. Brown, G. Derouaux, J. M. Gillespie, F. W. Kahnt, W. F. Lever, C. H. Liu, D. Mittleman, R. F. Mouton, K. Schmid and E. Uroma, *ibid.*, **72**, 465 (1950).

(4) F. R. N. Gurd and G. R. Murray, Jr., *ibid.*, **76**, 187 (1954).

(5) G. Schwarzenbach, W. Biedermann and F. Bangerter, *Helv. Chim. Acta*, **29**, 811 (1946).

(6) If the protein had contained more than a single sulfhydryl group or if lower degrees of binding had been studied, it is possible that the precaution of removing the protein would have been necessary.

Results

Comparison of Mercaptalbumin with Total Serum Albumin.—The previous studies on zinc binding² were made with total human serum albumin. The more homogeneous mercaptalbumin fraction⁷ was chosen for the present study. Besides differing in their sulfhydryl content,⁷ mercaptalbumin and total serum albumin do not contain the same number of anionic groups.⁴ The passage over ion-exchange resin in the preparation of mercaptalbumin appears to remove about four anionic groups, and it has been assumed⁴ that mercaptalbumin contains about 102 carboxyl groups per mole compared with the 106 apparently present in human serum albumin prepared without passage over ion-exchange resin.⁸ Isoionic mercaptalbumin was chosen for comparison with total human serum albumin to which had been added 5.8 moles of NaOH per mole of protein (ref. 2, Fig. 1, open circles). The pH values ranged from 5.60 to 5.44 for mercaptalbumin and from 5.74 to 5.41 for total serum albumin (ref. 2, Fig. 2, open circles). The results in Fig. 1 show that the value of \bar{v} , the average number of moles of zinc ion bound per mole of protein, are practically identical for the two protein preparations over the entire range of concentrations of unbound zinc ion.

Most of the measurements on mercaptalbumin were made after the addition of 15 moles of NaOH per mole of protein, corresponding on the average to perhaps 1 ± 1 hydrogen ion remaining bound to the imidazole groups. Taking the results for such systems at 0° (shown in Fig. 2), and making the arbitrary assumption that in each case exactly one hydrogen ion was bound to imidazole groups in the protein, values of the intrinsic association constant for zinc ions with the imidazole groups, k^0_{ZnIm} , were calculated (equation 5, ref. 2). Values for log k^0_{ZnIm} of 2.99, 2.79, 2.93 and 2.86 were found, compared with an average value of 2.82 for the same constant determined with total serum albumin.²

Effect of Temperature on Solubility.—At 0° in 0.15 M NaNO₃ a 1 or 2% solution of mercaptalbumin at pH near 6 containing 0.005 to 0.015 M zinc nitrate usually remained free of precipitate for weeks or months. At 0° the protein was precipitated by the addition of ethanol to 10% by volume. It redissolved immediately when the concentration of ethanol was reduced by dialysis against the original solvent containing zinc and sodium nitrates.

(7) W. L. Hughes, Jr., *Cold Spring Harbor Symposia Quant. Biol.*, **14**, 79 (1950).

(8) C. Tanford, *J. Am. Chem. Soc.*, **72**, 441 (1950).

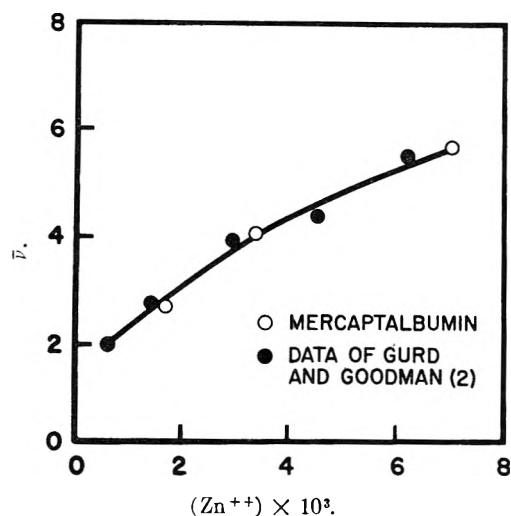


Fig. 1.—Comparison of zinc binding by mercaptalbumin and by total human serum albumin: O, mercaptalbumin; ●, data of Gurd and Goodman.²

At 25° in the same ethanol-free solvent a precipitate formed within five or six minutes; at 37° the precipitate formed within one or two minutes. This precipitation always occurred more rapidly at the higher temperature. The precipitate formed at 25° redissolved slowly if the protein suspension was returned to 0°, and the solution was usually clear within three hours after cooling. The precipitate formed at 25° was redissolved immediately (either at 0° or 25°) on the addition of 0.01 *M* ethylenediaminetetraacetate (EDTA) solution at pH 7.0. In contrast, the precipitate formed at 37° seldom redissolved completely on cooling to 0°, and after standing for one or two days at 37° contained some protein that was no longer soluble in EDTA solution.

The irreversible alteration of the solubility properties of the protein exposed to zinc ions at 37° appeared to be progressive with time. Most of the zinc binding studies to be reported below involved equilibration for six days, a time chosen to bring out any effects that such changes might have on the binding properties of the protein. The material that could no longer be dissolved simply by addition of EDTA solution was, however, soluble in EDTA if it was first brought to pH 9 or 10 by the addition of dilute NaOH or ammonia solution. However, when such a solution of protein that had been exposed to zinc ions at 37° was again dialyzed against a solution containing zinc and sodium nitrates, this time at 0°, the protein formed a heavy precipitate. By contrast, samples of the same stock solution of mercaptalbumin that were exposed for six days to zinc ions at 0 or 25°, and were then carried through the same series of operations, did not precipitate when dialyzed against the solution containing zinc and sodium nitrates. These observations show that the irreversible changes caused by the action of zinc ions at 37° rendered the protein more sensitive to the precipitating action of zinc ions than was the native mercaptalbumin. Furthermore, by this solubility test, the protein that had been exposed to zinc ions at 25° was not altered.

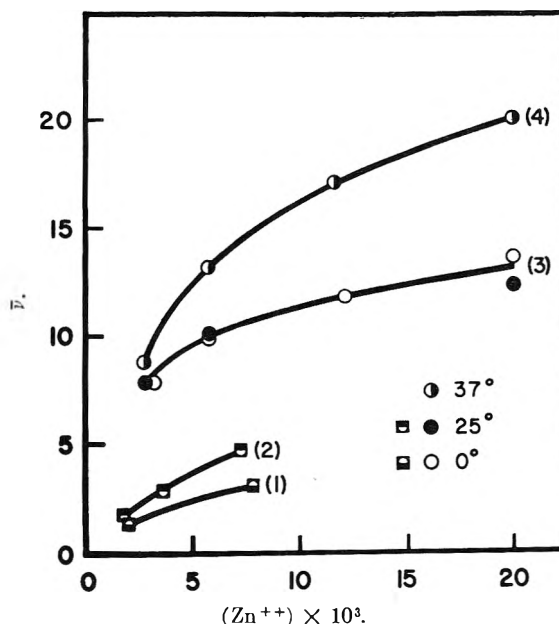


Fig. 2.—Binding of zinc ions by human serum mercaptalbumin: curve 1, 0°, pH 5.09 to 5.04; curve 2, 25°, pH 5.01 to 4.92; curve 3, O, 0° at pH 6.82 to 6.30, ●, 25° at pH 6.74 to 5.90; curve 4, 37°, pH 6.38 to 5.80.

Effect of Temperature on Binding of Zinc Ions.—

The results of measurements of zinc binding at 0, 25 and 37° are presented in Fig. 2. Curves 1 and 2, at 0 and 25°, respectively, were obtained with isoionic mercaptalbumin to which approximately 10 moles of nitric acid had been added per mole of protein. In order of increasing \bar{v} , the equilibrium pH values were: 5.09 and 5.04 at 0° (actually measured at 3.0–3.5°); and 5.01, 4.96 and 4.92 at 25° (actually measured at 24°). A small amount of protein precipitated in the experiment at 25° in which \bar{v} was 4.7. After the suspension had been removed from the cellophane bag it was stirred before sampling. The precipitate dissolved on dilution with water at 0° prior to analysis. In all cases the protein concentration was determined by measurement of the optical density at 280 $m\mu$ after dilution with 0.01 *M* EDTA buffer at pH 7.0.

Curves 3 and 4 in Fig. 2, showing measurements at all three temperatures, were obtained with isoionic mercaptalbumin to which approximately 15 moles of NaOH had been added per mole of protein before the equilibration with zinc ions for six days. Here the results at 0 and 25° were sufficiently alike to be plotted on a single curve. Considerable precipitation occurred in all the experiments at 25 and 37°. An aliquot of the suspension removed from the dialysis bag was diluted twenty-five-fold with dilute ammonia solution to give a uniform but cloudy suspension of pH about 10.5. For the optical density measurement an aliquot of this suspension was cleared by dilution with EDTA buffer of pH near 7. Another aliquot was used for zinc analysis.⁹

The remainder of the contents of the dialysis bag

(9) The alkaline suspension was uniform as judged by replication of the zinc analyses within $\pm 1.5\%$. Therefore, \bar{v} was determined with an accuracy that was practically independent of the difficulty in sampling the initial suspension obtained directly from the dialysis bag. The precision with which \bar{v} was calculated was probably $\pm 5\%$.

was centrifuged at room temperature and a pH measurement made on the supernatant solution, along with the measurements on the total solutions from the experiments at 0°. In order of increasing \bar{v} , the equilibrium pH values were: 6.82, 6.60, 6.58 and 6.30 at 0°; 6.74, 6.30 and 5.90 at 25°; and 6.38, 6.12, 5.92 and 5.80 at 37° (actually measured at 25°). Due to the small quantities of protein that remained in solution in all experiments except those in which the values of \bar{v} were lowest, the determination of \bar{v} for the soluble protein was very inaccurate, and the results were erratic. Whenever 60–80% of the protein remained in solution (corresponding to values of \bar{v} of 10 and less at 25 and 37°) the value of \bar{v} for the soluble protein was close to that for the total suspension.

