

THE JOURNAL OF PHYSICAL CHEMISTRY

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ISOMERISM IN INORGANIC CHEMISTRY—INTRODUCTORY REMARKS

BY HANS B. JONASSEN

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Received November 22, 1954

Isomerism in Inorganic Chemistry is a field of study that has been greatly neglected in most academic research circles in this country for many years. This subject brings to mind the name of Dr. John C. Bailar, Jr., whose continually expanding research in this field at the University of Illinois has kept interest alive. His early papers on this subject were in the *Journal of Chemical Education*,¹ and in the *Transactions of the Illinois State Academy of Science* in 1931.² These were followed by numerous papers, mostly in the *Journal of the American Chemical Society*.

His infectious enthusiasm for this topic excited the interest of his students and several of them have developed active research programs in this difficult but rewarding field. Several of his students, Drs. Basolo, Quagliano, Holtzclaw and Jonassen are participating in this program. It is, therefore, a great pleasure to dedicate this symposium to Dr. John C. Bailar, Jr., of the University of Illinois.

During the morning session Dr. Holtzclaw will discuss the differences in polarographic behavior of several pairs of octahedral *cis* and *trans* isomers. This will be followed by a paper given by Dr. Basolo in which the rates of acid hydrolysis of a series of chelated octahedral complexes will be discussed. Next Dr. Quagliano will give a report of the infrared data which he obtained on several *cis* and *trans* isomers of planar and octahedral complexes.

During the afternoon Dr. Martell will discuss stability of complex compounds as affected by isomeric changes in the ligand. Next, Dr. Dwyer will discuss another phase of isomerism, namely,

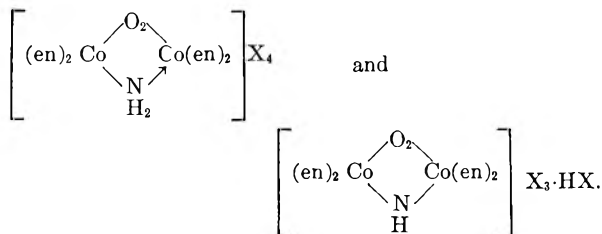
(1) John C. Bailar, Jr., *J. Chem. Ed.*, **8**, 310 (1931).

(2) John C. Bailar, Jr., *Transactions Ill. State Acad. Sci.*, **23**, 307 (1931).

optical activity in the extremely interesting complexes where hexadentate chelate groups are present. This will be followed by Dr. Yalman's work, reported by Mr. Kuwana, on structural isomerism involving nitro-nitrito isomerism. The last paper will discuss *cis* and *trans* isomerism in palladium(II) complex compounds.

To discuss all types of isomerism would take much more time than is allotted, but it might be well to append here a list of some other important varieties of isomerism that will not be covered in the papers scheduled for these sessions:

1. Coördination isomerism, such as in $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{en})_3][\text{Co}(\text{CN})_6]$.
2. Hydrate isomerism, such as in $[\text{Co}(\text{NH}_3)_2\text{H}_2\text{O}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$.
3. Polymerization isomerism, such as in $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$.
4. Valence isomerism, such as in



5. Structural isomerism, such as in thioselenates and selenosulfates.

6. Bond type isomerism, such as the two forms of HgI_2 and of nickelstilbenediamine complexes.

Perhaps in some future meeting these latter topics can be presented as learnedly as are the problems under present consideration in the papers which it is now our pleasure to hear.

THE FACTORS AFFECTING THE DIRECTIVE INFLUENCE OF THE NITRO GROUP IN THE NITRO COMPLEXES OF PALLADIUM(II). III. CHANGE IN ELECTRONEGATIVITY OF THE HALIDE GROUP¹

BY HANS B. JONASSEN AND THOMAS O. SISTRUNK

Contribution of the Richardson Chemistry Laboratories of Tulane University, New Orleans, Louisiana

Received November 22, 1954

A reaction mechanism postulated for the reaction of dichlorodiamminepalladium(II) with sodium nitrite has been extended to include the dibromo-, diiodo- and dicyanodiammine complexes of palladium(II). The effects of varying the halo group and the coordinated neutral group in the reactions of complexes of the type PdA_2X_2 with sodium nitrite were studied ($\text{A} = \text{NH}_3, \text{C}_2\text{H}_5\text{NH}_2, n\text{-C}_3\text{H}_7\text{NH}_2$; $\text{X} = \text{Br}^-, \text{I}^-, \text{CN}^-$). Evidence is offered in support of the previously postulated reaction mechanism.

Introduction

Even though the *cis* and *trans* configurations in the series of palladium(II) amines have been established from both chemical^{2,3} and physical⁴⁻⁶ properties, the mechanism by which the isomers are formed is less familiar.

After an intensive study of planar complexes, Tschernaiev⁷ formulated his rule of *trans* elimination which provides a criterion for predicting the formation of the *cis* or *trans* isomer in certain reactions. Mann,³ however, reported a complete reversal of Tschernaiev's rule in the formation of the dinitrodiamminepalladium(II) complex from the tetramminepalladium(II) ion.

An investigation of the factors influencing this reaction led Jonassen, *et al.*,^{8,9} to postulate a reaction mechanism for the dichlorodiamminepalladium(II) reaction which was in harmony with Tschernaiev's rule of *trans* elimination.

In order to determine the validity of this mechanism, it became necessary to study the directive effects when the coordinated electronegative groups were varied in the formation of $\text{PdA}_2(\text{NO}_2)_2$, ($\text{A} = \text{ammonia, ethylamine or } n\text{-propylamine}$) from the PdA_2X_2 complexes ($\text{X} = \text{Br}^-, \text{I}^-, \text{CN}^-$).

Experimental

A. Materials. 1. Preparation of Palladium(II) Bromide.—The palladium(II) bromide was prepared by a procedure analogous to that used for the preparation of palladium(II) chloride⁸ except that hydrobromic acid was used.

2. Preparation of Palladium(II) Iodide.—The palladous iodide was prepared by a method suggested by Gutbier and Krell.¹⁰ Palladium(II) chloride (5 g.) was dissolved in 200 ml. of hot water to which was added 9.5 g. of potassium iodide dissolved in 20 ml. of water. The black precipitate of palladium(II) iodide was collected by filtration, washed with 20 ml. of water, and dried in an oven at 100–110° for two hours. The yield was about 90%.

3. Preparation of Palladium(II) Cyanide.—Palladium(II) chloride (3.9 g.) was dissolved in 200 ml. of water. An

8 M solution of potassium cyanide was added to the dissolved palladous chloride until a yellow precipitate of palladous cyanide appeared. About 10 ml. of the potassium cyanide solution was required for the precipitation. The precipitate was removed by filtration, washed with 100 ml. of water, and dried over CaCl_2 . The yield of the amorphous palladium(II) cyanide was about 90%.

4. Other Reagents.—All other chemicals and reagents were of standard C.P. quality.

B. Crystallization of *cis* and *trans* Fraction.—The solution containing the dihalodiamminepalladium(II) complex in the presence of excess amine and sodium nitrite was placed in a desiccator over concentrated sulfuric acid. The time required for the formation of the first crystals of the dinitro complex varied from about 12 hours for the dinitrodiamminepalladium(II) complex at 35–40° to about 15 days for the formation of the idonitrodi-*n*-propylaminepalladium(II) compound at 10–12°. When a crop of crystals formed, the pH of the mother liquor was determined after which the crystals were removed by filtration. The filtrate was then returned to the desiccator. This procedure was repeated for each crop of crystals. The product was washed and dried.

C. Tests Used to Differentiate between the *cis* and *trans* Isomers.—Tests used to distinguish between the *cis* and *trans* isomers of the dinitrodiamminepalladium(II) complexes were essentially the same as those employed by Mann³ and Jonassen, *et al.*,^{8,9}

1. Potassium Iodide Test.—A yellow precipitate of diiododiamminepalladium(II) was formed when an aqueous solution of either the *cis* or *trans* isomer of dinitrodiamminepalladium(II) was treated with an aqueous saturated solution of potassium iodide. For the *trans*-dinitrodiamminepalladium(II) isomer the solution for the precipitate turned red within an hour. However, for the *cis* isomer, the solution above the precipitate remained almost colorless after standing for two hours or more. A mixture of the *cis* and *trans* isomers gave a *trans* test.

2. Melting Point.—As Table I shows, the melting points of a few of the isomers can be used for identification.

TABLE I

Compound	Decompn. point, °C.	Remarks
<i>cis</i> -Pd(NH ₃) ₂ (NO ₂) ₂	233–234	Dec. with non-violent evolution of a gas
<i>trans</i> -Pd(NH ₃) ₂ (NO ₂) ₂	230–231	Dec. with violent evolution of a gas
<i>cis</i> -Pd(C ₂ H ₅ NH ₂) ₂ (NO ₂) ₂	189–190	Decomposes
<i>trans</i> -Pd(C ₂ H ₅ NH ₂) ₂ (NO ₂) ₂	188–189	Melts to yellow liq. which dec. with violent evolution of gas
<i>trans</i> -Pd(<i>n</i> -C ₃ H ₇ NH ₂) ₂ (NO ₂) ₂	162–163	Melts to yellowish liq.
	167	Dec. with violent evolution of a gas
<i>trans</i> -Pd(<i>n</i> -C ₃ H ₇ NH ₂)(NH ₃)(NO ₂) ₂	148–149	Dec. with violent evolution of a gas

3. Ignition Test.—The *cis* isomers of dinitrodiamminepalladium(II) and dinitrodiethylaminepalladium(II) decomposed with non-violent gas evolution when ignited in a crucible. The remaining residue was dark gray and com-

(1) Abstracted in part from the Masters' Thesis and Doctoral Dissertation of Thomas O. Sistrunk. Present address: Ethyl Corporation, Baton Rouge, Louisiana.

(2) A. A. Grunberg and S. Schulman, *Compt. rend. acad. sci., (U.R.S.S.)*, 215 (1933).

(3) F. G. Mann, D. Crowfoot, D. Gattiker and W. Wooster, *J. Chem. Soc.*, 1642 (1935).

(4) E. G. Cox, H. Saenger and W. Wardlaw, *ibid.*, 182 (1934).

(5) E. G. Cox and G. H. Preston, *ibid.*, 1089 (1933).

(6) E. G. Cox, F. W. Pinkard, W. Wardlaw and K. C. Webster, *ibid.*, 459 (1935).

(7) I. Tschernaiev, *Ann. inst. platine, (U.R.S.S.)*, 4, 261 (1926).

(8) H. B. Jonassen and N. L. Cull, *J. Am. Chem. Soc.*, 73, 274 (1951).

(9) H. B. Jonassen, T. O. Sistrunk, J. R. Oliver and G. F. Helfrich, *ibid.*, 75, 5216 (1953).

(10) A. Gutbier and A. Krell, *Ber.*, 38, 2385 (1905).

pact. The *trans*-dinitrodiamminepalladium(II) complex decomposed with violent gas evolution, leaving a gray, spongy deposit. The *trans*-dinitrodiethylaminepalladium(II) isomer melted into a yellowish liquid which immediately decomposed vigorously. The *trans*-dinitrodi-*n*-propylaminepalladium(II) isomer melted into a liquid which decomposed vigorously about four degrees above its melting point.

D. Preparation of the Complexes. 1. **Dibromodiamminepalladium(II).**—Palladium(II) bromide (6.71 g.) was dissolved in 12 ml. of 40% hydrobromic acid. This solution was added while stirring to 40 ml. of a 5 *M* aqueous solution of ammonia and then heated over a water-bath until only a faint odor of ammonia was detectable. While hot, the solution was filtered into 10 ml. of water kept slightly acid to litmus by the addition of 40% hydrobromic acid. After some time crystals formed which were collected, redissolved in 30 ml. of a 5 *M* solution of aqueous ammonia and again filtered into a slight excess of hydrobromic acid. The resulting yellow precipitate was washed with two 10-ml. portions each of water, alcohol and ether and dried at 100–110°. The yield was about 90%.

Anal. Calcd. for Pd(NH₃)₂Br₂: Pd, 35.50. Found: Pd, 35.6.

2. ***cis*-Dinitrodiamminepalladium(II).**—The *cis*-dinitrodiamminepalladium(II) was prepared by a method outlined by Mann.³ An ammoniacal solution of dibromodiamminepalladium(II) was treated with a concentrated solution of sodium nitrite in the cold (10–15°). The first set of crystals formed were of the *cis* configuration.

Anal. Calcd. for Pd(NH₃)₂(NO₂)₂: Pd, 45.83. Found: Pd, 45.6.

3. ***trans*-Dinitrodiamminepalladium(II).**—The *trans*-dinitrodiamminepalladium(II) isomer was prepared in an analogous manner at 35° or above. The yield of the *trans* isomer decreased from 90% for the dichloro to 70% for the dibromo complex.

4. **Dibromodiethylaminepalladium(II).**—Forty ml. of 30% ethylamine was added slowly to 5 g. of palladium(II) bromide dissolved in 15 ml. of 40% hydrobromic acid. The mixture was heated for 20 minutes over a steam-bath and the hot solution filtered into 25 ml. of 40% hydrobromic acid. The yellow precipitate was separated by filtration, redissolved in 30 ml. of 30% ethylamine, and filtered into 45 ml. of 40% hydrobromic acid. The crystals were washed with two 10-ml. portions each of water, ethanol and ether and dried at 100–110° for two hours. The yield was approximately 70%. The crystals decomposed at 205–207°.

Anal. Calcd. for Pd(C₂H₅NH₂)₂Br₂: Pd, 29.91. Found: Pd, 29.9.