In keeping with the observations on solubility properties, it was found that relatively short periods of exposure to zinc ions at 37° did not affect the binding properties of the mercaptalbumin. A solution of mercaptalbumin in 0.15 *M* NaNO₃ that had been mixed with 15 moles of NaOH per mole of protein and a solution of sodium nitrate were sterilized by passage through an ultrafine sintered Pyrex glass disk with suction. Sterile glassware was used. The protein solution was divided in two parts, and zinc nitrate solution was added to one sample to a concentration of 0.009 *M*. The samples of mercaptalbumin with and without zinc ions were both incubated at 37° for four hours, and then were brought to 0°, placed in dialysis bags and equilibrated as usual with zinc ions at 0° for five days. During the equilibration at 0° the protein that had been exposed to both 37° and zinc ions redissolved. The final conditions were comparable to those of curve 3, Fig. 2. The value of \bar{v} was 11.3 for the protein that had been exposed to 37° in the presence of zinc ions; \bar{v} was 11.1 for the protein that had been exposed to 37° in the absence of zinc ions. The value of \bar{v} obtained by interpolation on curve 3, Fig. 2, was 10.5. The results show that short exposure to 37° in the presence or absence of zinc ions did not affect the zinc-binding properties of the mercaptalbumin when subsequently measured at 0°. In sharp contrast with these results are the high values of \bar{v} obtained after six days of exposure to zinc ions at 37° (curve 3, Fig. 2).

In general, the concentration of mercaptalbumin remaining in solution after equilibration with zinc ions was less the higher the value of \bar{v} . At 25° (curve 3, Fig. 2) the concentration of dissolved protein fell from 4.95×10^{-4} to 0.65×10^{-4} *M* as \bar{v} went from 7.6 to 12.3. At 37° (curve 4, Fig. 2) the concentration of dissolved protein fell from 4.64×10^{-4} to 0.05×10^{-4} *M* as \bar{v} went from 8.8 to 20.0. The total protein present in these series was 6.0 to 6.6×10^{-4} *M*.

Effect of Urea.—Kauzmann and Simpson¹⁰ have shown that bovine serum albumin undergoes reversible changes in optical rotation when exposed to urea solutions at temperatures between 0° and 40°. These changes were taken to reflect a reversible unfolding of the albumin molecule. In view

of these conclusions, the effect of urea on the binding of zinc ions by mercaptalbumin was studied.

The results of measurements of \bar{v} at 0° in 6 *M* urea are shown in Table I. Under these conditions the protein remained in solution throughout the equilibration. The table shows estimated values of \bar{v} in the absence of urea but under the same conditions of zinc ion concentration and pH. The results in the lower pH range were directly comparable to those in Fig. 1, which accordingly were used to estimate \bar{v} in the absence of urea, shown in the last column of Table I. The results in the higher pH range were obtained at pH values similar to those for curve 3, Fig. 2, and rough estimates of \bar{v} in the absence of urea were obtained from those results. At the higher pH there is a definite trend toward higher values of \bar{v} in the presence of urea. The effect of urea at 0° seems to be less marked, however, than that of raising the temperature to 37° in the absence of urea. Any detailed interpretation is impossible without knowledge of the effect of urea on the interaction of zinc ions with model compounds such as imidazole.¹¹

TABLE I
BINDING OF ZINC IONS AT 0° BY MERCAPTALBUMIN
DISSOLVED IN 6 *M* UREA CONTAINING 0.15 *M*
SODIUM NITRATE

Concn. unbound Zn ⁺⁺ , <i>M</i> × 10 ³	pH	Moles zinc ion bound per mole protein	
		Urea present	Urea absent (estd.)
1.86	5.54	3.7	2.8
3.82	5.48	4.0	4.2
8.06	5.40	6.4	6.0
16.1	5.30	8.8	—
2.22	7.0	10.9	8
5.50	6.68	13.6	10
11.75	6.48	14.5	12
19.5	6.65	17.3	14

At 25° in the presence of zinc nitrate and urea mercaptalbumin appears to be altered drastically. After exposure of the protein to 0.01 *M* zinc nitrate and 6 *M* urea at 25°, NaOH as well as ammonia was required to bring the protein back into solution. There was an indication that the binding was somewhat higher than in the same solvent at 0°. Urea appeared to delay slightly the onset of precipitation of the mercaptalbumin in the presence of zinc at 25 and 37°, but after equilibration for five days under such conditions it was not possible to redissolve the protein by removing the zinc ions with EDTA and raising the pH to 9.0 (see Effect of Temperature on Solubility).

Discussion

Up to about 25° the interaction of mercaptalbumin with zinc ions for the period of time that has been studied appears not to alter the protein permanently. However, the precipitation of the pro-

(11) The addition of zinc nitrate to a mixture of imidazole and imidazolium nitrate dissolved in 6 *M* urea caused a drop in pH roughly comparable to that observed in the absence of urea.¹² However, the tendency of urea to decompose spontaneously makes it difficult to interpret such experiments quantitatively.

(12) J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd. *J. Am. Chem. Soc.*, **76**, 3054 (1954)

(10) W. Kauzmann and R. B. Simpson, *J. Am. Chem. Soc.*, **75**, 5154 (1953).

tein in the presence of zinc ions at 25° shows a hysteresis effect in the slow and sometimes incomplete reversal that followed cooling to 0°. ¹³ It is not certain, therefore, that the measurements of $\bar{\nu}$ at 25° were made under conditions of true equilibrium. Nevertheless the results were consistent and reproducible. ¹⁶

The results in Fig. 2 show that increasing the temperature from 0 to 25° does not affect the binding very much. If it is assumed that imidazole groups in serum albumin are responsible for most of the binding of zinc ions, in competition with hydrogen ions, ^{2,18} then the effect of temperature on $\bar{\nu}$ should depend upon the way in which temperature changes alter the intrinsic association constants of the imidazole groups for H⁺ and Zn⁺⁺. For imidazole alone, Edsall, *et al.*, ¹² have estimated that at ionic strength 0.16, log k_1 for the association of Zn⁺⁺ is about 2.76 at 4.5° and 2.58 at 24°, whereas for H⁺ log K' is 7.50 at 4.5° and 7.11 at 23°. The smaller decrease in affinity constant with increasing temperature shown by Zn⁺⁺ as compared with H⁺ means that $\bar{\nu}$ may increase with rising temperature if enough sites become available (through loss of H⁺) to make up for the decreased affinity of the Zn⁺⁺ for any one site. The small increase in binding near pH 5.0 (curves 1 and 2 in Fig. 2) with increasing temperature may reflect such an effect, since in this pH range the competitive behavior of H⁺ is important. ^{2,8} Such an effect should not be so marked in the higher pH range corresponding to curve 3 in Fig. 2. Here so few hydrogen ions are bound to imidazole groups at 0° that a correspond-

ing proportional decrease in the number bound as the temperature is increased would make much less change in the number of sites available for the binding of zinc ions. The observed results are in qualitative agreement with this prediction.

It is interesting that cadmium ion, which combines with mercaptalbumin in a manner very similar to that of zinc ion, ¹⁵ also renders this protein less soluble at room temperature than at 0°. ¹⁹

Perhaps the most interesting aspect of the experiments with urea is that the increase in binding is small (Table I), indicating that no large number of groups potentially able to combine strongly with zinc ions is exposed by unfolding the protein molecule. It would be interesting to determine whether or not the presence of zinc ions affects the optical rotation of serum albumin in urea solution. It is noteworthy that in the presence of urea irreversible changes in solubility occurred on exposure to zinc ions even at 25°.

The irreversible changes that occur on exposure of the mercaptalbumin to zinc ions at 37° for several days are characterized by loss of solubility in solutions of zinc salts at 0° and by a distinct increase in the number of moles of zinc ion bound to the protein of a given concentration of zinc ion. The increased binding is of special interest in that the value of $\bar{\nu}$ exceeded 16, the number of histidine residues in human serum albumin. ^{2,8} Apparently some unidentified groups either become available for reaction for the first time under these conditions ²⁰ or undergo profound changes in affinity for zinc ions as a result of alterations in the structure of the mercaptalbumin molecule.

Acknowledgments.—Much of the material presented was made available through the kindness of Dr. Charlotte Fitting. The author wishes to express his indebtedness to the late Dr. E. J. Cohn and to Drs. G. Scatchard and J. L. Oncley for their advice and encouragement.

(13) Somewhat similar hysteresis effects have been observed ¹⁴ during the precipitation of crude casein by zinc salts and the subsequent redissolving of the protein. These results have been discussed elsewhere. ¹⁵

(14) F. M. Richards, personal communication.

(15) F. R. N. Gurd in "Ion Transport Across Membranes," edited by H. T. Clarke, Academic Press, Inc., New York, N. Y., 1954, p. 246.

(16) The reproducibility has been confirmed by Dr. Annemarie Weber ¹⁷ with more extensive studies under comparable conditions.

(17) A. Weber, personal communication.

(18) G. Scatchard, W. L. Hughes, Jr., F. R. N. Gurd and P. Wilcox in "Chemical Specificity in Biological Interactions," edited by F. R. N. Gurd, Academic Press, Inc., New York, N. Y., in press, Chapter XI.

(19) M. J. Hunter, personal communication.

(20) Values of $\bar{\nu}$ above 16 also have been observed ¹⁵ on equilibration with zinc glycinate solutions of pH above 8, where amino groups may be expected to play a part in binding zinc ions.

ACTIVITY COEFFICIENTS OF ELECTROLYTES IN MIXED AQUEOUS SOLUTION FROM ELECTROMOTIVE FORCE DATA

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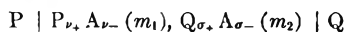
A method is presented by which the individual mean activity coefficients of each electrolyte solute and the osmotic coefficient of the solvent in a mixed aqueous solution may be calculated from electromotive force measurements on galvanic cells with electrodes reversible to ions of the same sign. The method is applied to data in the literature for mixed aqueous nitric acid-silver nitrate solutions. A simple method of obtaining solution activity coefficient ratios appropriate for ion exchange equilibria from solvent activity data also is presented.

Introduction

It has been shown by McKay¹ and by McKay and Perring² that the individual mean activity coefficients of two electrolyte solutes in an aqueous three-component solution may be calculated from measurements of vapor pressure alone, provided that such measurements cover the entire range of interest of both composition variables. Their work suggests in turn that the activities of all three components of such a mixed aqueous electrolyte solution may be calculated from measurements of the ratio of the two electrolyte activities, or of the ratio of appropriate powers of the two activities if the electrolytes are not of the same valence type. Such data are in principle available from electromotive force measurements on suitable galvanic cells, even for systems containing a common anion (or cation) for which no reversible electrode is available, or containing extremely volatile solutes. The method is therefore particularly suitable for the determination of activity coefficients in concentrated aqueous mixtures of nitric acid and metal nitrates.

Derivation of Relations

Consider an aqueous solution of the two electrolytes $P_{\nu_+}A_{\nu_-}$ (solute 1) and $Q_{\sigma_+}A_{\sigma_-}$ (solute 2). Let Z_P , Z_Q and Z_A be the charges on the respective ions, and let $\kappa_1 \equiv \nu_+Z_P = \nu_-Z_A$ and $\kappa_2 \equiv \sigma_+Z_Q = \sigma_-Z_A$ be the respective "total valence numbers" of the two electrolytes. For the galvanic cell



the reversible electromotive force E is given by

$$E = E^\circ - \frac{RT}{F} \ln \frac{a_1^{\nu_+/\kappa_1}}{a_2^{\nu_-/\kappa_2}} \quad (1)$$

where a_1 is the activity of $P_{\nu_+}A_{\nu_-}$ and a_2 is the activity of $Q_{\sigma_+}A_{\sigma_-}$. Equation 1 is more conveniently written in the form

$$\ln \frac{a_2^{\nu_-/\kappa_2}}{a_1^{\nu_+/\kappa_1}} = \frac{F}{RT} (E - E^\circ) \quad (2)$$

which gives explicitly the appropriate activity ratio to be determined from electromotive force data for the type of cell shown. If the two electrolytes are of the same valence type, then $\kappa_1 = \kappa_2 = \kappa$, and

$$\ln \frac{a_2}{a_1} = \frac{\kappa F}{RT} (E - E^\circ) \quad (3)$$

in which $\kappa = 1$ for 1:1 electrolytes, $\kappa = 2$ for 1:2, 2:1 and 2:2 electrolytes, $\kappa = 3$ for 1:3, 3:1 and 3:3

(1) H. A. C. McKay, *Nature*, **169**, 464 (1952).
(2) H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

electrolytes, and $\kappa = 6$ for 2:3 and 3:2 electrolytes.

In the discussion of aqueous solutions of two electrolytes of the same valence type, the most convenient composition variables are the total molality m and the solute mole fraction of one electrolyte, e.g., $x = m_1/m_1 + m_2 = m_1/m$. If the electrolytes are of different valence types, however, the most convenient variables are the total number of gram equivalent weights of solute per kilogram of solvent, for which the symbol N will be used, and the solute equivalent fraction y of component 1. (The concentration measure N , which has sometimes been termed the "weight normality," bears the same relation to normality that molality does to molarity.) If n_1 , n_2 and n_3 are the numbers of moles of the two electrolyte solutes and of the solvent, respectively, then the following relations exist

$$N = \frac{1000}{M} \frac{n_1\kappa_1 + n_2\kappa_2}{n_3}$$

$$y = \frac{n_1\kappa_1}{n_1\kappa_1 + n_2\kappa_2} \quad (4)$$

in which M is the formula weight of the solvent. If the two electrolytes are of the same valence type, N is proportional to the total molality m , and in fact $N = \kappa m$, while y is identical with the solute mole fraction x .

The calculation of the individual mean activity coefficients from the experimentally measured activity ratios depends on cross-differentiation relations (at constant temperature and pressure) of the type

$$\left(\frac{\partial \mu_1}{\partial n_2} \right)_{n_3, n_1} = \left(\frac{\partial \mu_2}{\partial n_1} \right)_{n_2, n_3} \quad (5)$$

where μ is the chemical potential. Each chemical potential is a function only of composition, that is, of the variables N and y ; hence one may write

$$\left(\frac{\partial \mu_1}{\partial n_2} \right)_{n_3, n_1} = \left(\frac{\partial \mu_1}{\partial N} \right)_y \left(\frac{\partial N}{\partial n_2} \right)_{n_3, n_1} + \left(\frac{\partial \mu_1}{\partial y} \right)_N \left(\frac{\partial y}{\partial n_2} \right)_{n_3, n_1} \quad (6)$$

The definitions of N and y given in (4) above yield by differentiation

$$\left(\frac{\partial N}{\partial n_2} \right)_{n_3, n_1} = \frac{1000}{M} \kappa_2, \text{ and } \left(\frac{\partial y}{\partial n_2} \right)_{n_3, n_1} = -\frac{1000}{M} \kappa_2 \frac{y}{N} \quad (7)$$

When these are substituted in equation 6 there results

$$\left(\frac{\partial \mu_1}{\partial n_2} \right)_{n_3, n_1} = \frac{1000}{M n_3} \kappa_2 \left[\left(\frac{\partial \mu_1}{\partial N} \right)_y - \frac{y}{N} \left(\frac{\partial \mu_1}{\partial y} \right)_y \right] \quad (8)$$

Similarly

$$\left(\frac{\partial \mu_2}{\partial n_1} \right)_{n_2, n_3} = \frac{1000}{M n_3} \kappa_1 \left[\left(\frac{\partial \mu_2}{\partial N} \right)_y + \frac{1-y}{N} \left(\frac{\partial \mu_2}{\partial y} \right)_y \right] \quad (9)$$

Finally when equations 8 and 9 are substituted in equation 5 one obtains after slight rearrangement

$$\frac{1}{\kappa_2} \left(\frac{\partial \mu_2}{\partial y} \right)_N = y \left[\frac{\partial}{\partial y} \left(\frac{\mu_2}{\kappa_2} - \frac{\mu_1}{\kappa_1} \right) \right]_N - N \left[\frac{\partial}{\partial N} \left(\frac{\mu_2}{\kappa_2} - \frac{\mu_1}{\kappa_1} \right) \right]_y \quad (10)$$

Now in general

$$\mu = \mu^\circ + RT \ln a \quad (11)$$

in which μ° does not depend on composition, and thus

$$\frac{1}{\kappa_2} \left(\frac{\partial \ln a_2}{\partial y} \right)_N = y \left(\frac{\partial}{\partial y} \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right)_N - N \left(\frac{\partial}{\partial N} \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right)_y \quad (12)$$

Equation 12 may be integrated at constant N to yield

$$\frac{1}{\kappa_2} \ln \frac{a_2}{a_2^\circ} = \int_0^y \left[y \left(\frac{\partial}{\partial y} \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right)_N - N \frac{\partial}{\partial N} \left(\ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right)_y \right] dy \quad (13)$$

in which a_2° is the activity of component 2 in its pure solution in solvent component 3, at the same value of N as in the mixed solution. This result may be simplified by integration of the first term by parts and combination of the results in the form

$$\frac{1}{\kappa_2} \ln \frac{a_2}{a_2^\circ} = y \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} - \int_0^y \left[\frac{\partial}{\partial N} \left(N \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right) \right]_y dy \quad (14)$$

If now equation 14 is evaluated at $y = 1$ and the result subtracted from equation 14, one obtains

$$\frac{1}{\kappa_1} \ln \frac{a_1}{a_1^\circ} = - (1 - y) \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} - \int_y^1 \left[\frac{\partial}{\partial N} \left(N \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right) \right]_y dy \quad (15)$$

where a_1° is the activity of component 1 in its pure solution in solvent component 3, at the same value of N as in the mixed solution. Thus in equations 14 and 15 the individual activities of the two electrolyte solutes are expressed in terms of the activity ratio which may be measured as a function of the composition variables N and y .