5. ***cis*-Dinitrodiethylaminepalladium(II).**—The *cis*-dinitrodiethylaminepalladium(II) isomer was prepared in a manner similar to the preparation of the *cis*-dinitrodiamminepalladium(II) isomer by Mann.³ A solution of 65 ml. of 33% ethylamine in 40 ml. of water was used to dissolve 5.6 g. of dibromodiethylaminepalladium(II), and to this was added 40 ml. of water containing 10 g. of sodium nitrite. This solution was placed in an evaporating dish in a desiccator over concentrated sulfuric acid. The first crystals formed at 10–12° and had the *cis* configuration. The precipitate was collected by filtration, washed with two 10-ml. portions each of water, ethanol, ether and dried at 100–110° for two hours. The yield of the *cis* isomer was only about 10%.

Anal. Calcd. for Pd(C₂H₅NH₂)₂(NO₂)₂: Pd, 36.93. Found: Pd, 37.0.

6. ***trans*-Dinitrodiethylaminepalladium(II).**—The *trans* isomer was prepared in the same manner as the *cis*-dinitrodiethylaminepalladium(II) complex at a temperature of 35–40°. The yield was about 90%.

7. **Dibromodi-*n*-propylaminepalladium(II).**—A rose red precipitate formed when 5 g. of palladium(II) bromide dissolved in 15 ml. of 40% hydrobromic acid was added while stirring to 30 ml. of equal volumes of *n*-propylamine and water.

Since only the yellow forms of the dibromo- or dichloro-diammine complexes have been used in this investigation, this form was prepared as follows: Thirty milliliters of water was added and the solution heated over a water-bath for 20 minutes. The rose red precipitate dissolved leaving a small light gray precipitate. The hot solution was filtered into 30 ml. of hydrobromic acid. A yellow precipitate

formed which was purified by redissolving it in 25 ml. of 2 *M* *n*-propylamine and again filtering the solution into 20 ml. of hydrobromic acid. The yellow dibromodi-*n*-propylaminepalladium(II) was separated by filtration, washed with two 10-ml. portions each of water, ethanol and ether, and dried in an oven at 100–110°. A 40% yield of crystals, decomposing at 204–205°, was obtained.

Anal. Calcd. for Pd(*n*-C₃H₇NH₂)₂Br₂: Pd, 27.73. Found: Pd, 27.5.

8. ***trans*-Dinitrodi-*n*-propylaminepalladium(II).**—Dibromodi-*n*-propylaminepalladium(II) (10.74 g.) was dissolved in 800 ml. of a hot 0.17 *M* solution of *n*-propylamine and 5 g. of sodium nitrite dissolved in 10 ml. of water was added. The solution was placed in a desiccator over concentrated sulfuric acid at a temperature of 10–12°. After about 8 days, a set of crystals was removed. The filtrate was placed in the desiccator. After 13 days the next set of crystals was removed by filtration, washed with two 10-ml. portions each of ethanol and ether, and dried over calcium chloride. This was found to be the *trans*-dinitroamine-*n*-propylaminepalladium(II) complex. The yield was approximately 20%.

Anal. Calcd. for Pd(*n*-C₃H₇NH₂)(NH₃)(NO₂)₂: Pd, 38.82. Found: Pd, 38.9.

9. **Diiododiamminepalladium(II) (Red Form).**—The red diiododiamminepalladium(II) was prepared by dissolving 10.4 g. of palladium(II) iodide in 300 ml. of 3 *M* ammonia. The solution was stirred mechanically for 30 minutes before it was filtered. Forty per cent. hydriodic acid was added to the filtrate until the solution was neutral to litmus. A yellow precipitate was collected by filtration, washed with two 20-ml. portions each of water, ethanol and ether. Upon drying the precipitate over calcium chloride, the crystals became dark red in color. The yield was about 90%.

Anal. Calcd. for Pd(NH₃)₂I₂ (red form): Pd, 27.04. Found: Pd, 26.9.

10. **Diiododiamminepalladium(II) (Yellow Form).**—The yellow form of the diiododiamminepalladium(II) complex was prepared by adding an aqueous 1 *M* solution of hydriodic acid to the ammonia solution of palladium(II) iodide until no more yellow diiododiamminepalladium(II) formed. This required only about one third of the HI necessary for complete neutralization of the excess ammonia remaining in the solution. The solution was cooled in an ice-bath before filtering. The yellow crystals were washed with two 20-ml. portions of ether and dried over calcium chloride in an evaporated desiccator. The yield was about 80%.

It is of interest to note that the red form was converted to the yellow form merely by dissolving the red diiododiamminepalladium(II) in excess ammonia and treating the tetrammine ion as described above.

Anal. Calcd. for Pd(NH₃)₂I₂ (yellow form): Pd, 27.04. Found: Pd, 27.2.

11. **Iodonitrodiamminepalladium(II).**—The red form of diiododiamminepalladium(II), 9.29 g., was dissolved in a solution of 15 ml. of concentrated ammonia in 55 ml. of water and 12 g. of sodium nitrite in 20 ml. of water was added. The combined solution was placed in a desiccator over concentrated sulfuric acid at 25–30°. As crystals formed, they were removed by filtration, washed with two 10-ml. portions each of water, ethanol and ether and dried over calcium chloride. The yield of iodonitrodiamminepalladium(II) was about 70%.

Anal. Calcd. for Pd(NH₃)₂NO₂I: Pd, 34.01; N, 13.4. Found: Pd, 34.2; N, 13.3.

12. **Diiododiethylaminepalladium(II).**—One hundred and fifty milliliters of a hot solution containing 50 ml. of 33% ethylamine in 100 ml. of water was added to 8.128 g. of palladium(II) iodide, but the palladium(II) iodide was only partially dissolved. The solution was cooled to 50° and 150 ml. of 9.2 *M* ethylamine was added to the warm suspension. This was heated just to the boiling point and stirred vigorously for 30 minutes to expel part of the excess ethylamine. Most of the remaining palladium(II) iodide dissolved during this treatment. The hot, light yellow solution was filtered and the filtrate made neutral to litmus with hydriodic acid. The solution was cooled in an ice-bath after which the yellow crystals were collected by filtration, washed with two 10-ml. portions each of water, ethyl alcohol and diethyl ether, and dried over calcium chloride. The yield was about 95%.

Anal. Calcd. for $\text{Pd}(\text{C}_2\text{H}_5\text{NH}_2)_2\text{I}_2$: Pd, 23.67. Found: Pd, 23.9.

13. **Iodonitrodiethylaminepalladium(II) Tetrahydrate.**—Eighty milliliters of 33% aqueous ethylamine was dissolved in 50 ml. of water and added to 8.94 g. of diiododiethylaminepalladium(II). A very small light gray precipitate formed which was removed by filtration. A solution of 11.3 g. of sodium nitrite in 50 ml. of water was added to the filtrate. This was placed in a desiccator over concentrated sulfuric acid at room temperature. As the red crystals of $\text{Pd}(\text{C}_2\text{H}_5\text{NH}_2)_2(\text{I})(\text{NO}_2)\cdot 4\text{H}_2\text{O}$ formed, they were removed by filtration, washed with two 5-ml. portions each of water, ethyl alcohol and ether, and dried over calcium chloride. The yield was about 70%.

Anal. Calcd. for $\text{Pd}(\text{C}_2\text{H}_5\text{NH}_2)_2\text{NO}_2\text{I}\cdot 4\text{H}_2\text{O}$: Pd, 24.26; N, 9.6. Found: Pd, 24.4; N, 9.8.

14. **Diiododi-*n*-propylaminepalladium(II).**—Palladous iodide (7.165 g.) was dissolved in a mixture of 200 ml. of *n*-propylamine in 150 ml. of water to give a light green solution. The solution was evaporated to about one-half its original volume and filtered while hot. A grayish-white precipitate formed in the filtrate, which redissolved upon heating. The hot solution was made slightly acid to litmus with HI. A yellowish-red precipitate of diiododi-*n*-propylaminepalladium(II) formed. After the solution cooled, the precipitate was collected by filtration, washed with two 10-ml. portions each of ethyl alcohol and ether, and dried over calcium chloride. The yield was about 90%.

Anal. Calcd. for $\text{Pd}(\text{n-C}_3\text{H}_7\text{NH}_2)_2\text{I}_2$: Pd, 22.28. Found: Pd, 22.2.

15. **Iodonitrodi-*n*-propylaminepalladium(II) Tetrahydrate.**—This compound was prepared in a manner similar to the preparation of the corresponding complexes of ammonia and ethylamine. Diiododi-*n*-propylaminepalladium(II) (7.63 g.) was dissolved in a solution of 230 ml. of 2 *M* *n*-propylamine. A small light gray precipitate was formed and was removed by filtration. A solution of 11.0 g. of sodium nitrite in 20 ml. of water was added to the filtrate. A large white precipitate formed and was removed by filtration. The filtrate was placed in a desiccator over concentrated sulfuric acid at room temperature.

The crystals were removed as they formed, washed with a 5-ml. portion each of ethyl alcohol and ether, and dried over calcium chloride. The yield was only about 6%.

Anal. Calcd. for $\text{Pd}(\text{n-C}_3\text{H}_7\text{NH}_2)_2(\text{NO}_2)\text{I}\cdot 4\text{H}_2\text{O}$: Pd, 22.71; N, 8.95. Found: Pd, 22.9; N, 8.9.

16. **Dinitrobisdiethylaminepalladium(II).**—The dinitrobisdiethylaminepalladium(II) complex was prepared by a method similar to the preparation of dinitrodiamminepalladium(II).³ To a solution of 32 ml. of diethylamine in 330 ml. of water was added 4.50 g. of dichlorobisdiethylaminepalladium(II). This was heated just to boiling for two minutes. A slight amount of decomposition of the complex occurred at this temperature. When the solution cooled, a small white precipitate formed, and this was removed by filtration. A solution of 7.2 g. of sodium nitrite in 12 ml. of water was added to the filtrate. The filtrate was evaporated in a desiccator over concentrated sulfuric acid at room temperature. As crystals formed, they were removed from the solution, washed with a 5-ml. portion each of ethyl alcohol and ether, and dried over calcium chloride. The yield was about 65%.

Anal. Calcd. for $\text{Pd}[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2(\text{NO}_2)_2$: Pd, 30.93. Found: Pd, 30.6.

17. **Dicyanodiamminepalladium(II).**—The dicyanodiamminepalladium(II) was prepared by the method of Feigl and Heisig.¹¹ Palladium(II) cyanide (2.43 g.) was suspended in 75 ml. of water, and 50 ml. of 6 *M* aqueous ammonia was added. The solution was filtered to remove the small traces of impurities. The filtrate was evaporated to about one-third of its original volume. The white precipitate of dicyanodiamminepalladium(II) was removed by filtration, washed with 100 ml. of water and dried over calcium chloride. The yield was about 30%.

Anal. Calcd. for $\text{Pd}(\text{NH}_3)_2(\text{CN})_2$: Pd, 55.34. Found: Pd, 55.1.

F. **Reactions of PdA_2Br_2 with Sodium Nitrite.**—The method used for this study was analogous to the procedure outlined by Jonassen, *et al.*^{8,9}

Compounds of the type PdA_2Br_2 (where A = ammonia, ethylamine or *n*-propylamine) were dissolved in a solution of the corresponding amine so that the mole ratio of palladium to amine was about 1:8. To the dissolved complex was added 4 *M* sodium nitrite, giving a mole ratio of sodium nitrite to palladium of about 8:1. The solution was divided into three equal volumes and one was placed in a desiccator over concentrated sulfuric acid at each of the temperatures 10–12, 25–30 and 35–40°. The crystals were successively collected, washed and dried according to the directions given under the respective preparations. The results obtained from this study are summarized in Table II.

TABLE II

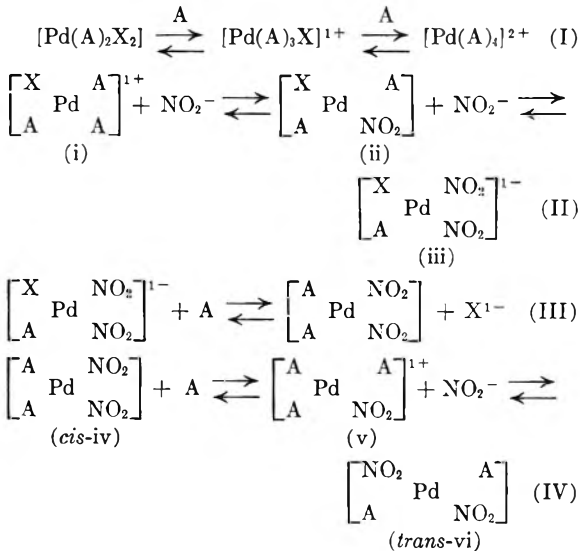
FORMATION OF $\text{Pd}(\text{A})_2(\text{NO}_2)_2$ FROM $\text{Pd}(\text{A})_2\text{Br}_2$

A	Total % <i>cis</i>	Total % <i>trans</i>	Temp., °C.
Ammonia	40.3	34.2	10–12
Ammonia	15.8	56.0	25–30
Ammonia	0.0	64.8	35–50
Ethylamine	3.3	89.3	10–12
Ethylamine	0.0	70.8	25–30
Ethylamine	0.0	66.7	35–40
<i>n</i> -Propylamine	0.0	0.0	10–12
<i>n</i> -Propylamine	0.0	38.5	25–30
<i>n</i> -Propylamine	0.0	26.4	35–40

No data are listed for the cyano or iodo complex since no dinitrodiamminepalladium(II) was formed in those reactions.