The activities a_1 and a_2 are most commonly referred to a molality basis and the corresponding mean activity coefficients likewise. Thus from the usual definitions one may write (where $\nu = \nu_+ + \nu_-$)

$$a_1 = \left(\frac{N y}{Z_P} \right)^{\nu_+} \left(\frac{N}{Z_A} \right)^{\nu_-} \gamma_{1\pm}^\nu = \frac{N^\nu}{Z_P^{\nu_+} Z_A^{\nu_-}} y^{\nu_+} \gamma_{1\pm}^\nu, \text{ and} \\ a_1^\circ = \frac{N^\nu}{Z_P^{\nu_+} Z_A^{\nu_-}} \gamma_{1\pm}^{\circ\nu} \quad (16)$$

in which $\gamma_{1\pm}^\circ$ is the mean activity coefficient in a pure solution of solute component 1 in solvent component 3, at the same value of N as in the mixed solution. (The \pm sign is omitted from γ_{\pm} for the sake of clarity.) Thus

$$\frac{a_1}{a_1^\circ} = y^{\nu_+} \left(\frac{\gamma_{1\pm}}{\gamma_{1\pm}^\circ} \right)^\nu, \text{ and } \frac{a_2}{a_2^\circ} = (1 - y)^{\nu_+} \left(\frac{\gamma_2}{\gamma_2^\circ} \right)^\nu \quad (17)$$

With these relations and equation 2, equations 14 and 15 become

$$\ln \frac{\gamma_1}{\gamma_1^\circ} = \frac{Z_A}{Z_P + Z_A} \left\{ \frac{Z_P F}{RT} \left[-(1 - y)(E - E^\circ) + \int_y^1 \left(\frac{\partial}{\partial N} N(E - E^\circ) \right)_y dy \right] - \ln y \right\} \quad (18)$$

and

$$\ln \frac{\gamma_2}{\gamma_2^\circ} = \frac{Z_A}{Z_Q + Z_A} \left\{ \frac{Z_Q F}{RT} \left[y(E - E^\circ) - \int_0^y \left(\frac{\partial}{\partial N} N(E - E^\circ) \right)_y dy \right] - \ln (1 - y) \right\} \quad (19)$$

in which

$$\frac{Z_A}{Z_P + Z_A} = \frac{\nu_+}{\nu} \text{ and } \frac{Z_A}{Z_Q + Z_A} = \frac{\sigma_+}{\sigma}$$

In the special case of electrolytes of the same valence type

$$\frac{\nu_+}{\nu} = \frac{\sigma_+}{\sigma}, \quad y = x = \frac{m_1}{m}, \text{ and } \left(\frac{\partial}{\partial N} N(E - E^\circ) \right)_y = \left(\frac{\partial}{\partial m} m(E - E^\circ) \right)_x$$

It will sometimes be convenient to define a derived dependent variable G as

$$G(N, y) = \frac{F}{RT} \left[E - E^\circ + \frac{RT}{F} \ln \left(\frac{N y}{Z_P} \right)^{1/Z_P} + \frac{RT}{F} \ln \left(\frac{Z_Q}{N(1 - y)} \right)^{1/Z_Q} \right] = - \ln \frac{\gamma_1^{1/Z_P + 1/Z_A}}{\gamma_2^{1/Z_Q + 1/Z_A}} \quad (20)$$

In terms of G equations 18 and 19 become

$$\ln \frac{\gamma_1}{\gamma_1^\circ} = \frac{Z_P Z_A}{Z_P + Z_A} \int_y^1 \left[(1 - y) \frac{\partial G}{\partial y} + N \frac{\partial G}{\partial N} \right] dy \quad (21)$$

and

$$\ln \frac{\gamma_2}{\gamma_2^\circ} = \frac{Z_Q Z_A}{Z_Q + Z_A} \int_0^y \left[y \frac{\partial G}{\partial y} - N \frac{\partial G}{\partial N} \right] dy \quad (22)$$

There remains the problem of calculating the solvent activity from the experimentally determined solute activity ratio. This may be done in a similar manner through the relationships

$$\left(\frac{\partial \mu_1}{\partial n_3} \right)_{n_1, n_2} = \left(\frac{\partial \mu_3}{\partial n_1} \right)_{n_2, n_3} \text{ and } \left(\frac{\partial \mu_2}{\partial n_3} \right)_{n_1, n_2} = \left(\frac{\partial \mu_3}{\partial n_2} \right)_{n_1, n_3} \quad (23)$$

but is perhaps more rapidly accomplished through the use of the Gibbs-Duhem equation at constant temperature and pressure

$$n_1 \left(\frac{\partial \mu_1}{\partial y} \right)_N + n_2 \left(\frac{\partial \mu_2}{\partial y} \right)_N + n_3 \left(\frac{\partial \mu_3}{\partial y} \right)_N = 0 \quad (24)$$

Using the relations in (4) above one obtains after rearrangement

$$\left(\frac{\partial \mu_3}{\partial y} \right)_N = - \frac{MN}{1000} \left[y \left(\frac{\partial \mu_1}{\partial y} \right)_N + \frac{1 - y}{\kappa_2} \left(\frac{\partial \mu_2}{\partial y} \right)_N \right] \quad (25)$$

or

$$\left(\frac{\partial \ln a_3}{\partial y} \right)_N = - \frac{MN}{1000} \left[y \left(\frac{\partial \ln a_1}{\partial y} \right)_N + \frac{1 - y}{\kappa_2} \left(\frac{\partial \ln a_2}{\partial y} \right)_N \right] \quad (26)$$

If now equations 14 and 15 are differentiated and the results substituted in equation 26, appropriate rearrangement yields

$$\left(\frac{\partial \ln a_3}{\partial y} \right)_N = - \frac{M}{1000} \left(\frac{\partial}{\partial^{1/N}} \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right)_y \quad (27)$$

Integration of equation 27 at constant N leads to

$$\ln \frac{a_3}{a_3^*} = - \frac{M}{1000} \int_0^y \left(\frac{\partial}{\partial^{1/N}} \ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} \right)_y dy \quad (28)$$

where a_3^* is the solvent activity in a pure solution of solute component 2 in solvent component 3, at the same value of N as in the mixed solution. In terms of the measured electromotive force of the galvanic

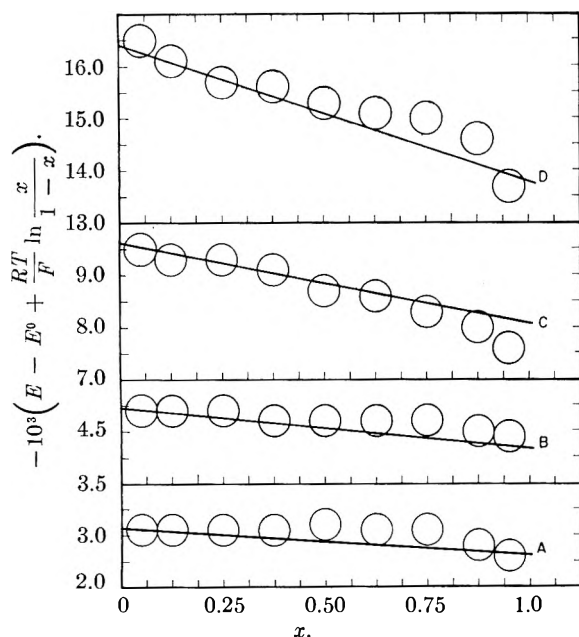


Fig. 1.—Electromotive force data for aqueous HNO_3 - AgNO_3 solutions. Curves A, B, C and D refer to ionic strengths of 0.1, 0.2, 0.5 and 1.0 molal, respectively.

cell considered, the substitution of equation 2 in equation 28 yields the final result

$$\ln \frac{a_3}{a_3^*} = -\frac{M}{1000} \frac{F}{RT} \int_0^y \left(\frac{\partial}{\partial^1 N} (E - E^0) \right)_y dy \quad (29)$$

It is evident that completely analogous results may be obtained throughout for systems with a common cation.

Applications of Relations

Suitable data for the application of the calculation methods here proposed are rather sparse. Solution activity coefficient ratios have been determined from electromotive force measurements on suitable cells by Bonner, Davidson and Argersinger³ for aqueous nitric acid-silver nitrate solutions, and by Bonner and Unietis⁴ for aqueous nitric acid-mercurous nitrate solutions. Measurements were obtained in the former for nine compositions at each of only four ionic strengths; in the latter for six compositions at each of five ionic strengths. Thus in neither case is the desired activity ratio well defined as a function of both composition variables. Nevertheless, certain interesting results may be obtained by application of the proposed methods to the nitric acid-silver nitrate data. (The silver nitrate system was chosen in preference to the mercurous nitrate system because of the slightly greater number of experimental measurements available, as well as because of the somewhat greater smoothness of the experimental curves.)

As seen in Figs. 1 and 2, the data may be fairly well represented by the expression

$$\begin{aligned} E - E^0 + \frac{RT}{F} \ln \frac{x}{1-x} &= -0.01 \sqrt{m} [0.68 + \\ &0.96 \sqrt{m} - x(0.109 + 0.151 \sqrt{m})] \quad (30) \\ &= -2 \frac{RT}{F} \ln \frac{\gamma_1}{\gamma_2} = \frac{RT}{F} G \end{aligned}$$

(3) O. D. Bonner, A. W. Davidson and W. J. Argersinger, Jr., *J. Am. Chem. Soc.*, **74**, 1047 (1952).

(4) O. D. Bonner and F. A. Unietis, *ibid.*, **75**, 5111 (1953).

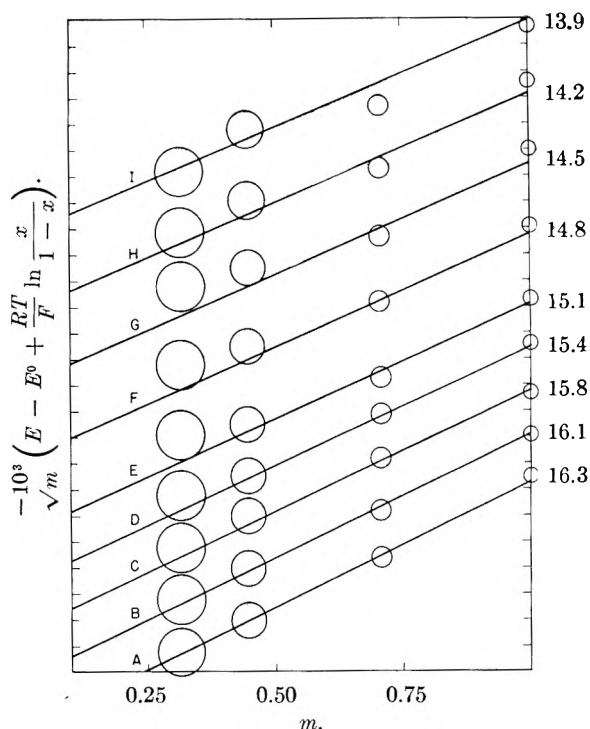


Fig. 2.—Electromotive force data for aqueous HNO_3 - AgNO_3 solutions. Curves A through I refer, respectively, to solute mole fractions of 0.050, 0.125, 0.250, 0.375, 0.500, 0.625, 0.750, 0.875 and 0.950, and have been successively displaced vertically by 2 units (A through E) or 3 units (F through I), as indicated by the intercepts at $m = 1$. The interval on the vertical coordinate axis is 1.0 unit for all curves.

where x is the mole fraction of nitric acid (solute component 1) in the mixed solute, and m is the total molality, or in this case, ionic strength. This relation suggests a linear variation of the logarithms of the activity coefficients with composition at constant ionic strength, as given by Harned's rule,⁵ although a quadratic variation is not excluded. The relation further implies a simple not unreasonable dependence of the linear or quadratic variation constants on ionic strength. Although the experimental data deviate from the simple expression given, especially near $x = 0$ and $x = 1$, it was not considered justified to use a more involved expression, particularly in view of the small number of ionic strengths studied.

When this relation is substituted in equation 20 and the result in equations 21 and 22, one obtains after appropriate simplification

$$\begin{aligned} \log \frac{\gamma_1}{\gamma_1^0} &= - \left(\frac{0.025}{\sqrt{m}} + 0.069 \right) m(1-x) + \\ &\frac{0.0024}{m^{3/2}} (m(1-x))^2 \quad (31) \end{aligned}$$

and

$$\log \frac{\gamma_2}{\gamma_2^0} = + \left(\frac{0.029}{\sqrt{m}} + 0.081 \right) mx + \frac{0.0024}{m^{3/2}} (mx)^2 \quad (32)$$

Thus a quadratic variation of $\log \gamma$ with composition is obtained; and, the two quadratic constants being equal, the variation of $\log \gamma_1/\gamma_2$ is linear. McKay found a similar result for the lith-

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 459.

ium chloride-potassium chloride and sodium chloride-cesium chloride systems. The explicit dependence of the four variation constants on the ionic strength is indicated; the dependence of the linear term constants resembles that observed in the cesium chloride-hydrochloric acid system⁶ rather than that in the sodium chloride-hydrochloric acid system. However, it should be observed that these results are obtained over a limited and not very low ionic strength range, and they are not to be considered valid at very low values of m .

If equations 21 and 22 are combined for the case under consideration there results the relation

$$2 \ln \frac{\gamma_1^\circ}{\gamma_2^\circ} = -G(m,1) + \int_0^1 \left(x \frac{\partial G}{\partial x} - m \frac{\partial G}{\partial m} \right) dx \quad (33)$$

or in terms of the constants of equation 30

$$\frac{1}{\sqrt{m}} \log \frac{\gamma_1^\circ}{\gamma_2^\circ} = 0.079 + 0.150 \sqrt{m} \quad (34)$$

In Fig. 3 experimental data are plotted for nitric acid and silver nitrate, taken from Conway's compilation⁷; the straight line is that of equation 34 derived entirely from the nitric acid-silver nitrate mixed solution measurements. Except at the lower ionic strengths, the agreement is good.

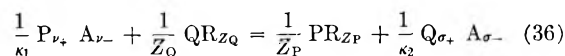
The osmotic coefficient in the mixed solution is obtained by substitution of equation 30 in equation 29, integration, and application of the general relation between osmotic coefficient, ϕ , and solvent activity. The result is

$$\phi - \phi_2^\circ = 10^{-4} m^{3/2} x [0.44 + 1.23 \sqrt{m} - x(0.035 + 0.097 \sqrt{m})] \quad (35)$$

where ϕ_2° is the osmotic coefficient in pure aqueous silver nitrate solution of molality m .

Appendix

Equation 27 provides a direct means of calculating activity ratios or activity coefficient ratios appropriate to ion-exchange reactions from measurements of solvent activity alone, a procedure similar to that suggested by McKay.² In the cation-exchange reaction for which the balanced equation is (R represents the univalent exchanger anion)



(6) Reference 5, p. 469.

(7) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., London, 1952. pp. 75, 79.

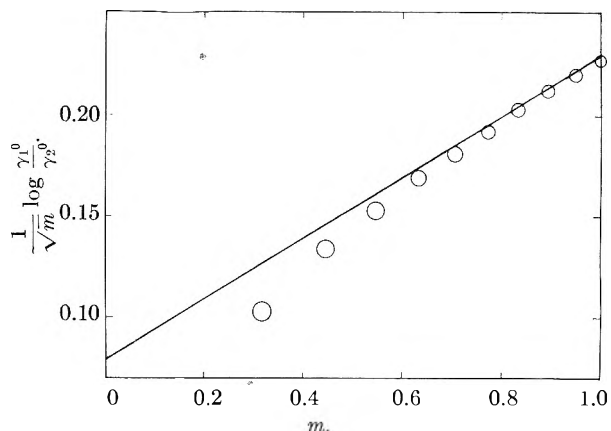


Fig. 3.—Activity coefficient ratios for aqueous HNO₃ and AgNO₃ solutions. Experimental points derive from measurements on separate pure solutions, straight line from eq. 34 based on measurements on mixed solutions.

the equilibrium constant expression contains the term $a_2^{1/\kappa_2}/a_1^{1/\kappa_1}$. If equation 27 is reversed and added to the identity

$$-\left(\frac{\partial}{\partial 1/N} \ln N^{1/Z_Q - 1/Z_P} \right)_y = \left(\frac{1}{Z_Q} - \frac{1}{Z_P} \right) N \quad (37)$$

there results the expression

$$\left[\frac{\partial}{\partial 1/N} \ln \left(\frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} N^{1/Z_Q - 1/Z_P} \right) \right]_y = -\frac{1000}{M} \left(\frac{\partial \ln a_3}{\partial y} \right)_N + \left(\frac{1}{Z_Q} - \frac{1}{Z_P} \right) N \quad (38)$$

Equation 38 may now be integrated at constant y from $N = 0$ to $N = N$, since the value at the lower limit is finite; the result is

$$\ln \frac{a_2^{1/\kappa_2}}{a_1^{1/\kappa_1}} N^{1/Z_Q - 1/Z_P} = \ln \left(\frac{1-y}{Z_Q} \right)^{1/Z_Q} \left(\frac{Z_P}{y} \right)^{1/Z_P} + \int_0^N \left[\frac{1000}{M} \left(\frac{\partial \ln a_3}{\partial y} \right)_N - \left(\frac{1}{Z_Q} - \frac{1}{Z_P} \right) N \right] \frac{dN}{N^2} \quad (39)$$

Equation 39 is easily solved for $a_2^{1/\kappa_2}/a_1^{1/\kappa_1}$. If only the activity coefficient ratio is desired, equation 39 leads, with equation 16 and its analog for a_2 , to the result

$$\ln \frac{\gamma_2^{1/Z_Q + 1/Z_A}}{\gamma_1^{1/Z_P + 1/Z_A}} = \int_0^N \left[\frac{1000}{M} \left(\frac{\partial \ln a_3}{\partial y} \right)_N - \left(\frac{1}{Z_Q} - \frac{1}{Z_P} \right) N \right] \frac{dN}{N^2} \quad (40)$$

Acknowledgment.—The author wishes to express his indebtedness to Dr. Arthur W. Davidson for many helpful discussions and criticisms.

ETHANE HYDROGENATION-CRACKING ON IRON CATALYSTS WITH AND WITHOUT ALKALI

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The kinetics of the hydro-cracking of ethane on iron catalysts with and without alkali additions have been studied. A general expression of the form $-d[C_2H_6]/dt = kp^r_{C_2H_6}p^s_{H_2}$ has been obtained. The exponent r is 1 or a fraction; s changes from negative to positive as potash is added to fused iron oxides, containing traces of acidic impurities, from which the catalysts were prepared by reduction. A general formulation of the reaction kinetics is presented to include all the data here recorded and earlier work with nickel on the hydro-cracking of ethane and propane. It postulates as a slow step the breaking of a C-C bond by interaction of an adsorbed hydrocarbon radical $(C_2H_x)_a$ with hydrogen on the surface. The mechanism proposed suggests an interpretation of the role of alkalis in Fischer-Tropsch synthesis on iron catalysts.