Discussion of Results

A reaction mechanism postulated by Jonassen and Cull⁸ not only explains all the observations made during this investigation, but is also in complete accord with Tschernaiev's concept of "trans elimination"



A. **Change in Halide Group.**—If the above mechanism is correct, replacement of the chloro group by the bromo or iodo group should make it easier to form the *trans*-nitrohalo complex (ii) because of the greater *trans*-labilizing power of these groups compared to the chloro group.¹²

The greater double bond character of the palladium-bromide bond would be expected to make it more difficult to displace the bromo group by the amine than was the case with the chloro group, thus decreasing the concentration of the *cis*-

(11) F. Feigl and G. Heisig, *J. Am. Chem. Soc.*, **73**, 5630 (1951).

(12) J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50**, 201 (1952).

dinitro isomer in step II to an extent insufficient for precipitation. This in turn would lead only to the precipitation of the *trans*-dinitro isomer. A comparison of the data from the previous work⁸ with Table II shows that an appreciable decrease in the yields of the *cis* isomer has occurred.

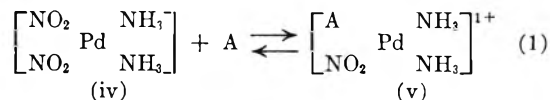
Due to the still greater double bond character in the metal-iodide bond for the iodo complex, the equilibrium between (i), (ii) and (iii) should be displaced toward the *trans*-iodonitrodiammine complex (ii). For this complex the concentration of (ii) became so large that *trans*-nitroiododiamminepalladium(II) precipitated under the experimental conditions; thus no dinitrodiammine complex was obtained.

However, *trans*-nitroiododiamminepalladium(II) (ii) dissolved when excess nitrite ion and ammonia were added and the *trans*-dinitrodiamminepalladium(II) isomer precipitated from the solution after long standing at 10–12°. This is additional evidence for the postulated reaction mechanism.⁸

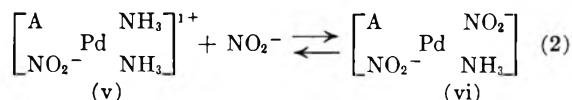
Experiments with the cyano group, one of the most powerful *trans*-labilizing ones, resulted only in the reprecipitation of dicyanodiamminepalladium(II) from the amine solution of the complex in the presence of excess sodium nitrite. Since the cyano group was so tightly held in dicyanodiamminepalladium(II), ammonia could not replace the more stable group from the coördinating sphere to form the intermediate (i) of Reaction II. Since this intermediate was postulated as necessary to obtain the dinitro isomers (iv) and (vi), these should not be formed even in the presence of excess nitrite ions, as was verified experimentally.

B. Effects of Temperature Variations.—The greater solubility of the *cis* isomer at elevated temperatures explains why no *cis* isomer is obtained at elevated temperatures, and only the less soluble *trans* isomer precipitates.

C. Reaction of *cis*-Dinitrodiamminepalladium(II) with *n*-Propylamine.—If *cis*-dinitrodiamminepalladium(II) were dissolved in an aqueous solution of *n*-propylamine, the following reactions could be expected to take place if reaction IV of the postulated reaction mechanism represents the over-all reaction. (A represents *n*-propylamine)



In the presence of an excess of nitrite ion in the reaction mixture, the following reaction should then occur



Upon evaporation over concentrated sulfuric acid, dinitroamine-*n*-propylaminepalladium(II) precipitated as postulated.

The NO₂⁻ group in (iv) was replaced by the neutral group A, resulting in the mixed triamine ion (v). When allowed to react with another NO₂⁻ group the *trans* effect led to the mixed ammine *trans*-dinitro compound.

Reaction IV thus represents a valid mechanism for the formation of the *trans* isomer from the *cis* isomer where the neutral groups, A, may or may not be the same. This seems to verify the original mechanism⁸ which postulated the formation of the *trans* isomer by displacement of one of the *cis*-nitro groups by the excess of amine present in solution.

Acknowledgment.—The authors are indebted to the Office of Naval Research which gave financial support for this and continuing investigations.

INFRARED STUDIES OF INORGANIC COÖRDINATION COMPOUNDS. II. INFRARED AND RAMAN SPECTRA OF 1,2-DITHIOCYANATOETHANE IN RELATION TO A NEW TYPE OF OPTICAL ISOMERISM OF COÖRDINATION COMPOUNDS

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From the infrared and Raman spectra of 1,2-dithiocyanatoethane it has been shown that the molecules are present in the *trans* form in the solid state, but exist in the *trans* and *gauche* forms in chloroform solution. By the comparison of these spectra with that of 1,2-dithiocyanatoethanedichloroplatinum(II), it has been concluded that the chelate ligand is in the *gauche* form which gives rise to a new type of optical isomerism of coördination compounds. Conclusive evidence has been provided against the presence of the *cis* form, tacitly assumed for chelate ligands of the type XH₂C-CH₂X.

Introduction

Considerable evidence based on spectroscopic,

thermal and electric measurements has been accumulated to indicate that 1,2-disubstituted ethanes, XH₂C-CH₂X, exist in the *trans* and *gauche* forms in the gaseous and liquid states and in solutions, and they exist only in the *trans* form

(1) Presented in part before the 125th meeting of the American Chemical Society, March, 1954. Supported in part under AEC Contract AT(11-1)-38. Radiation Project of the University of Notre Dame.

in the solid state.² The *trans* form has the symmetry of C_{2h} and the *gauche* form the symmetry of C_2 , the latter being obtained from the former by $ca. \pm 120^\circ$ internal rotation about the C-C axis. Quagliano and Mizushima³ have indicated that when a ligand of this type is present in coordination complexes it gives rise to a new type of optical isomerism, since the *gauche* form exists in two forms which are non-superposable mirror images (see Fig. 1). This is of great interest concerning the stereochemistry of coordination compounds, and therefore it is desirable to demonstrate conclusively the presence of the *gauche* form and the absence of the *cis* form, the latter tacitly assumed to be present in such complexes. As will be shown in this paper, such evidence is provided by measurements of the infrared and Raman spectra together with consideration of the selection rule.

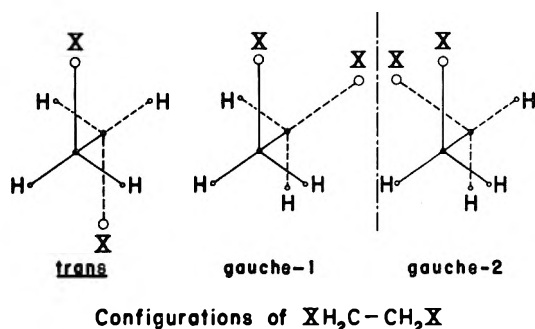


Fig. 1.—Stable forms of XH_2C-CH_2X as viewed along the C-C axis.

Experimental Results and Discussion

In Table I are listed the infrared and Raman spectra of 1,2-dithiocyanatoethane, $NCSH_2C-CH_2-SCN$, in the solid state. The former have been obtained using the KBr disk⁴ and Nujol mull techniques with a Perkin-Elmer spectrophotometer Model 21, and the latter with a spectrometer of high luminosity of our own construction.⁵

It is readily seen from this table that none of the infrared frequencies coincides with any of the Raman frequencies, except for the accidental coincidences. For example, the symmetric and antisymmetric $C\equiv N$ frequencies have the same value. Therefore, it can definitely be concluded that 1,2-dithiocyanatoethane in the solid state is in the *trans* form, the only form with a center of symmetry among all the conceivable structures formed by internal rotation about the C-C axis.

All the absorption bands observed in the spectrum of 1,2-dithiocyanatoethane in the solid state have been found in the spectrum of its saturated chloroform solution at practically the same frequencies, except for the bands at or near the strong absorption bands of chloroform. Due

(2) For the summary of this work see, *e.g.*, S. Mizushima, "Internal Rotation," Academic Press, New York, N. Y., 1954, or "Peter C. Reilly Lectures in Chemistry," Volume 5 (1951), The University of Notre Dame Press, Notre Dame, Indiana. See also S. Mizushima, Y. Morino, I. Watanabe, T. Shimanouchi and S. Yamaguchi, *J. Chem. Phys.*, **17**, 591 (1949).

(3) J. V. Quagliano and S. Mizushima, *J. Am. Chem. Soc.*, **75**, 6084 (1953).

(4) M. M. Stimson and M. J. O'Donnell, *ibid.*, **74**, 1805 (1952).

(5) See for example first reference of (2).

TABLE I
INFRARED AND RAMAN FREQUENCIES ASSIGNED TO THE
FUNDAMENTAL VIBRATIONS OF 1,2-DITHIOCYANATOETHANE
AND 1,2-DITHIOCYANATOETHANEDICHLOROPLATINUM(II)

Raman Solid	Infrared		Assignment
	Solid	Co- ordina- tion complex CHCl ₃ soln.	
292 (4)			<i>trans</i> $\nu(C-C-S)$ A_g
	660(m)	660(m)	<i>trans</i> $\nu(C-S)$ B_u
673 (2b)			<i>trans</i> $\nu(C-S)$ A_g
	680(m)	677(m)	<i>trans</i> $\nu(C-S)$ B_u
722 (6)			<i>trans</i> $\nu(C-S)$ A_g
	749(s)	a	<i>trans</i> $\nu(C-S)$ A_u
		847(s)	<i>gauche</i> CH_2 -rock. B
		929(m)	<i>gauche</i> CH_2 -rock. A
1037 (2)			<i>trans</i> $\nu(C-C)$ A_g
	1052(m)	a	<i>gauche</i> $\nu(C-C)$ A
	1110(m)	1100(w)	<i>gauche</i> CH_2 -twist. A or B
	1145(m)	1140(m)	<i>trans</i> $\nu(C-H)$ -twist. A_u
	1220(s)	1215(s)	<i>trans</i> $\nu(C-H)$ -wag. B_u
	1280(m)	1285(s)	<i>gauche</i> CH_2 -wag. A or B
1291 (3)			<i>trans</i> CH_2 -wag. A_g
	1410(s)	1419(s)	<i>gauche</i> CH_2 -bend. A or B
	1423(s)		<i>trans</i> $\nu(C-H)$ -bend. B_u
1422 (1)		1423(s)	<i>trans</i> $\nu(C-H)$ -bend. A_g
	2155(s)	2170(s)	<i>trans</i> $\nu(C\equiv N)$ B_u
2160 (7)			<i>trans</i> $\nu(C\equiv N)$ A_g
	2165(s)	2170(s)	<i>gauche</i> $\nu(C\equiv N)$ A and B
2947 (3)		a	$\nu(C-H)$
	2960(w)	a	
2986 (2b)		a	
3010 (1b)	2993(sh)	a	
	3140(s)	a	

a The frequency region where the absorption peak cannot be measured accurately due to the absorption of chloroform.

to the inevitable small difference in the absorption path of chloroform between the sample and reference cells, the absorption bands of 1,2-dithiocyanatoethane in the region of strong absorptions of the solvent may not be detected or may be deformed to such an extent that the exact position of the absorption peak is unobtainable. Taking this into account it is concluded that the *trans* configuration also exists in chloroform solution.

In addition to the *trans* absorption bands referred to above, many others are present in the spectrum of the chloroform solution and these should be assigned to the normal vibrations of another stable molecular form of 1,2-dithiocyanatoethane. Furthermore, these absorption bands are essentially the same as those found in the spectrum of the coordination complex, 1,2-dithiocyanatoethanedichloroplatinum(II), in which none of the bands due to the *trans* form has been observed. This shows that the ligand of the complex is present in this other stable form and not in the *trans* form. The most important point of this problem lies, therefore, in the determination of the spacial configuration of the other stable form of 1,2-dithiocyanatoethane. Such a type of chelate has been tacitly assumed to be present in the *cis* form in metal coordination complexes but, as will be shown below, 1,2-dithiocyanatoethane ligand is present in the *gauche* form with the symmetry of C_2 .

The normal frequencies of 1,2-dichloroethane as an eight-body problem have been calculated and all the observed frequencies could be assigned to the normal vibrations of the *trans* and the *gauche*

molecules.⁶ In the solid state only the *trans* form exists, whereas both *trans* and *gauche* forms are present in solutions and in the liquid and gaseous states as referred to above. Thus a strong absorption band of the *trans* form at 768 cm.⁻¹ and two strong absorption bands of the *gauche* form at 880 and 941 cm.⁻¹ are assigned to the CH₂-rocking vibrations, one of the two rocking vibrations of the *trans* form being forbidden in infrared absorption by the selection rule. It is impossible that the *cis* form be present in place of the *gauche* form, since the *cis* form would show only one CH₂-rocking frequency at about 740 cm.⁻¹ corresponding to the B₂-vibration of C_{2v}. The other CH₂-rocking frequency of the hypothetical *cis* form, corresponding to A₂-vibration of C_{2v} (calculated to be 937 cm.⁻¹), is forbidden in the absorption.⁷

It will be shown in the next section that the CH₂-rocking frequencies of 1,2-dithiocyanatoethane are not much different from those of 1,2-dichloroethane. Thus we can assign the strong band of the *trans* form at 749 cm.⁻¹ and the two strong bands of the other form at 847 and 929 cm.⁻¹ to the CH₂-rocking vibrations. This shows that the other stable form of 1,2-dithiocyanatoethane is the *gauche* form and definitely not the *cis* form, since the latter would show only one absorption band in the frequency region referred to above. It should be noted that no frequency other than CH₂-rocking vibration can appear for this kind of molecule in this frequency region, as has been shown by one of us.⁸ Therefore, conclusive evidence is presented that the ligand in the coordination complex is in the *gauche* form, which gives rise to a new type of optical isomerism presented in our previous note,³ since this form consists of two non-superposable mirror images.

The values of interatomic distances of this complex are also compatible with the *gauche* form of the ligand. The fact that the C≡N frequency of the ligand at 2160 cm.⁻¹ is not appreciably changed on complex formation indicates that coordination takes place through the sulfur atoms; furthermore, the complex shows the usual color and chemical properties characteristic of Pt-S coordination compounds. On the basis of the sum of bond radii, the bond length of Pt-S is calculated to be 2.36 Å., from which the distance between two sulfur atoms of the ligand in the planar square complex is found to be 3.35 Å. This corresponds to the distance between the two sulfur atoms, when the ligand is in the *gauche* form. If the ligand were in the *cis* form, the distance between the two sulfur atoms would amount to 2.75 Å., which would be too small to be the distance between the two non-bonded sulfur atoms. Studies of other coordination compounds containing ligands with internal rotation axes are under investigation.

Normal Vibrations.—The normal vibrations of a molecule as 1,2-dithiocyanatoethane can be approximately divided into two groups, the skeletal

vibrations⁹ and the hydrogen vibrations.¹⁰ For the calculations of these vibrations we shall use the Urey-Bradley field which has been shown to be useful in the treatment of such molecules.¹¹ The corresponding force constants for the calculation of skeletal vibrations are shown in Table II, and those for the calculation of hydrogen vibrations in Table III.

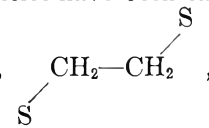
TABLE II
FORCE CONSTANTS IN 10⁵ DYNES/CM. FOR SKELETAL VIBRATIONS

Stretching force constant	Deformation force constant	Repulsive force constant
$K(\text{CH}_2-\text{CH}_2) = 3.7$	$H\alpha(\text{CH}_2-\text{CH}_2-\text{S}) = 0.15$	$F_q(\text{CH}_2 \dots \text{S}) = 0.50$
$K(\text{CH}_2-\text{S}) = 2.6$		$F_q' = -1/10 F_q$

TABLE III
FORCE CONSTANTS IN 10⁵ DYNES/CM. AND INTRAMOLECULAR TENSION IN 10¹¹ DYNES/CM. FOR HYDROGEN VIBRATIONS

Deformation force constant	Repulsive force constant	Intramolecular tension
$H\alpha(\text{H}-\text{C}-\text{H}) = 0.40$	$F_q(\text{H} \dots \text{H}) = 0.10$	$\kappa = 0.10$
$H\alpha(\text{H}-\text{C}-\text{S}) = 0.04$	$F_q(\text{H} \dots \text{S}) = 0.80$	
$H\alpha(\text{H}-\text{C}-\text{C}) = 0.15$	$F_q(\text{H} \dots \text{C}) = 0.40$	

These force constants have been shown to yield the computed frequency values in good agreement with those observed for molecules with similar structures.^{9,10}

The skeletal frequencies have been calculated as a four-body problem,  at azi-

muthal angles of internal rotation, 0, 90, 120 and 180°, where 0° corresponds to the *trans* form and 180° to the hypothetical *cis* form. The results are shown in Table IV. The computed values of

TABLE IV
COMPUTED VALUES OF SKELETAL FREQUENCIES AT DIFFERENT AZIMUTHAL ANGLES OF INTERNAL ROTATION

Mode	0° (<i>trans</i>)	90°	120° (<i>gauche</i>)	180° (<i>cis</i>)	obsd. for <i>trans</i>
$\delta(\text{C}-\text{C}-\text{S})$	291	300	251	129	292
A $\nu(\text{C}-\text{S})$	724	670	664	672	722
$\nu(\text{C}-\text{C})$	997	996	996	996	1037
B $\delta(\text{C}-\text{C}-\text{S})$	222	385	410	406	^a
$\nu(\text{C}-\text{S})$	718	698	710	736	680

^a This frequency is Raman inactive and is too low to be observed with NaCl optics.

hydrogen deformation frequencies consisting of the bending, wagging, twisting and rocking frequencies⁶ are listed in Table V.

Based on these computed values, we can assign the observed frequencies as shown in the last column of Table I. We have not calculated the C-H and C≡N stretching frequencies, but undoubtedly these can be assigned to the bands observed at about 3000 cm.⁻¹ and those at 2160 cm.⁻¹, respectively. Furthermore, it should be noted that our calculation includes only two C-S

(6) I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953); I. Nakagawa, *J. Chem. Soc. Japan*, **74**, 848 (1953); **75**, 178 (1954).

(7) S. Mizushima, I. Nakagawa, I. Ichishima and T. Miyazawa, *J. Chem. Phys.*, forthcoming publication.

(8) I. Nakagawa, to be published shortly.

(9) S. Mizushima, T. Shimanouchi, I. Nakagawa and A. Miyake, *J. Chem. Phys.*, **21**, 215 (1953).

(10) I. Nakagawa, to be published shortly.

(11) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949)

TABLE V
COMPUTED VALUES OF HYDROGEN DEFORMATION FRE-
QUENCIES FOR THE *trans* AND *gauche* FORMS

Mode	<i>trans</i>	<i>gauche</i>
CH ₂ -bending	A _g 1455	A 1455
	B _u 1455	B 1455
CH ₂ -wagging	A _g 1300	A 1201
	B _u 1302	B 1332
CH ₂ -twisting	A _u 1098	A 1103
	B _g 1104	B 1100
CH ₂ -rocking	A _u 760	A 911
	B _g 929	B 858

vibrations, whereas actually there are four C-S vibrations for one molecular form. Therefore, the

assignment shown in Table I includes more C-S frequencies than are expected from our calculation of skeletal frequencies.

In the frequency region from 750 to 1500 cm.⁻¹ we observe only the various hydrogen deformation frequencies except for the C-C stretching frequencies. Among the deformation frequencies, the CH₂-rocking frequencies are most important in our structural problem as referred to in the preceding section. Now we have shown definitely that the absorption band at 749 cm.⁻¹ of the solid must be assigned to the rocking vibration of the *trans* form, or A_u vibration of C_{2h}, and those at 855 and 918 cm.⁻¹ of the chloroform solution and those at 847 and 929 cm.⁻¹ of the complex, to the rocking vibrations of the *gauche* form, or B and A vibrations of C₂.

THE RESOLUTION AND RACEMIZATION OF POTASSIUM ETHYLENEDIAMINETETRAACETATOCOBALTATE(III)

BY F. P. DWYER, E. C. GYARFAS AND D. P. MELLOR

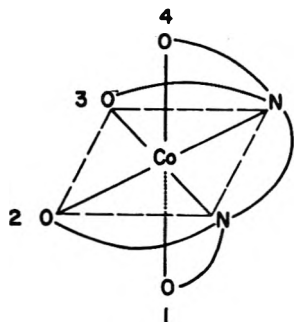
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The complete resolution of the ethylenediaminetetraacetatocobaltate(III) ion has been carried out through the optically active tris-ethylenediaminecobalt(III) cation, and the rate of racemization determined at 100°. Replacement of the sexadentate ligand with ethylenediamine can be effected with partial retention of configuration.

Recently, active solutions of one of the enantiomeric forms of the ethylenediaminetetraacetatocobaltate(III) ion were obtained by Busch and Bailar,¹ through the strychnine salt or by adsorption on optically active quartz. The separation can be effected even more conveniently with *d*-tris-ethylenediaminecobalt(III) chloride which yields the crystalline diastereoisomer *d*-[Co(en)₃] *d*-[Co(enta)₂]Cl·4H₂O. After elimination of the resolving agent as the sparingly soluble salt of the tri-iodide anion, pure crystalline *d*-potassium ethylenediaminetetraacetatocobaltate(III) was obtained. The other enantiomer was obtained in a similar manner using *l*-tris-ethylenediaminecobalt(III) chloride.

In aqueous solution the active forms were stable at 30° for two weeks. Racemization occurred, however, at 100°, with an approximate half-life of 170 minutes.



Sexadentate function has been postulated for the ethylenediaminetetraacetate group in many suitable metal complexes such as Fe(III), Cr(III) and Co(III) and the infrared studies of Busch and Bailar¹ support this view for the Co(III) complex. The anhydrous salt has been found to be diamagnetic, a result already obtained by Klemm² for the dihydrate. Schwarzenbach,³ however, has demonstrated that the cobalt complex may have the ethylenediaminetetraacetate group as a quinquadentate, a molecule of water, hydroxyl or some other anion occupying the sixth position. This is not at variance with the magnetic data, since even the hydrated cobalt(III) ion is diamagnetic. Nevertheless it may be inferred that at least one Co-O bond is easily broken, and racemization could occur at elevated temperatures through a 5-covalent intermediate. The demonstration of Busch and Bailar¹ that the *active* bromo-(ethylene diaminetetraacetato)-cobaltate(III) ion may be transformed into *active* ethylenediaminetetraacetatocobaltate(III) ion with silver nitrate is not definitive, since the reaction was performed at room temperature. However, it seems more probable that racemization occurs by rupture of at least two Co-O bonds such as 1 and 4 (Fig. 1), when the resulting 4-covalent intermediate can have a plane of symmetry. Recombination can then generate either antipode, but the possibility of intramolecular change of the still asymmetric intermediates following rupture of bonds in the *cis* position 2,3 or 3,4,^{1,2} cannot be precluded.

(1) D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **75**, 4574 (1953).

(2) W. Klemm, *Z. anorg. Chem.*, **252**, 229 (1944).

(3) G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 839 (1949).

Potassium ethylenediaminetetraacetatocobaltate (III) reacted rapidly with 50% ethylenediamine at 30–35° with the formation of the tris-ethylenediaminecobalt(III) ion. With the active forms, partial retention of configuration occurred in the reaction. If it is assumed that it is the Co–O bonds that rupture first, it is evident that ethylenediamine acting as a monodentate ligand can replace any of the four oxygen atoms, and subsequently fill another *cis* position.

In this process, replacement may be partly effected so as to maintain the configuration provided the asymmetric 5-covalent or 4-covalent intermediates do not undergo rapid intramolecular racemization at this temperature. Thus, the experiment, though interesting, gives no information on the mechanism of replacement or of racemization.

Experimental

Rotations were measured in a 1 dm. tube at 20°.

d-Tris-ethylenediaminecobalt(III), *d*-Ethylenediaminetetraacetatocobaltate (III) Chloride Tetrahydrate.—Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared by heating a mixture of cobalt(II) chloride hexahydrate (8 g.), potassium acetate (20 g.) and ethylenediaminetetraacetic acid (10 g.) in water (60 ml.) to nearly boiling and adding gradually to the deep red solution 3% hydrogen peroxide (30 ml.). Addition of alcohol to the cooled deep violet red solution gave an almost quantitative yield of the salt. This method is superior to that of Brintzinger, Thiele and Muller.⁴ At 105° the salt was dehydrated (loss of H₂O (calcd.), 8.5, found 8.3%). The anhydrous salt was diamagnetic $\psi_g = 0.17 \times 10^{-6}$ c.g.s. units.

The potassium salt (5 g.) in water (70 ml.) was treated with *d*-tris-ethylenediaminecobalt(III) chloride (1.5 g.), potassium chloride (2 g.), cooled to 10° and fractionally precipitated with alcohol. The precipitate of the diastereoisomer crystallized on scratching and standing. The least soluble fractions, which were dextro in the Hg₅₄₆₁ line, were recrystallized from water by adding alcohol, and gave pink needles. A solution in water, 0.02%, gave $\alpha_{5461} = +0.09^\circ$, but showed no rotation in the N_{AD} line.

Anal. Calcd. for C₂₆H₅₆N₁₀O₂₀ClCo₃: C, 30.0; H, 5.42; N, 13.46. Found: C, 30.1; H, 5.49; N, 13.36.

l-Tris-ethylenediaminecobalt(III), *l*-Ethylenediaminetetraacetatocobaltate(III) Chloride Tetrahydrate.—This was prepared in the same manner as the other diastereoisomer, using *l*-tris-ethylenediaminecobalt(III) chloride.

(4) H. Brintzinger, H. Thiele and U. Muller, *Z. anorg. Chem.*, **261**, 285 (1943).

Anal. Calcd. for C₂₆H₅₆N₁₀O₂₀ClCo₃: C, 30.0; H, 5.42; N, 13.46. Found: C, 30.0; H, 5.42; N, 13.1.

d-Potassium Ethylenediaminetetraacetatocobaltate(III) Trihydrate.—The appropriate diastereoisomer (1 g.) in water (20 ml.) was treated with potassium iodide (2 g.) and glacial acetic acid (5 drops) and cooled to 4°. Hydrogen peroxide (5 ml. of 3%) was added gradually and the dark brown precipitate of Co(en)₃I₃ filtered off. Addition of alcohol gave the required potassium salt, which after dissolution in a little water and reprecipitation with alcohol yielded purplish red micaceous plates. A 0.02% aqueous solution gave $\alpha_{5461} +0.20^\circ$, $\alpha_D -0.03^\circ$, $\alpha_{4100} -0.19^\circ$ whence $[\alpha]_{5461}^{20} +1000^\circ$, $[\alpha]_{20D}^{20} -150^\circ$, $[\alpha]_{4100}^{20} -950^\circ$. The molecular rotations, $([M]_D)_{\lambda}^T = [\alpha]_{\lambda}^T \cdot M \times 10^{-2}$, were, respectively, +4,400°, -660° and -4,180°. The values quoted by Busch and Bailar are calculated $[M] = [\alpha] \cdot M$. It will be evident that the complex anion has a considerable anomalous rotatory dispersion but the molecular rotations are less than a tenth of those found for the cobalt complexes of the Schiff bases from the dithiadiamines.⁵

Anal. Calcd. for C₁₀H₁₈N₂O₁₁CoK: C, 27.27; H, 4.09; N, 6.36. Found: C, 27.3; H, 4.0; N, 6.4.

l-Potassium Ethylenediaminetetraacetatocobaltate(III) Trihydrate.—This was prepared in the same manner as the dextro compound above. A 0.02% solution gave $\alpha_{5461} -0.20^\circ$; $\alpha_D +0.03^\circ$, $\alpha_{4100} +0.19^\circ$.