The catalytic hydrogenation of ethane has been studied on nickel^{1,2} and cobalt³ catalysts, where the reaction rate corresponds to an expression of the type

$$-dp_{C_2H_6}/dt = kp_{C_2H_6}^r p_{H_2}^s \quad (1)$$

No investigation has been made so far on iron catalysts. Fused iron catalysts, of the synthetic-ammonia type, are particularly interesting because of the great importance that they have gained in the last decade for hydrocarbon synthesis.⁴

A fundamental problem which arises in connection with these iron catalysts is the role of the alkali promoter, which is known to have great importance in the synthesis and which could therefore affect a reaction such as the present one. Accordingly it was decided to investigate ethane hydrogenation on reduced fused iron catalysts with and without alkali, mainly to determine whether and how the kinetics of such a reaction is influenced by alkali.

Experimental

Apparatus.—A static system, similar to the one described by Kemball and Taylor² has been used. The reaction vessel of about 220 cc., electrically heated, was provided with an air-jacket and a mercury regulator to keep the temperature constant within 1°.

Gases.—Cylinder hydrogen was purified over palladized asbestos at 300°, calcium chloride, ascarite, magnesium perchlorate and phosphorus pentoxide. Cylinder ethane was dried over calcium chloride and phosphorus pentoxide, and then doubly distilled from liquid nitrogen traps.

Catalysts.—The catalysts⁵ were prepared by fusion of Alan Wood magnetite ore⁶ with the addition of potassium or lithium carbonate. Concentrations of the alkali promoters, determined by means of chemical analysis, were as follows (basis iron): Catalyst AW, no alkali added; catalyst F1K, 0.05% K₂O; Catalyst F1L, 0.6%, Li₂O; catalyst F2K, 0.6% K₂O.

Analyses.—The analyses were carried out⁷ in a Nier-type mass spectrograph, and based on a calibration curve obtained from hydrogen-containing mixtures of ethane and methane.

Reduction Experiments.—A preliminary study was conducted on the reduction by hydrogen of catalysts AW, F2K and of two other catalysts, MW and MK, prepared,

respectively, by fusion of mill scale, and of mill scale plus potassium carbonate (to give 0.6% K₂O, basis iron).⁵ The study was made by means of a flow system, in a vertical chamber, using approximately 4 g. of the catalysts, mesh 40 to 100, with hydrogen flowing at the rate of 3 liters/hr. at atmospheric pressure, in the temperature range from 300 to 430°. The reaction was followed by weighing the water produced, and it was linear with time up to about 70%. A comparison of the reduction rates showed no appreciable difference between them, the activation energies being also the same within the experimental error (14.1, 15.7, 15.8, 15.6 kcal. for catalysts AW, F2K, MW, MK, respectively).

Procedure.—Approximately 1 g. of catalyst, mesh 40 to 100, contained in a porcelain boat, was reduced at 460° for about 70 hours, with hydrogen flowing over it. The catalyst was then evacuated overnight at the same temperature by means of a mercury diffusion pump, and cooled down to reaction temperature under continuous pumping. A given amount of the mixture of ethane and hydrogen was then let into the reaction chamber. After one hour a sample of about 40 cc. was withdrawn for the analysis, and the catalyst pumped out at reaction temperature for half an hour. An excess of hydrogen was always used to avoid carbon deposition and abnormal kinetics.² Calculation of ethane and hydrogen exponents was made by keeping constant one of the working pressures and by varying the other. Owing to a tendency to poisoning it was found necessary to use a "bracketing" technique, repeating the conditions of the first run after one of the parameters had been varied, disregarding therefore those results which were not taken in a condition of satisfactory reproducibility.

Experimental Results

All the experiments are reported in Tables I to V; Table VI gives a summary for the various catalysts reporting the experimental values for ethane and hydrogen exponents and the apparent activation energies; k' has been calculated according to the formula

$$\log k' = \log xp_{0C_2H_6} - r \log \bar{p}_{C_2H_6} - s \log \bar{p}_{H_2} \quad (2)$$

where x is the fraction of reacted ethane, and $xp_{0C_2H_6}$ is therefore the total amount of ethane reacted in 1 hour, expressed in cm., $p_{C_2H_6}$ and p_{H_2} are the mean working pressures of ethane and hydrogen, respectively; k' therefore represents the reacted ethane in cm./hr., for 1 cm. ethane and 1 cm. hydrogen, and for each catalyst is proportional to the rate constant.

Table I reports the data obtained for catalyst F2K. After run F2K a5 the catalyst was kept *in vacuo* for a few days; the activity then decreased to about 1/4 and the behavior was not reproducible. A period of reduction of 12 hours at 460° followed by overnight evacuation markedly increased the activity, failing however to bring it to the previous value. Set F2K b is a check for reproducibility per-

(8) Analysis of the fused mill scale gave the following percentages: Fe, 69.1; SiO₂, 0.1; Al₂O₃, 0.2; TiO₂, 0.03; MgO, 0.02; CaO, 0.1.

(1) K. Morikawa, W. S. Benedict and H. S. Taylor, *THIS JOURNAL*, **58**, 1795 (1936).

(2) C. Kemball and H. S. Taylor, *ibid.*, **70**, 345 (1948).

(3) E. H. Taylor and H. S. Taylor, *ibid.*, **61**, 503 (1939).

(4) H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 222.

(5) All the catalysts and their analyses were obtained through the courtesy of the M. W. Kellogg Company, Jersey City, N. J.

(6) Analysis of the fused Alan Wood ore had given the following percentage composition: Fe, 73.0; Al₂O₃, 0.76; SiO₂, 0.73; TiO₂, 0.17; MgO, 0.08; CaO, 0.04; Na₂O, 0.004.

(7) The analyses were made possible through the courtesy of Professor John Turkevich, who kindly permitted the use of his mass spectrograph.

TABLE I

ETHANE HYDROGENATION ON CATALYST F2K

Run	Temp., °C.	$p_{C_2H_6}$, cm.	p_{H_2} , cm.	$x p_{C_2H_6}$, ^a cm./hr.	k' ^b
F2K a1	247	1.26	3.85	0.106	0.0454
2	258	1.24	3.75	.165	.0736
3	258	1.25	3.80	.155	.0684
4	247	1.24	3.75	.103	.0449
5	236	1.25	3.80	.069	.0294
b1	258	1.26	3.74	.115	.0494
2		1.26	3.74	.116	.0497
3		1.27	3.78	.072	.0324
4		1.08	5.78	.048	.0196
5		1.27	3.78	.051	.0212
c1	247	1.28	3.87	.0865	.0459
2		1.30	8.80	.112	.0464
3		1.31	3.99	.0905	.0468
4		0.58	3.97	.0508	.0468
5		1.29	3.91	.0895	.0475
6	278	1.29	3.91	.258	.135
7	249	1.32	4.03	.102	.0522
8	262	1.32	4.03	.157	.0820
9	284	1.32	4.03	.308	.169
10	274	1.27	3.83	.227	.126
d8	230	3.87	5.11	.154	.037
9		2.41	3.19	.093	.036
10		1.50	1.98	.055	.035
11		0.94	1.13	.033	.033
e1 ^c	265	1.28	3.82	.285	.120 ^d
2		1.28	3.82	.251	.106 ^d

^a x = percentage of ethane reacted in 1 hr. ^b k' = ethane reacted cm./hr. for 1 cm. C_2H_6 and 1 cm. H_2 . ^c Runs e1, e2 performed in a circulating system. ^d Calculated k' to volume conditions and amount of catalyst of runs in static system.

TABLE II

ETHANE HYDROGENATION ON CATALYST AW

Run	Temp., °C.	$p_{C_2H_6}$, cm.	p_{H_2} , cm.	$x p_{C_2H_6}$, ^a cm./hr.	k' ^b
AW a1	225	1.27	3.78	0.560	1.24
2				.573	1.28
3				.559	1.24
4				.553	1.22
11	234	1.28	3.72	.175	0.274
12		0.69	3.71	.107	.301
13		1.28	3.72	.170	.266
14		1.28	3.72	.170	.266
15		2.61	7.59	.221	.294
b1	231	1.34	4.11	0.902	2.58
2	192	1.37	4.18	.148	0.316
3		1.39	8.61	.0725	.258
4		1.33	4.07	.130	.271
5		0.66	4.09	.0321	.134
6		1.38	4.22	.0352	.071
7		1.31	3.99	.0248	.050
8	207	1.26	3.89	.266	.614
9	188	1.22	3.78	.015	.231
10		1.25	3.85	.0985	.214
11	208	1.30	4.00	.283	.646
12	222	1.31	4.04	.434	1.04
13	201	1.26	3.89	.193	0.439
14	178	1.26	3.89	.0466	.098
15		0.63	3.92	.0230	.098
16		1.28	3.97	.0421	.089
17		1.27	8.83	.0238	.089

^{a,b} See footnotes of Table I.