Anal. Calcd. for C₁₀H₁₈N₂O₁₁CoK: C, 27.27; H, 4.09; N, 6.36. Found: C, 27.4; H, 4.06; N, 6.4.

Racemization.—A 0.02% aqueous solution was maintained at 100° in a thermostat, in a vessel fitted with a reflux condenser. Samples withdrawn at intervals were rapidly chilled and the rotations observed at 20°. Results were calculated from the expressions $K = 2.3/2t \log \alpha_0/\alpha_t$, and $T_{1/2} = 2.3/2K \log 2$, where K is the unimolecular rate constant, α_0 is the initial rotation, α_t is the rotation after time t minutes, and $T_{1/2}$ is the half-life. The mean value of K was found to be $2.06 \times 10^{-3} \text{ min.}^{-1}$, whence the mean half-life is 168 min.

Reaction with Ethylenediamine.—The finely powdered dextro salt (0.2 g.) was shaken with 50% ethylenediamine (3 ml.) at 30° for two minutes, when the initial violet red color had changed to orange. The solution was diluted to 50 ml. and the rotation observed. This gave $\alpha_D +0.15^\circ$. From the stoichiometry of the reaction, and the specific rotation of the Co(en)₃⁺⁺⁺ ion,⁶ the calculated rotation, assuming no loss of configuration, is 0.56°. The identity of the product was checked by isolation of trisethylenediaminecobalt(III) iodide.

Anal. Calcd for C₆H₂₄N₆I₃·Co·3H₂O: Co, 8.74. Found: Co, 8.8.

(5) F. P. Dwyer and F. Lions, *J. Am. Chem. Soc.*, **69**, 2917 (1947); F. P. Dwyer, N. S. Gill, E. C. Gyarfás and F. Lions, *ibid.*, **74**, 4188 (1952).

(6) A. Werner, *Ber.*, **45**, 124 (1912).

PROPERTIES OF ACIDOCOBALTAMMINES. III.
cis-NITRITOTETRAMMINES¹

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cis-Nitritoaquo-, nitroaquo, and dinitritotetramminecobalt(III) nitrates were prepared, and the rates of their conversion to *cis*-nitroaquo-, *trans*-nitroaquo- and *cis*-dinitrotetramminecobalt(III), respectively, were studied. The formation of *cis*-dinitrotetramminecobalt(III) salts from cobalt(II) is discussed.

Although *trans*-dinitrotetramminecobalt(III) salts can be prepared directly from those of cobalt(II),² salts of the *cis*-dinitrotetramminecobalt(III) series are only obtained from carbonatotetramminecobalt(III).^{3,4}

The purpose of the present paper is to examine more closely the formation of the *cis*-dinitrotetramminecobalt(III) ion in order to discover why it cannot be made directly from cobalt(II) in large quantities.

Results

Three new complex nitrates in the *cis*-tetramminecobalt(III)⁵ series were prepared. Two of these, *cis*-nitritoaquo and *cis*-dinitrito nitrate, were prepared directly from carbonate and *cis*-diaquo nitrate. Attempts to obtain these *cis*-nitrito complex ions from *trans*-diaquo nitrate were unsuccessful.

The third compound, *cis*-nitroaquo nitrate, was obtained when *cis*-nitritoaquo nitrate was allowed to stand in the dry state. Upon standing in aqueous solution both of these compounds were converted into *trans* nitroaquo nitrate. However, either in the dry state or in aqueous solution *cis*-dinitrito nitrate forms *cis*-dinitro nitrate. The theoretical intermediate compound, *cis*-nitritonitro nitrate, could not be identified by means of its absorption spectrum during the conversion of the dinitrito to the dinitro complex. Attempts to prepare *cis*-nitritonitro nitrate from both *cis*- and *trans*-nitroaquo nitrate were also unsuccessful.

The chemical properties of the *cis*-nitritoaquo, *cis*-nitroaquo, *cis*-dinitrito and of *trans*-diaquo nitrate were determined. Each of these ions reacted with concentrated hydrochloric acid at room temperature to form *trans*-dichloro chloride and with 50% nitric acid at 80° to form nitroaquo nitrate. The *cis*-nitritoaquo nitrate, and *cis*-nitroaquo nitrate as well as *cis*-diaquo nitrate react with weakly acid solutions of sodium nitrite at room temperature to form *cis*-dinitro nitrate. However *trans*-diaquo nitrate reacts with weakly acid solutions of sodium nitrite to form *trans*-dinitro nitrate.

First-order reaction rates were observed for the

(1) The work on this paper was supported by a Cottrell grant from the Research Corporation of America.

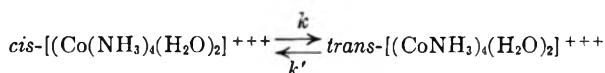
(2) S. M. Jorgensen, *Z. anorg. Chem.*, **5**, 469 (1894).

(3) S. M. Jorgensen, *ibid.*, **5**, 163 (1894); **17**, 473 (1898).

(4) C. Duval, *Compt. rend.*, **182**, 636 (1926), obtained a mixture of nitrocobaltamines including *cis*-dinitrotetramminecobalt(III) directly from cobalt(II) without isolating the intermediate carbonatotetramminecobalt(III).

(5) Unless otherwise noted all of the compounds to be discussed belong to the tetramminecobalt(III) series. For purposes of abbreviation this part of the name of the compounds will be eliminated.

conversion of the *cis*-diaquo complex into the *trans*-form, for the conversion of the *cis*-nitritoaquo ion to the more stable *cis*-nitroaquo ion and for the intramolecular rearrangement of the *cis*-dinitrito ion to form the stable *cis*-dinitro complex. Although the latter reaction may take place in two steps, only one was observed at this time. These results are listed in Table I. Each figure is an average of four measurements. The equilibrium constant for the reaction



was found to be 6.0 ± 0.5 at both 20 and 30°. No equilibrium was observed for the *cis*-*trans* conversion of the nitroaquo ion.

TABLE I

RATES OF REACTION IN THE *cis*-TETRAMMINE SERIES

Reactant	Product	$k \times 10^2, \text{min.}^{-1}$		E_a kc./mole
		20°	30°	
Diaquo	<i>trans</i> -Diaquo	0.72	3 3	25,000
Nitritoaquo	<i>cis</i> -Nitroaquo		2 3	
Dinitro	<i>cis</i> -Dinitro	1.1	1.9	8,300
Nitroaquo	<i>trans</i> -Nitroaquo		0.05	

Discussion

The configuration of nitroaquotetramminecobalt(III) nitrate reported here was determined by comparing its chemical properties with those of *trans*-nitroaquo nitrate⁶ and *cis*- and *trans*-dinitro nitrate. The reaction products of these four salts with sodium nitrite and concentrated HCl at 30° and with 50% HNO₃ at 80° are given in Table II. The similarity in the properties of *cis*-dinitro nitrate and the nitroaquo nitrate obtained here as well as their generic relationship indicate that the latter has the *cis* configuration. Attempts to determine the configuration of this compound by comparing its absorption spectrum in the ultraviolet region with that of the *trans* isomer were inconclusive.

TABLE II

REACTIONS OF Compound	Reagent HCl	HNO ₃	Nitrates NaNO ₂
A. Products of the <i>cis</i> Series			
Nitroaquo	Dichloro	Diaquo	<i>cis</i> -Dinitro
Dinitro	Dichloro	Diaquo	
B. Products of the <i>trans</i> Series			
Nitroaquo	Chloronitro	Nitroaquo	<i>trans</i> -Dinitro
Dinitro	Chloronitro	Nitroaquo	

(6) S. M. Jorgensen, *Z. anorg. Chem.*, **7**, 289 (1894); J. Meyer and K. Grohler, *ibid.*, **155**, 99 (1926).

Because the nitritocobaltamines are more sensitive to mineral acids than the nitro isomers⁷ these reactions cannot be used to establish their configuration. It has been assumed, however, that the nitrito-nitro conversion does not involve a change in the configuration of the complex ion.⁸ If this assumption is correct, then the nitritoquo and dinitrito ions will have the same configuration as the *cis*-nitroquo and *cis*-dinitro ions, respectively.

In addition to *cis*-nitritoquo tetramminecobalt(III) nitrate and dinitritotetramminecobalt(III) nitrate, salts of *cis* and *trans*-dinitrito-bis-(ethylenediamine)-cobalt(III)⁹ and dinitritodipyridiamminecobalt(III)^{9,10} as well as nitritopentamminecobalt(III)¹¹ are well known. The occurrence of nitrito-nitro-bis-(ethylenediamine)-cobalt(III) has also been reported.¹² The formation of these compounds which are unstable and undergo rearrangements in the dry state to form the corresponding stable nitro complexes, indicates that the preparation of all nitro complexes from aquo ions in aqueous solution may involve the formation of intermediate nitrito complexes.

The stepwise formation of *cis*-dinitrotetramminecobalt(III) and the apparent greater stability of the *trans* isomers of the nitroquo and *trans*-diaquo complex ions provided added information as to why the *cis*-dinitro salts are not prepared directly from cobalt(II). In the preparation of *trans*-dinitrotetramminecobalt(III) salts² air is passed through a mixture of cobalt(II) and ammonium salts, sodium nitrite and aqueous ammonia for four hours. During this time the pH of the mixture decreases from approximately 9 to 7. The solution is then allowed to stand for 12 hours before the reaction product is filtered, washed free of nitropentamminecobalt(III) and a little of the more soluble *cis*-dinitro salts and then recrystallized. During the initial period of oxidation the only mononuclear cobaltamines present will be hydroxopentamminecobalt(III) and some dihydroxotetramminecobalt(III).¹³ As the ammonia is expelled and the concentration of the aquo ions increases, they will begin to react at a measurable rate with sodium nitrite at a pH of 7.¹⁴ Any nitropentamminecobalt(III) which is formed can react further with sodium nitrite to form *trans*-dinitrotetramminecobalt(III),¹⁵ while *trans*-diaquo tetramminecobalt(III) also reacts with sodium nitrite to form the *trans*-dinitro complex ion. Furthermore, because of the slow conversion of *cis*-nitritoquo tetramminecobalt(III) to the more stable

trans form, some of the reaction product of the *cis*-diaquo ion with sodium nitrite will be found as *trans*-dinitrotetramminecobalt(III). As a result of these various reactions very little *cis*-dinitrotetramminecobalt(III) will be obtained from cobalt(II).

Experimental

Preparation of Compounds.—Carbonatotetramminecobalt(III) nitrate was used as the starting material for all of the other cobaltamines. *cis*-Diaquo and *cis*-dinitro nitrates were prepared in the usual way. *trans*-Dinitro nitrate was prepared from *trans*-diaquo nitrate by means of the procedure used for the preparation of *cis*-dinitro nitrate from carbonate and *cis*-diaquo nitrates.

A. *trans*-[Co(NH₃)₄(H₂O)₂](NO₃)₃.—This compound was prepared by the partial precipitation of the equilibrium mixture of *cis*- and *trans*-diaquo nitrates by the addition of an equal volume of 50% nitric acid at room temperature and then chilling the reaction mixture. The red product was filtered, washed with alcohol and ether, and dried in a desiccator. The product obtained was recrystallized by dissolving in water at 5° and reprecipitating with nitric acid until a constant absorption spectrum was obtained. The final product may still contain a small percentage of the *cis* isomer.

Anal. Calcd. for *trans*-[Co(NH₃)₄(H₂O)₂](NO₃)₃: Co, 17.28. Found: Co, 17.19, 17.24.

Absorption spectrum maximum at 306, 357, 512 min. at 285, 326 and 417 mμ.

B. *cis*-[Co(NH₃)₄H₂O(ONO)](NO₃)₂.—A solution of 5 g. of carbonatotetraamminecobalt(III) nitrate and 10 g. of sodium nitrite in 100 ml. of water is cooled in an ice-salt bath at 0°. Twenty-five ml. of 10 N nitric acid is now added and the solution maintained at 0–2°. After five minutes, a carmine red precipitate is transferred to a sintered glass filter with the aid of suction and washed with two 5-ml. portions of cold 2 N nitric acid, followed by cold alcohol and ether. The product must be stored in a refrigerated desiccator; yield 2.4 g. or 48%.

Anal. Calcd. for [Co(NH₃)₄H₂O(ONO)](NO₃)₂: Co, 18.71. Found: Co, 18.65, 18.69.

Absorption spectrum maximum at 335 and 510 min. at 303 and 442 mμ.

C. *cis*-[Co(NH₃)₄(ONO)₂]NO₃.—Five grams of carbonatotetramminecobalt(III) nitrate is dissolved in 40 ml. of water at 5° with the aid of 3.5 ml. of 16 N concentrated nitric acid. Ten grams of solid sodium nitrite is then added and the solution stirred for ten minutes at 5°. The red precipitate is filtered, washed with two 5-ml. portions of cold 2 N nitric acid, alcohol and ether. The dry product should be kept cold.

Anal. Calcd. for [Co(NH₃)₄(ONO)₂]NO₃: Co, 19.84. Found: Co, 19.80, 19.83.

Absorption spectrum maximum at 355 and 510 min. at 335 and 444 mμ.

D. *cis*-[Co(NH₃)₄H₂ONO₂]NO₃.—*cis*-Nitritoquo tetramminecobalt(III) is allowed to stand at room temperature for four days. Absorption spectrum maximum at 242, 330 and 472 min. at 232, 292 and 420 mμ.

Spectrophotometric Measurements.—The absorption spectra of the unstable complexes were determined over the range of 220–600 mμ by means of a Beckman Model DU spectrophotometer using quartz cells of 1-cm. path length. Measurements were made as quickly as possible at 1° by circulating water from an ice-bath through the compartment surrounding the cells. Freshly prepared samples were examined repeatedly over small ranges until constant results were obtained. During the kinetic measurements thermostated water was circulated through the cell compartment which was thus maintained at 20 ± 0.1° or 30 ± 0.1°.