TABLE III

ETHANE HYDROGENATION ON CATALYST AWK

Run	Temp., °C.	$p_{C_2H_6}$, cm.	p_{H_2} , cm.	$x p_{C_2H_6}$, ^a cm./hr.	k' ^b
AWK a25	258	1.30	4.15	0.0862	0.0590
26		0.60	4.05	.0505	.0559
27		1.27	4.08	.0736	.0515
28		1.27	8.58	.0787	.0509
29		1.28	4.12	.0709	.0492
30	282	1.28	4.12	.178	.126
31	259	1.31	4.19	.0932	.0640
32	272	1.30	4.15	.166	.0953

^{a,b} See footnotes of Table I.

TABLE IV

ETHANE HYDROGENATION ON CATALYST F1K

Run	Temp., °C.	$p_{C_2H_6}$, cm.	p_{H_2} , cm.	$x p_{C_2H_6}$, ^a cm./hr.	k' ^b
F1K a2	204	1.25	3.70	0.245	0.434
3		1.23	8.32	.143	.441
4		1.25	3.70	.275	.491
5		0.56	3.79	.140	.528
6		1.23	3.65	.292	.531
7		1.25	3.70	.251	.444
8	177	1.27	3.78	.046	.0762
9	192	1.26	3.74	.116	.197
10	220	1.25	3.70	.484	.920
11	198	1.25	3.70	.180	.312

^{a,b} See footnotes of Table I.

TABLE V

ETHANE HYDROGENATION ON CATALYST F1L

Run	Temp., °C.	$p_{C_2H_6}$, cm.	p_{H_2} , cm.	$x p_{C_2H_6}$, ^a cm./hr.	k' ^b
F1L a1	254	1.29	3.91	0.486	0.745
2	219	1.27	3.83	.168	.234
3		1.28	8.62	.105	.199
4		1.27	3.83	.152	.213
5		0.58	3.87	.0829	.220
6		1.29	3.91	.157	.218
7	245	1.27	3.83	.127	.176
8	219	1.30	3.95	.0272	.036
9		1.27	3.83	.155	.202
10	245	1.26	3.79	.382	.571
11	201	1.28	3.87	.0736	.100
12	259	1.28	3.87	.750	1.27
13	233	1.30	3.92	.339	0.493
14		1.29	8.66	.226	.443
15		1.24	3.76	.289	.423
16		2.47	7.48	.410	.446
b1	222	1.29	3.86	0.227	.316
2		1.29	8.71	.170	.325
3		1.28	3.82	.228	.318

^{a,b} See footnotes of Table I.

TABLE VI

EFFECT OF ALKALI ON KINETIC EXPONENTS AND APPARENT ACTIVATION ENERGY FOR ETHANE HYDROGENATION

Catalyst	Alkali promoter	Kinetic exponents C_2H_6	H_2	E^a
AW	None	1.0	-0.7	25.6
F1K	K_2O (0.05%)	0.9	-0.7	25.2
F1L	Li_2O (0.6%)	0.8	-0.4	21.0
F2K	K_2O (0.6%)	0.7	+0.3	19.3
AWK	K_2O^b	0.6	+0.1	20.1

^a E = apparent activation energy. ^b Alkali-promoted by soaking into KOH solution.

formed on a second sample of the same catalyst; here again the activity, very constant at first, dropped to a lower value. The catalyst was then treated with hydrogen at 50 cm. pressure, and after some hours the gas was analyzed by means of the mass spectrograph to observe a possible removal of carbon as methane. Seven of these treatments were successively made from 258 to 391° until no further presence of methane was detected. The total amount of carbon removed was only about 0.1 mg., which approximately corresponds to 2% of the total surface, if this is assumed to be of the order of 5 sq. m./g.^{9,10} Evacuation for 1 hour at 391° followed this hydrogen treatment, but the catalyst did not show any measurable activity at the same temperature (258°) at which the reaction had proceeded before. In set F2K c the behavior of the catalyst was very reproducible and the kinetic exponents as well as the temperature coefficient were calculated. A check is given by set F2K d, where runs were made with a constant hydrogen to ethane ratio, varying the total pressure: the constancy of k' calculated according to the kinetic values given in Table VI for this catalyst is a control of the correctness of these values.

Table II reports the data obtained for catalyst AW. Two sets of runs were made on two different samples both having been reduced according to the standard procedure previously recorded. After run AW a4 the catalyst had been left *in vacuo* for a few days and the activity diminished. Measurements were then made to calculate the ethane and hydrogen exponents, leading to the values of +0.8 and -0.6, respectively, but they are to be considered only as indicative. Runs AW a11 to a15 show the fair constancy of k' when calculated according to the kinetic values given above. The decrease in activity noticeable after run AW b5 is due to an accidental failure of the mercury diffusion pump. A period of 36 hours of reduction at 460° followed by overnight evacuation restored the previous activity.

Following experiment AW a15 the catalyst was taken out of the reaction chamber, and treated with KOH solution in a way similar to that described by Love and Emmett.¹¹ Reduction of this catalyst (now designated as AWK) was carried for 40 hours at 460° followed by overnight evacuation at reduction temperature. A first set of experiments showed that the activity had very markedly decreased, but it was not constant, eventually becoming negligible. An additional period of 48 hours of reduction followed as usual by evacuation restored the activity first shown by the catalyst AWK, and the behavior was fairly reproducible. The experimental results are given in Table III. Table IV gives the results obtained on catalyst F1K, and Table V those obtained on catalyst F1L. Two sets were made on the last catalyst. The poisoning observed after first run F1L a6 was due to accidental failure of the mercury diffusion pump, but in

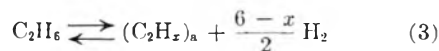
this case also a reduction period of 24 hours followed by evacuation restored the previous activity (see run F1L a9).

In order to see whether the much lower activity shown by catalyst F2K could be attributed to less reduction inherent in our reduction technique, we decided to investigate the same reaction in a circulating closed system where the catalyst, placed in a vertical chamber, could be reduced by hydrogen flowing through it,¹² and where therefore as shown by McGeer and Taylor,¹³ we could expect a better reduction. The good agreement between run F2K e1, e2 (Table I), obtained with the new reduction technique, can be seen, and indicates that the difference between activities shown in our conditions is a real one.¹⁴

Decomposition of Ethane Alone.—A few experiments on the decomposition of ethane alone were made on catalysts AW and F2K. The reaction was first order with respect to ethane pressure on both catalysts, and proceeded at higher temperatures than the hydrogenating cracking. It is interesting to note that the temperature difference for having $k'_{dec.} = k'_{hydr.}$ ($k'_{dec.}$ being also referred to 1 cm. pressure of ethane) was about 100° for both catalysts. Unfortunately, owing to the poor reproducibility, no sufficient data were obtained to calculate activation energies, but their values yielded *circa* 20 to 25 kcal./mole.

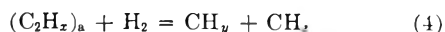
Discussion

Since it was shown by Morikawa, Benedict and Taylor¹ that the exchange reaction of ethane and deuterium on a nickel catalyst occurred in a lower temperature range than the interaction to yield methane, and with a lower activation energy, it has been natural to assume that the slow step in the hydrocracking of saturated hydrocarbons on metal catalysts involved the breaking of the C-C bonds. The high mobility of the hydrogen atoms of adsorbed paraffins, as evidenced by the relative ease of exchange with deuterium on metal films such as nickel¹⁵ suggests an equilibrated reaction of the type



where x is an integer and $(C_2H_x)_a$ is an adsorbed dehydrogenated radical.

If, now, we postulate that the slow step consists in breaking this radical into fragments and that a molecule of hydrogen is involved in the process.



we can interpret the kinetic data of this work as well as those of previous work. We further assume that the resulting fragments CH_y and CH_z are rapidly removed to the gas phase as methane. It is

(12) Total volume of the system was 310 cc., circulation of gas was assured by a two stage alternating mercury pump (displacement 10 cc./sec.), 2 g. of catalyst was used. Reduction was carried at 460° for 72 hours, the hydrogen flowing with a space velocity of 4500 and having been purified in exactly the same way as described before.

(13) J. P. McGeer and H. S. Taylor, *J. Am. Chem. Soc.*, **73**, 2743 (1951).

(14) Possible differences in surface area between the two catalysts is outside the order of magnitude of the observed one. See ref. 10.

(15) C. Kemball, *Proc. Roy. Soc. (London)*, **A2107**, 539 (1951); **A217**, 376 (1953).

(9) W. K. Hall, W. H. Tarn and R. B. Anderson, *J. Am. Chem. Soc.*, **72**, 5436 (1950).

(10) P. H. Emmett and S. Brunauer, *ibid.*, **59**, 1553 (1937).

(11) The catalyst was soaked into 0.8 cc. of a 0.1 *m* KOH solution; after 3 hr. it was dried up to 100°, and then placed in the reactor. See K. S. Love and P. H. Emmett, *ibid.*, **63**, 3297 (1941).

immaterial to our discussion whether the hydrogen molecule strikes the radical from the gas phase or attacks it via the surface so long as the fraction of the surface covered with hydrogen is proportional to the hydrogen gas pressure. Because the slow step is occurring, by postulate, on the surface, we can apply the classical Langmuir kinetic treatment. The fraction of the surface θ covered with C_2H_2 radicals by the equilibrium (3) is given by equating the velocities in the two directions

$$v_1 = \alpha_1 p_{C_2H_6} (1 - \theta) = v_2 = \alpha_2 p_{H_2}^{6-x/2} \theta$$

whence

$$\theta = \frac{\alpha(p_{C_2H_6}/p_{H_2}^{6-x/2})}{1 + \alpha(p_{C_2H_6}/p_{H_2}^{6-x/2})}$$

with $\alpha = \alpha_1/\alpha_2$. As is well known such an expression can be replaced in a restricted pressure range by

$$\theta = \alpha^n (p_{C_2H_6}/p_{H_2}^{6-x/2})^n$$

where $0 < n < 1$.