Kinetic Measurements.—The rates of conversion of *cis*-nitritoquo and the *cis*-dinitrotetramminecobalt(III) into the corresponding *cis*-nitro isomers and the *cis*-*trans* isomerization of the diaquo complex ion were determined by following the change in the optical densities of their solutions containing 0.001 M perchloric acid. The wave lengths chosen corresponded to a maximum absorption difference between the two forms. Both of the nitrito com-

(7) R. Weiland, "Complex Compounds," Stuttgart, 1924, pp. 44, 64.

(8) A. Werner, *Ber.*, **40**, 769, 779 (1907).

(9) A. Werner, *ibid.*, **40**, 769, 779, 785 (1907).

(10) B. Adell, *Acta Chem. Scand.*, **4**, 1 (1950).

(11) S. M. Jorgensen, *Z. anorg. Chem.*, **5**, 169 (1893); B. Adell, *Compt. rend.*, **262**, 272 (1944). Although C. Duval and J. Lecompte, *Bull. soc. chim.*, [5] **12**, 678 (1945), question the formation of this compound, the work of Adell has been duplicated in this Laboratory, while that of Duval has been shown to be in error.

(12) F. Basolo, B. D. Stone, J. C. Bergmann and R. G. Pearson, *J. Am. Chem. Soc.*, **76**, 3079 (1954); R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, *ibid.*, **76**, 5920 (1954).

(13) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen, 1941, p. 253.

(14) R. G. Yalman and T. Kuwana, *THIS JOURNAL*, in press.

(15) N. R. Dhar, *Akad. Amsterdam. Versl.*, **28**, 551 (1920).

plexes were studied at 330 $m\mu$ and their rate constants were determined from typical first order plots of $\log(D_\infty - D_0)/(D_\infty - D_t)$. The diaquo ions were examined at 285 $m\mu$ using the relationship $\ln(D_0 - D_{eq})/(D_t - D_0) = k(1 + (1/K))$ where D_{eq} is the observed optical density when equilibrium is established between the two isomers and K is the equilibrium constant. The latter value was determined from the relationship $K = (e_{cis} - e_{eq})/(e_{trans} - e_{eq})$ in solutions containing 0.001 M $HClO_4$.

Because of the similarity between the absorption spectra

of *cis*- and *trans*-nitroaquotetramminecobalt(III) ions the rate of conversion of the *cis* to *trans* isomer had to be estimated by treating solutions of the complex with hydrochloric acid and determining the relative amounts of red nitrochloro- and green dichlorotetramminecobalt(III) formed. This method is crude and only provided an order of magnitude of the reaction rate.

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POLAROGRAPHIC BEHAVIOR OF ISOMERIC INORGANIC COÖRDINATION COMPOUNDS

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A study was made of several *cis* and *trans* isomers to determine whether differences in polarographic behavior at the dropping mercury electrode are sufficient to distinguish between the *cis* and *trans* isomers in solution. Experiments to establish satisfactory conditions and polarographic reductions of several pairs of isomers, with and without supporting electrolyte, are reported.

Several physical methods for distinguishing isomers of inorganic coördination compounds in solution have been studied. This paper describes studies which have been made from the polarographic point of view, both in the absence and in the presence of supporting electrolyte.

Polarographic Studies in the Absence of Supporting Electrolyte.—The possibility of distinguishing between isomers polarographically in the absence of supporting electrolyte depends upon the measurement of postulated differences in the migration current component of the limiting current. A *cis* ion containing two negative groups and four neutral groups coördinated about the central metal ion has an appreciably larger internal dipole than the corresponding symmetrical *trans* isomer. The *cis* isomer, with greater resulting orientation in the unsymmetrical field around the dropping mercury electrode, would thereby be expected to migrate to the electrode at a different rate than the *trans* form. The migration current, a significant part of the limiting current in the absence of supporting electrolyte, would then be different for the *cis* ion than for the *trans*.

Laitinen and Holtzclaw¹ investigated the conditions under which polarograms could be obtained in the absence of supporting electrolyte. Dinitrotetramminecobalt(III) chloride was selected for

the first experiments. Table I shows that in the presence of gelatin and camphor, as maximum suppressors, the limiting current for the *cis* compound is consistently higher than for the *trans* in both reduction steps. Gelatin and camphor each suppressed the maxima partially and improved stability of the solution but had a significant effect upon limiting current values.

The polarographic runs were made within 30 minutes after the dry salt was dissolved in conductivity water. A change in limiting current values was noted with time, probably due to aqua-

TABLE II

EFFECT OF TIME UPON LIMITING CURRENT 0.001 M *cis*- AND *trans*-DINITROTETRAMMINECOBALT(III) CHLORIDE

Concn. of ethanol, %	Approx. time since preparation of soln.	Limiting current, $\mu a.$	
		Co(III) \rightarrow Co(II)	Co(II) \rightarrow Co
No supporting electrolyte			
<i>trans</i> Isomer			
None	30 min.	2.20	16.50
None	45 min.	2.06	16.56
None	14 hr.	1.84	8.86
None	95.5 hr.	0.83	1.56
5	30 min.	1.85	17.02
5	45 min.	1.79	17.08
5	2.5 hr.	1.79	14.77
15	30 min.	2.03	14.99
15	45 min.	2.03	14.69
25	30 min.	1.97	14.53
25	45 min.	1.97	14.23
25	22 hr.	1.66	4.17
75	30 min.	2.26	No wave
75	45 min.	2.44	No wave
<i>cis</i> Isomer			
None	30 min.	3.48	17.82
None	45 min.	3.18	17.37
None	9 hr.	2.06	7.14
None	12 hr.	2.14	6.99
25	30 min.	2.44	17.02
25	45 min.	2.44	17.02

TABLE I

EFFECT OF GELATIN AND CAMPHOR ON LIMITING CURRENT 0.001 M *cis*- AND *trans*-DINITROTETRAMMINECOBALT(III) CHLORIDE

Isomer	Nature	No supporting electrolyte		
		Maximum suppressor Concn., %	Co(III) \rightarrow Co(II)	Co(II) \rightarrow Co
<i>cis</i>	None	..	3.48	17.82
<i>trans</i>	None	..	2.20	16.50
<i>cis</i>	Gelatin	0.01	3.81	15.24
<i>trans</i>	Gelatin	.01	3.51	14.42
<i>cis</i>	Camphor	0.01	3.16	15.60
<i>trans</i>	Camphor	.01	3.09	15.37

(1) H. F. Holtzclaw Jr. Ph.D. Thesis. University of Illinois, 1947.

tion followed by hydrolysis of the aquo complex and precipitation of cobalt oxide. Table II indicates the effect of time upon the limiting current in solutions of the dry salt dissolved in conductivity water with and without ethanol. The presence of ethanol has the desirable effects both of decreasing the maxima and decreasing the aquation effect. The visible maximum in the first wave is removed when at least 25% ethanol is used and the maximum in the second wave is decreased markedly. In 75% ethanol, no second wave occurs. In the presence of at least 25% ethanol, the limiting current is satisfactorily constant over a period of 30 to 45 minutes required to dissolve the dry salt, remove oxygen from the solution and make the polarogram.

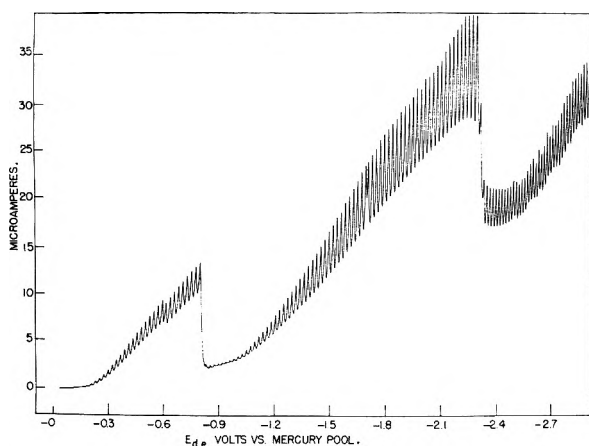


Fig. 1.—0.001 *M* *trans*-[Co(NH₃)₄(NO₂)₂]Cl in conductivity water; no supporting electrolyte.

Waves in the absence of supporting electrolyte differ considerably from those with a supporting electrolyte. Figures 1 and 2 show typical polarograms illustrative of the effect of ethanol upon the maxima.

Table III summarizes polarographic values obtained by Holtzclaw and Sheetz² for three pairs of isomers in the absence of supporting electrolyte. *cis*-Dinitrotetramminecobalt(III) chloride has consistently produced higher limiting current values than the corresponding *trans* isomer in the absence of supporting electrolyte. The *trans* isomers of dinitrobisethylenediaminecobalt(III) nitrate and nitroisothiocyanatobisethylenediaminecobalt(III)

TABLE III

LIMITING CURRENTS IN THE ABSENCE OF A SUPPORTING ELECTROLYTE

Concentration, 0.001 *M*. Reduction step Co(III) to Co(II) only

Compound	Limiting current, μ a.	Solvent
<i>cis</i> -[Co(NH ₃) ₄ (NO ₂) ₂]Cl	2.28	<i>a</i>
<i>trans</i> -[Co(NH ₃) ₄ (NO ₂) ₂]Cl	2.20	<i>a</i>
<i>cis</i> -[Co(en) ₂ (NO ₂) ₂]NO ₃	3.09	<i>b</i>
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂]NO ₃	3.48	<i>b</i>
<i>cis</i> -[Co(en) ₂ (NCS)(NO ₂)]Cl·H ₂ O	3.00	<i>b</i>
<i>trans</i> -[Co(en) ₂ (NCS)(NO ₂)]Cl·H ₂ O	3.12	<i>b</i>

^a 75 ml. of 95% ethanol diluted with water to 100 ml. Water.

(2) D. P. Sheetz, Ph.D. Thesis, University of Nebraska, 1952.

chloride monohydrate show higher limiting currents than the corresponding *cis* forms.

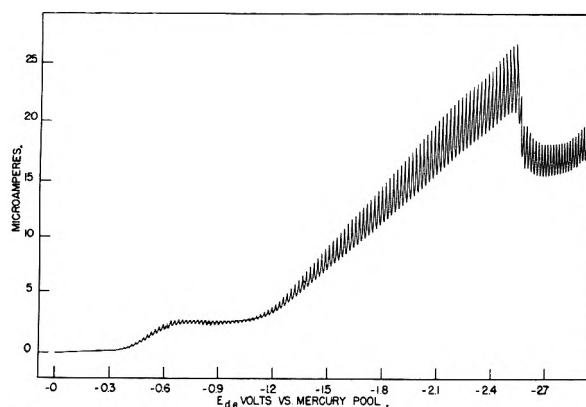


Fig. 2.—0.001 *M* *trans*-[Co(NH₃)₄(NO₂)₂]Cl in 25% ethanol; no supporting electrolyte.

cis- and *trans*-dichlorobispropylenediaminecobalt(III) chloride were prepared and studied but were found to be too unstable in dilute solution for satisfactory polarographic results.

The formation of electrolyte during the reduction (nitrite ions, for example) and stirring effects associated with maxima which may not disappear even at more negative potentials are troublesome factors arising in the absence of supporting electrolyte. It seems apparent that difficulties inherent in the experimental method make polarographic reductions in the presence of supporting electrolyte, described in the next section, more promising as a method of distinguishing between *cis* and *trans* isomers in solution.

Polarographic Studies in the Presence of Supporting Electrolyte.—Herda³ measured half-wave potentials of several cobalt coordination compounds, a few of which possessed *cis* and *trans* isomers. Later work by Laitinen, Bailar, Holtzclaw and Quagliano⁴ showed that relative trends were indicated in Herda's work but the absolute values were affected significantly by the presence of 0.02% gelatin, used to suppress maxima, and a minute drop of octyl alcohol, used to prevent foaming of the gelatin solution.

Willis, Friend and Mellor,⁵ using *N* and 0.1 *N* potassium sulfate and 0.1 *N* sodium acetate without the use of maximum suppressing agents, studied the polarographic behavior of a number of cobalt coordination compounds, including two pairs of *cis* and *trans* isomers. The *cis*-dinitrotetramminecobalt(III) ion showed a more positive first half-wave potential than the *trans* form. The second half-wave potential was the same for both forms, within experimental error, this being ascribed by the authors to aquation of the cobalt(II) complex before reduction to metallic cobalt. *cis*- and *trans*-dichlorotetramminecobalt(III) ions were shown to aquate readily and to give identical half-wave potentials corresponding to those expected for an aquated form of cobalt(III). The authors

(3) M. G. Herda, M.S. Thesis, University of Illinois, 1943.

(4) H. A. Laitinen, J. C. Bailar, Jr., H. F. Holtzclaw, Jr., and J. V. Quagliano, *J. Am. Chem. Soc.*, **70**, 2999 (1948).

(5) J. B. Willis, J. A. Friend and D. P. Mellor, *ibid.*, **67**, 1680 (1945).

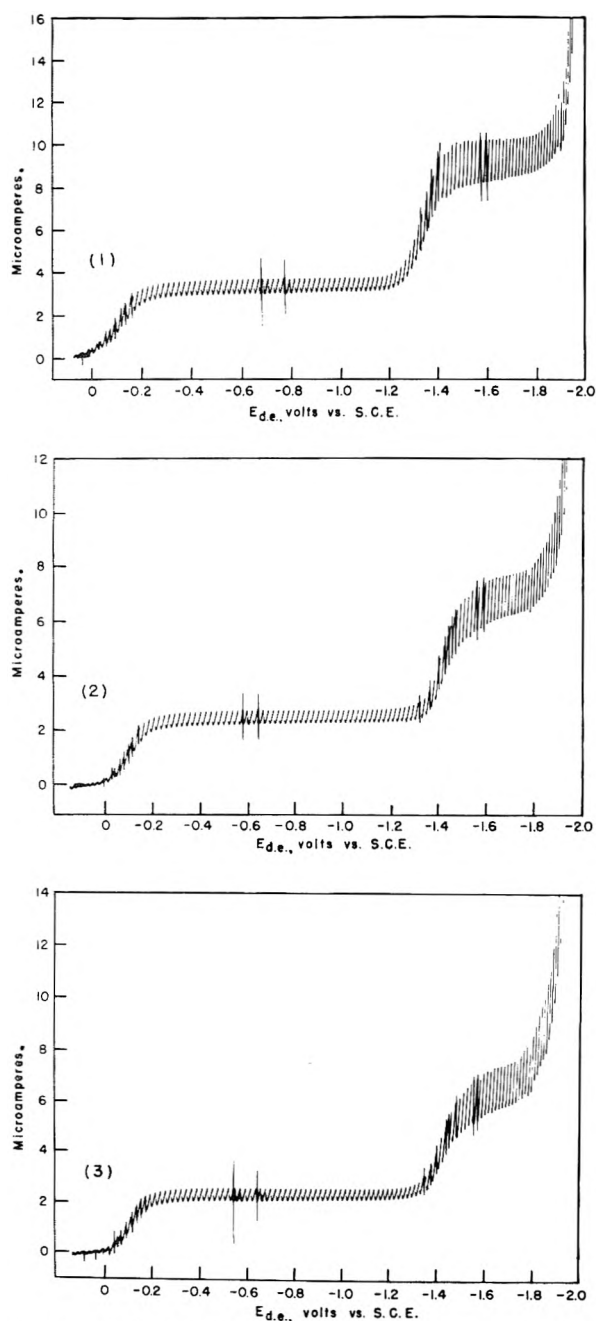


Fig. 3.—0.001 *M cis*-[Co(NH₃)₄(NO₂)₂]Cl in 0.1, 0.5 and 0.9 *M* potassium sodium tartrate, respectively.

showed, further, an effect upon their results when concentration of sulfate as supporting electrolyte was varied.

Studies were undertaken on various coordination compounds to determine more accurately optimum experimental conditions.^{4,6-8}

Figures 3 and 4 show the tendency for increasing concentrations of potassium sodium tartrate and potassium citrate to move the half-wave potentials of *cis*-dinitrotetramminecobalt(III) chloride to more negative values and to decrease the diffusion currents. Analogous results are obtained with the

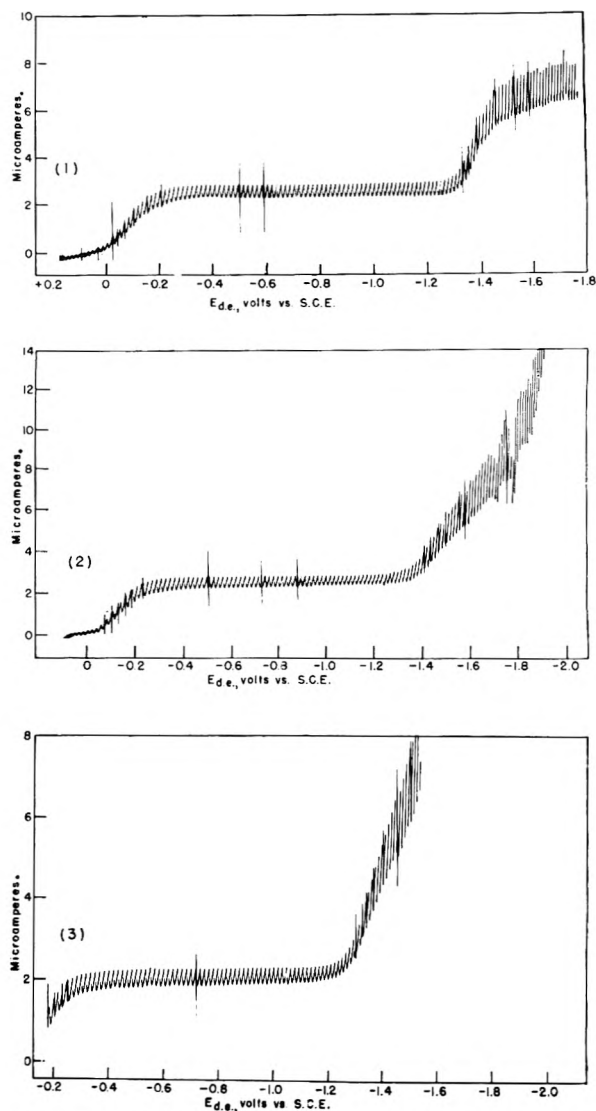


Fig. 4.—0.001 *M cis*-[Co(NH₃)₄(NO₂)₂]Cl in 0.1, 0.5 and 0.9 *M* potassium citrate, respectively.

trans isomer.⁶ Potassium sulfate causes a similar shift but of lower magnitude. Potassium chloride and potassium nitrate are satisfactory supporting electrolytes, having very little tendency to affect half-wave potentials or diffusion currents. The effects of various supporting electrolytes have been ascribed to "super complexing,"^{4,6} in which the supporting electrolyte ions are aggregated around the central complex ion by electrostatic attraction, and to a combination of "super complexing" and changes in solution viscosity.⁸

Holtzclaw and Sheetz⁹ have investigated the polarographic behavior of several *cis* and *trans* isomers of cobalt and chromium. All reductions studied were found to be irreversible. Table IV gives half-wave potentials and diffusion current data for the Co(III) to Co(II) wave. In general, the *cis* isomer has a more positive half-wave potential than the corresponding *trans* when two negative groups and four neutral groups are coordinated to the cobalt. An appreciably greater dipole exists within the coordination sphere of the *cis* ion

(6) H. F. Holtzclaw, Jr., *J. Am. Chem. Soc.*, **73**, 1821 (1951).

(7) H. A. Laitinen and P. Kivalo, *ibid.*, **75**, 2198 (1953).

(8) H. A. Laitinen, A. J. Frank and P. Kivalo, *ibid.*, **75**, 2865 (1953).

(9) H. F. Holtzclaw, Jr., and D. P. Sheetz, *ibid.*, **75**, 3053 (1953).

TABLE IV

POLAROGRAPHIC REDUCTION OF COBALT COÖRDINATION COMPOUNDS IN THE PRESENCE OF SUPPORTING ELECTROLYTE 0.1 *M* potassium chloride as supporting electrolyte unless otherwise noted; concn. reducible ion, 0.001 *M*; *m* = 1.397 mg. per second; temp. = 25.0 ± 0.1°; *n* = 1, Co(III) → Co(II).

Compound	$E_{1/2}$, v. vs. S.C.E.		Diffusion current, μ a.		Total	$\frac{i_d}{m^{2/3}t^{1/6}}$
	First wave	Aquation wave	First wave	Aquation wave		
Isomers containing greater internal dipole in <i>cis</i> form than in <i>trans</i>						
<i>cis</i> -[Co(NH ₃) ₄ (NO ₂) ₂]Cl	-0.05				2.84	1.69
<i>trans</i> -[Co(NH ₃) ₄ (NO ₂) ₂]Cl	- .21				2.96	1.77
<i>cis</i> -[Co(en) ₂ (NO ₂) ₂]NO ₃ ^a	- .24	-0.41	2.10	0.70	2.80	1.66
<i>trans</i> -[Co(en) ₂ (NO ₂) ₂]NO ₃ ^a	- .27	- .40	1.97	.88	2.85	1.69
<i>cis</i> -[Co(en) ₂ (NCS)(NO ₂)]Cl·H ₂ O ^{a,b}	- .04	- .38	2.15	.56	2.71	1.62
<i>trans</i> -[Co(en) ₂ (NCS)(NO ₂)]Cl·H ₂ O ^{a,b}	- .12	- .36	2.38	.44	2.82	1.67
Isomers containing the same or no internal dipole in both <i>cis</i> and <i>trans</i>						
<i>cis</i> -[Co(en) ₂ (NH ₃)(NO ₂)]Br ₂ ^c	-0.21	-0.40	1.86	0.93	2.80	1.66
<i>trans</i> -[Co(en) ₂ (NH ₃)(NO ₂)](NO ₃) ₂ ^d	- .20	- .40	1.86	.90	2.76	1.64
<i>cis</i> -[Co(en) ₂ (NH ₃)(NCS)](CNS) ₂ ^e	- .13	- .39	<i>e</i>	<i>e</i>	<i>e</i>	<i>e</i>
<i>trans</i> -[Co(en) ₂ (NH ₃)(NCS)](CNS) ₂	- .10	- .39	1.59	1.23	2.82	1.67
<i>cis</i> -[Co(en) ₂ (NH ₃) ₂]I ₃	- .31				2.74	1.63
<i>trans</i> -[Co(en) ₂ (NH ₃) ₂]Cl ₃ ·H ₂ O ^f	- .31				2.84	1.69

^a Two drops of 0.1% methyl red per 100 ml. of solution added as a maximum suppressor. ^b Supporting electrolyte: 0.1 *M* KNO₃. ^c Solution 0.002 *M* with respect to KNO₃. ^d Solution 0.002 *M* with respect to NaBr. ^e Contaminated with KSCN. ^f Solution 0.003 *M* with respect to KI.

than in the *trans* in this type of compound. Electrostatic repulsion of the adjacent centers of electronegativity may make the *cis* isomer less stable than the *trans* and hence easier to reduce. Those compounds for which the internal dipole should be about the same for both the *cis* and *trans* isomer (that is, those containing only one or no negative groups in the coördination sphere) do not show easier reduction on the part of the *cis* isomer.

Chatt suggests¹⁰ a somewhat different explanation based upon *trans* effect. Those ligands which have high *trans* influence are thought to coördinate by double bonds which utilize electrons from filled *d*-orbitals of the metal. Thus, the electron density on the metal atom is decreased and low valency states are stabilized. Nitro groups and thiocyanato groups, which have fairly high *trans* influence, might be expected to show more extensive double bonding when in the *cis* positions than when *trans* to each other. Hence, the lower valence state should be more stable when two groups of high *trans* influence are in *cis* positions. Those compounds in the second half of Table IV would not exhibit this difference inasmuch as they contain only one group of high *trans* influence.

The diffusion current constants in Table IV indicate that the relative rates of diffusion for the *cis* ions tend to be slightly lower than for the corresponding *trans* isomers.

Two distinct polarographic waves occurred for the Co(III) to Co(II) reduction step of compounds containing two ethylenediamine groups. The second of the two waves, occurring at about -0.40 volt *versus* the saturated calomel electrode, is attributed to an aquated complex in which one or more of the coördinated groups other than ethylenediamine are replaced by water. Evidences for this postulate are: (1) The second of the two waves consistently occurs at about -0.40 volt *versus* S.C.E. (2) Hydrated cobalt complexes similar to those postulated, *cis*- and *trans*-aquo-

hydroxobisethylenediaminecobalt(III) bromide and *cis*-diaquobisethylenediaminecobalt(III) bromide, each give half-wave potentials of -0.40 volt *versus* S.C.E. (3) Compounds known to aquate readily in dilute solution, *cis*-chloronitrobisethylenediaminecobalt(III) nitrate and *cis*- and *trans*-dichlorobisethylenediaminecobalt(III) chloride, each produce a wave at -0.40 volt *versus* S.C.E. (4) A contaminant would not likely be the same for all compounds studied nor would it seem probable that the half-wave potential would be the same (-0.40 volt) for different contaminants. Further evidence that contamination is not responsible for the second wave is given by five successive recrystallizations of *cis*-dinitrobisethylenediaminecobalt(III) nitrate which produced no change in polarographic behavior. It follows that the first wave is for the original complex species and the second for the aquated complex.

The relative heights of the two waves vary with different runs on a given compound but the total diffusion current for the two waves taken together is always the same, indicating that the concentration of each species is dependent upon age of the solution but the total concentration of reducible cobalt is independent of time.

Kivalo¹¹ has independently noted similar behavior, with a second wave at -0.40 volt, in the Co(III) to Co(II) reduction step of trimethylenediaminebisethylenediaminecobalt(III) chloride in 0.1 *N* sodium nitrate.

cis- and *trans*-diamminebisethylenediaminecobalt(III) ions show evidence of the second wave at -0.40 volt, but the first wave is sufficiently negative to merge partially, making accurate evaluation of the second wave impractical. All other ethylenediamine complexes studied give well characterized aquation waves, as reported in Table IV. The fact that no equation wave occurs for *cis*- and *trans*-dinitrotetramminecobalt(III) chloride is thought to be because of more extensive

(10) J. Chatt, private communication.

(11) P. Kivalo, private communication.

aquation involving displacement of ammonia molecules as well as nitrite ions and resulting in precipitation of cobalt oxide. No visible precipitation occurs under like circumstances with the ethylenediamine complexes.

Table V gives data for the isomeric glycine and alanine chelates of cobalt. The glycine isomers showed striking differences in polarographic behavior upon changing from a neutral to an acid solvent. The alanine isomers, extremely insoluble in water, were run in acid solution only. In a given solvent, the two isomers of each compound showed no significant differences in behavior.