The rate of the over-all reaction with reaction (4) the slow step becomes

$$r = k\theta p_{H_2}$$

or

$$r = k' p_{C_2H_6}^n p_{H_2}^{1-n} \left[\frac{1-n}{2} \frac{6-x}{2} \right] \quad (5)$$

All the kinetic data hitherto accumulated show that the rate of hydrocracking of ethane is proportional to some fractional power m of the partial pressure of ethane. To test the expression (5) we set $m = n$ and test the adequacy of (5) by the agreement between the observed value of the exponent of p_{H_2} and the value calculated from (5) with selected values of x . *A priori*, it appears reasonable to assume values of 0, 2 and 4 for x corresponding to acetylenic, acetylene and ethylene residues on the surface. Moreover, we expect that the stripping of hydrogens from the hydrocarbon (low values of x) should be more marked for highly dehydrogenating surfaces. In this manner we have obtained the summary presented in Table VII of the data of this work on iron catalysts and that of Kemball and Taylor on nickel.

TABLE VII

CALCULATED EXPONENTS OF p_{H_2} IN ETHANE HYDROCRACKING

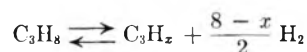
Catalyst	Exponent of $p_{C_2H_6}$	Value of x	Exponent of p_{H_2} Calcd. with (5)	Obsd.
Supported Ni	0.7	0	-1.1	-1.2
AW no alkali	1.0	2	-1.0	-0.7
F1K 0.05% K_2O	0.9	2	-0.8	-0.7
F1L 0.06% Li_2O	0.8	2	-0.6	-0.4
F2K 0.6% K_2O	0.7	4	+0.3	+0.3
AWK impregnated with K_2O	0.6	4	+0.4	+0.1

The agreement is very satisfactory, if it is remembered that the kinetic exponents are only approximate. The physical meaning of this scheme is quite informative. Thus, a nickel catalyst ($x = 0$) is pictured as a potent dehydrogenating surface. Iron, with no or little potash, or with lithia, is less hydrogenating ($x = 2$) as is well known. The really interesting feature however is that the effect of potash is to decrease the hydrogenating capacity ($x =$

4) of the iron surface. Essentially, its effect is to maintain the paraffinic molecule on the surface as dimeric CH_2 radicals without further breakdown to less hydrogenated carbon radicals.

This result is well worthy of further comment especially in connection with the still unexplained role of potash in the Fischer-Tropsch synthesis on iron catalysts. It must be emphasized that the introduction of potash into the catalysts studied in this work markedly decreases their ability to rupture C-C bonds. Consequently, the explanation of the beneficial effect of potash in the hydrocarbon synthesis must not be sought in its promoting of C-C bond formation. It now appears that its function is to preserve at the surface the CH_2 radicals which finally yield the higher molecular weight saturated hydrocarbons. The poor showing of nickel as a Fischer-Tropsch catalyst also follows from this scheme, since on Ni, $x = 0$ and paraffinic molecules are stripped down to carbon with only methane as the final product. Moreover, it is known⁴ that lithia does not possess in the synthesis the virtue of potash. This becomes clear from our table where it is seen that lithia is unable to protect the CH_2 polymeric radicals; in other words x remains equal to 2 just as on iron without alkali.

The kinetics of the hydrocracking of propane on nickel, as studied by Morikawa, Trenner and Taylor,¹⁶ also follow from this scheme. Here, the equilibrated reaction is



The rate expression representing the data is

$$r = k p_{C_3H_8}^{0.9} \times p_{H_2}^{-2.6} \quad (6)$$

By a reasoning analogous to that above for propane, we now obtain

$$r = k p_{C_3H_8}^n \times p_{H_2}^{1-n} \left[1 - n \frac{8-x}{2} \right]$$

As before let us put $n = 0.9$ and $x = 0$ since we deal here also with a nickel catalyst. The calculated hydrogen exponent is then -2.6 , identical with the observed. In the earlier publication¹⁶ it was difficult to rationalize the high negative exponent for hydrogen. This comes quite naturally from the present postulated mechanism.

A few words will give further weight to our considerations. It was shown in this work that ethane alone decomposes at a higher temperature than ethane-hydrogen mixtures. This suggests that hydrogen is involved in the slow step of the cracking reaction as we have indeed postulated. No heterogeneity of the surface has been assumed in our derivation. This does not mean that the surface is not heterogeneous but recognizes the fact that, in a kinetic experiment, the pressure variation at constant temperature is so small that the surface behaves as if it were homogeneous. This will be shown elsewhere in detail in the case of the decomposition of stibine on an antimony film, and in ammonia synthesis catalysis.

The less potent activity of iron catalysts contain-

(16) K. Morikawa, N. Trenner and H. S. Taylor, *THIS JOURNAL*, **59**, 1103 (1937).

ing potash finds substantiation in the recent work of Kummer and Emmett.¹⁷ They found that a Fe-Al₂O₃ catalyst performs the H₂-D₂ exchange rapidly at -195° (time for 1/2 conversion, $t_{1/2}$ = 3-10 sec.). On an iron catalyst that is promoted

(17) J. T. Kummer and P. H. Emmett, *THIS JOURNAL*, **56**, 258 (1952).

with both aluminum oxide and potassium oxide the rate is scarcely appreciable at that temperature ($t_{1/2}$ ca. 6000 sec.).

Acknowledgment.—This work was supported in part by the Office of Naval Research, under Contract No. N6-onr-27018. We wish to express our best thanks for this assistance.

COMMUNICATION TO THE EDITOR

ALPHA-PARTICLE IONIZATION AND EXCITATION IN GAS MIXTURES

Sir:

In a recent publication¹ it was shown that the ion yield (M/N) for the polymerization of acetylene by α -particles in individual mixtures with six different inert gases is constant only when related to the energy of ionization (ionization potential), but not in relation to the total energy (W) expended in the mixture. From this it was deduced that the excess energy (excitation?) contributed nothing to the reaction. The argument was based on the inequality of the ratio for different inert gases (ionization potential/total energy) as derived from the then accepted data.²

Recently several workers³ have reexamined the total ionization produced by alpha particles in a number of inert gases and find the total energy (W) necessary to produce an ion pair strongly dependent on the purity of the gas. Very small quantities of certain impurities can greatly lower W by contributing ions not depending on the ionization of the principal component. When the impurities are removed by strenuous purification the net result⁴ is that the ratio of W to ionization potential has the constant value 1.71 ± 0.034 for each of the five inert gases.

Evidently this invalidates the argument that

(1) S. C. Lind, *THIS JOURNAL*, **56**, 920 (1952).

(2) Rutherford, Chadwick and Ellis, "Radiation from Radioactive Substances," Cambridge University Press, New York, N. Y., 1930, p. 81.

(3) W. P. Jesse and J. Sadauskis, *Phys. Rev.*, **90**, 1120 (1953); T. E. Bortner and G. S. Hurst, *ibid.*, **90**, 160 (1953); **93**, 1236 (1954).

(4) W. P. Jesse, private communication in advance of publication.

excitation or metastable states cannot contribute to chemical action taking place under alpha radiation. While it does not prove that they do or do not take part, it shows that if they do participate they must do so in some constant proportion to the ionization. What the ratio may be is difficult to ascertain in view of the lack of methods to determine quantitatively the number of excited or metastable states. Ionization can be definitely measured and therefore continues to be the best index of yield in gas reactions taking place under ionizing radiation. In fact, if both ions and metastable states contribute to the reaction both may feed into a common product, a free radical or atom, as the next stage in the kinetic mechanism.

The fact that the rates of polymerization of acetylene in mixtures with six different inert gases were found proportional to the total ions produced by alpha rays in acetylene plus the ions in the inert may mean that the gases used contained no disturbing impurities.⁵

Finally, what is the probability that the excited states of inert gases, including nitrogen, should contribute to produce chemical action in some proportion to the accompanying ionization.⁶

OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

S. C. LIND⁷

RECEIVED JULY 22, 1954

(5) This may well have been the case since the gases were purified in the Cryogenic Laboratory of the Bureau of Mines in Washington where the techniques of gas purification had been highly developed in the separation of helium from natural gas.

(6) Dr. R. L. Platzman expects to answer this question by utilizing existing data for the polymerization of acetylene by radon in mixtures with the inert gases.

(7) Carbide and Carbon Chemicals Company, Oak Ridge, Tennessee.

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AZEOTROPIC DATA

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Table I. Binary Systems

Formula	B-Component Name	B.P., ° C.	B.P., ° C.	Wt. % A	Azeotropic Data	Ref.
	Argon	-186			Nonazeotrope, V-1.	164
	Nitrogen, 500-1500 mm.	-195			Nonazeotrope	255
	Silver Chloride	1590			Nonazeotrope	263
	Lead chloride	954				
	Boron Chloride	11.5				
	Boron hydride	-92.5				
		-100				
		-92				
		100				
		106				
		77.2				
		62				
		60				
		65				
		80				
		42				
		52				
		62				
		263				
		262				
		262				
		590				
		590				
		590				
		590				
		590				
		262				
		262				
		590				

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