TABLE V

POLAROGRAPHIC REDUCTION OF AMINO ACID DERIVATIVES
 $m = 1.397$ mg. per second; $n = 1$, Co(III) \rightarrow Co(II)

Compound	Concn., moles/l.	Supporting electrolyte	$E_{1/2}$, v. vs. S.C.E.	i_d , $\mu\text{a.}$	$\frac{i_d}{m^2/t^{1/2}}$
α -Co(CH ₂ NH ₂ COO) ₂ ·2H ₂ O	0.001	a	-0.04	2.78	1.63
β -Co(CH ₂ NH ₂ COO) ₂ ·H ₂ O	Almost saturated	a	-.03		
α -Co(CH ₂ NH ₂ COO) ₂ ·2H ₂ O	.001	b	+.04	2.24	1.35
β -Co(CH ₂ NH ₂ COO) ₂ ·H ₂ O	.001	b	+.04	2.28	1.37
α -Co(CH ₃ CHNH ₂ COO) ₂	.001	b	-.08	1.83	1.10
β -Co(CH ₃ CHNH ₂ COO) ₂	.001	b	-.07	1.96	1.15

^a 0.1 M KCl. ^b 25 ml. of 70.72% HClO₄ per 100 ml. of solution.

In addition to the cobalt compounds previously described, one or more isomers of the following ions were synthesized by Holtzclaw and Sheetz and studied for use in polarographic work but were found generally to be too unstable in dilute aqueous solution or too easily reduced for satisfactory results: dibromobisethylenediaminecobalt(III), dichlorobispropylenediaminecobalt(III), dichlorotetramminecobalt(III), dinitrooxalatodiammineco-

baltate(III), aquoamminebisethylenediaminecobalt(III), chloroamminebisethylenediaminecobalt(III), chloroaquobisethylenediaminecobalt(III), bisisothiocyanatobisethylenediaminecobalt(III), chloronitrobisethylenediaminecobalt(III), chloroisothiocyanatobisethylenediaminecobalt(III), dinitroethylenediaminepropylenediaminecobalt(III) and disulfatotetramminecobaltate(III).

Three chromium complex ions which appeared to have some promise of yielding usable results polarographically, dibromobisethylenediaminechromium(III), bisisothiocyanatobisethylenediaminechromium(III), and dichlorobisethylenediaminechromium(III), were prepared by Holtzclaw and Sheetz but were found to be too unstable in dilute solution or to reduce at too positive potentials for satisfactory results.

Experimental

Compounds were prepared by methods in the literature or modifications thereof except *trans*-dinitrobisethylenediaminecobalt(III) nitrate, for which a new method was developed.¹² Solutions were made by dissolving the dry salt in the appropriate solvent. Conductivity water of approximately 800,000 ohms specific resistance was used for the work in the absence of supporting electrolyte.

Potential measurements in the absence of supporting electrolyte were not critical and were made *versus* mercury pool to avoid contamination with electrolyte from the saturated calomel electrode.

Potentials in the presence of supporting electrolyte were measured against an external saturated calomel electrode by means of a standard potentiometer circuit. Cell temperature was maintained at $25.0 \pm 0.1^\circ$. Reversibility of electrode reactions was tested by determining the slopes of the plots of $\log i/(i_d - i)$ *versus* potential. Half-wave potentials were taken from the logarithmic plots.

A Fisher Elecdropode and Sargent Models XII and XXI Polarographs were used in the various stages of the investigations.

(12) H. F. Holtzclaw, Jr., D. P. Sheetz and B. D. McCarty, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p. 176.

MECHANISM OF SUBSTITUTION REACTIONS IN COMPLEX IONS. V. EFFECT OF CHELATION ON THE RATES OF ACID HYDROLYSIS OF SOME COBALT(III) COMPLEX IONS^{1,2}

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Contribution from the Chemistry Laboratories of Northwestern University, Evanston, Illinois

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Rates of acid hydrolysis have been measured for three series of complex ions of the types *cis*-[CoA₂Cl₂]⁺, *trans*-[CoA₂Cl₂]⁺ and [CoA₃Cl]⁺², in which the extent of chelation by the A groups is varied. It was found that in general the rate of acid hydrolysis decreased with increase in chelation. Arguments are presented to show that these results can be accounted for either on the basis of a dissociation (S_N1) or a displacement (S_N2) mechanism. It is, however, suggested that the observations are somewhat more consistent with an S_N1 process.

The difficulties encountered in any attempt to establish the mechanism of an acid-hydrolysis reaction for hexacovalent complexes was discussed in a

(1) Previous paper, F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, *J. Am. Chem. Soc.*, **76**, 3079 (1954).

(2) This investigation was supported by a grant from the United States Atomic Energy Commission under contract AT(11-1)89-Project No. 2.

(3) Based upon a portion of the thesis submitted by C. R. Boston to Northwestern University in August, 1953, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

recent review.⁴ Brown, Ingold and Nyholm⁵ suggest that the most obvious interpretation of the kinetic data on the acid-hydrolysis and base-hydrolysis reactions of [Co(NH₃)₅X]⁺² (X = Cl⁻, Br⁻, NO₃⁻) is that all these reactions take place by an S_N2 mechanism. Their interpretation is based upon the assumption that the base hy-

(4) F. Basolo, *Chem. Revs.*, **52**, 459 (1953).

(5) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2673 (1953).

hydrolyses involve an S_N2 process because these are known to be second-order reactions with first-order dependence on the concentration of the complex and on the concentration of the hydroxide ion. However, there exists also the possibility that the hydroxide ion dependence is due to an acid-base reaction with the ammine complex⁶ and that the resulting conjugate base reacts by a dissociation mechanism of the conjugate base. This mechanism is called $S_{N1}CB$ in reference 5.

In a previous paper in this series,⁷ it was reported that the rates of acid hydrolysis of several analogous cobalt(III) complexes increased with an increase in steric hindrance. The suggestion was made that these results were consistent with an S_{N1} mechanism. This paper presents the results of a similar study wherein an investigation was made to determine the effect of chelation on the rates of hydrolysis of some cobalt(III) complex cations.

Experimental

Preparation of Compounds.—All of the chemicals used in the synthesis of these complex compounds are commercially available. Diethylenetriamine and triethylenetetramine were purified by distillation over sodium at reduced pressure, whereas the purified tetraethylenepentamine was kindly furnished us by Professor Hans B. Jonassen.⁸ The known compounds were prepared essentially by the methods described in the literature (for references see footnotes to Tables I and II) and characterized by chloride analysis.

(a) Chloroamminetriethylenetetraminecobalt(III) Perchlorate.—A slurry of 5 g. of *cis*-[CotrienCl₂]Cl⁹ and 5 cc. of water contained in a mortar at room temperature was allowed to react with 10 cc. of concentrated aqueous ammonia. The reaction mixture was ground continuously until it had assumed a homogeneous pink color (approximately 20 min.). The pink crystalline slurry was transferred into 50 cc. of absolute ethanol and the insoluble product collected on a suction filter and washed free of ammonia with absolute ethanol. The crystals were then dissolved in 10 cc. of hot concentrated hydrochloric acid and the solution was digested on a steam-bath for 15 min. After allowing this solution to cool to room temperature, 3 cc. of concentrated perchloric acid was added. The crystalline product that separated was collected in a sintered-glass filter funnel, washed with a small amount of cold water followed by alcohol and finally ether. The salt was dried at 60°.

Anal. Calcd. for [CotrienNH₃Cl](ClO₄)₂: Cl, 7.95. Found: Cl, 7.83.

This complex is designated as the *cis* isomer in Table II, because it has been found difficult to cause the three chelate rings of trien to lie in one plane of an octahedral complex.¹⁰

(b) Chlorodiethylenetriamine-(ethylenediamine)-cobalt(III) Chloride.—A reaction mixture containing 5 g. of [Coen-NH₃(NO₂)₃],¹¹ 1.87 g. of trien and 75 cc. of water was kept on a steam-bath and continuously agitated until the solid completely dissolved (45 min.). The solution was then allowed to concentrate to 10 cc. and at this point 20 cc. of concentrated hydrochloric acid was added and the solution was boiled for approximately 1 hr. During this time oxides of nitrogen were liberated and the solution took on a pink appearance. An excess of ethanol and ether was added to the cold solution and this resulted in the separation of an oil. The oil became solid upon standing overnight. This pink

solid was collected on a filter, washed with alcohol and ether then air-dried at room temperature.

Anal. Calcd. for [Coen(dien)Cl]Cl₂: Cl (ionic), 21.6. Found: Cl (ionic), 21.7.

(c) Chlorotetraethylenepentaminecobalt(III) Chloride.—A mixture of 1.84 g. of [Co(NH₃)₂(NO₂)₃],¹² 18.5 cc. of 0.4 *M* tetraen, and 15 cc. of water was placed on a steam-bath and occasionally stirred until the solid completely dissolved (approximately 30 min.). The solution was then evaporated to 5 cc. and 15 cc. of concentrated hydrochloric acid was added and this acid solution was kept on the steam-bath for approximately 1 hr. Addition of excess alcohol and ether to the pink solution caused an oil to separate which did not solidify. Therefore the oil was extracted several times with absolute alcohol and the hygroscopic residue that remained was dried at 110°.

Anal. Calcd. for [CotetraenCl]Cl₂: Cl (ionic), 20.0; Cl (total), 30.0. Found: Cl (ionic), 20.4; Cl (total), 29.7.

Although the chloride analyses are in accord with the expected values for the compound [CotetraenCl]Cl₂, the kinetic data (Fig. 3) show this to be a mixture of two components. That this material is a mixture is not surprising because it is extremely soluble and could therefore not be purified by recrystallization.

Determination of Rates of Acid Hydrolysis.—The techniques employed to follow the rates of these reactions were described in a previous publication.⁷ Reactions of the dichloro compounds (Table I) were studied in 0.1 *M* HNO₃ solutions to minimize any interference due to replacement of the second chloro group. The concentration of the complex was approximately 0.005 *M*. Since these reactions are fairly rapid they were followed spectrophotometrically at 25 ± 0.1°. Measurements were made at 600 mμ because at this wave length there is a maximum change in optical density as the dichloro complexes change to the chloroaquo products.

The chloropentaminecobalt(III) complexes (Table II) react more slowly and their rates of reaction were followed by determining the rates of chloride ion formation. This was accomplished by the titration of small aliquots of the reaction mixture, taken at various times, with a standard solution of Hg(NO₃)₂ to a turbidity end point of Hg[Fe(CN)₆NO]. Reaction mixtures were approximately 0.005 *M* complex and 0.1 *M* HNO₃ and a temperature of 35 ± 0.1° was maintained.

Results

Rate constants were calculated for the spectrophotometric method by plotting $\log(D_{\infty} - D_0)/(D_{\infty} - D)$ vs. time, where D represents optical density. The initial optical density, D_0 , was determined by extrapolation to zero time. In each case the change in optical density was followed until a "leveling off" occurred and this was taken as D_{∞} . Such a point is reached because in acid solution the rate of acid hydrolysis of the second chloro group is extremely slow compared to that of the first. Duplicate measurements were made in every case with about 5% precision. A typical plot of data collected by this method is shown in Fig. 1 and average values of rate constants are given in Table I.

Rate constants were calculated for the titration method by plotting $\log[\text{chlorocomplex}]$ vs. time. Again duplicate measurements were made with about 5% precision and in every case but one the data gave good straight line plots for first-order reactions (Fig. 2). However as shown in Fig. 3 a straight line plot is not obtained with the material believed to be [CotetraenCl]Cl₂. It would appear from this plot that there are two components present, one reacting appreciably more rapidly than the other. If it is assumed that this

(6) J. S. Anderson, N. L. Spoor and H. V. A. Briscoe, *Nature*, **139**, 508 (1937); *J. Chem. Soc.*, 361 (1943).

(7) R. G. Pearson, C. R. Boston and F. Basolo, *J. Am. Chem. Soc.*, **75**, 3089 (1953).

(8) E. H. Gause, T. B. Crumpler and H. B. Jonassen, *ibid.*, **73**, 5457 (1951).

(9) The following symbols will be used in this paper: en = H₂NCH₂CH₂NH₂; dien = H₂NCH₂CH₂NHCH₂CH₂NH₂; trien = H₂NCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂; tetraen = H₂NCH₂CH₂NHCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂.

(10) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

(11) A. Werner, *Helv. Chim. Acta*, **1**, 10 (1918).

(12) H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1909, p. 182.

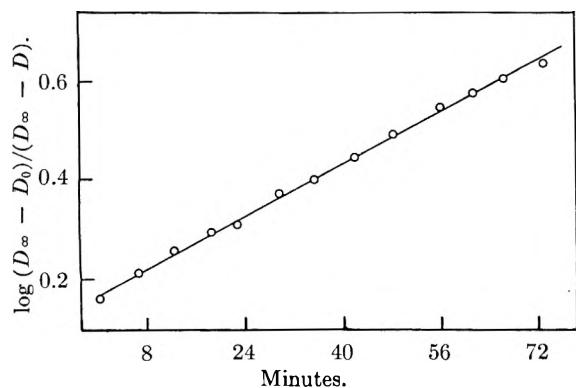


Fig. 1.—Plot of spectrophotometric data for rate of acid hydrolysis of *cis*-[Coen₂Cl₂]Cl.

consists of two parallel first-order reactions producing a common product, it is possible to resolve the plot into its two components, calculate a rate constant for each constituent and determine the

TABLE I

RATES OF ACID HYDROLYSIS OF SOME DICHLOROTETRAMINECOBALT(III) COMPLEXES AT 25° AND pH 1

No. ^a	Complex	$k \times 10^2$ (min. ⁻¹)
1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂] ⁺	Very fast
2	<i>cis</i> -[Coen(NH ₃) ₂ Cl ₂] ⁺	1.4
3	<i>cis</i> -[Coen ₂ Cl ₂] ⁺	1.5
4	<i>cis</i> -[CotrienCl ₂] ⁺	0.9
5	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂] ⁺	11
6	<i>trans</i> -[Coen(NH ₃) ₂ Cl ₂] ⁺	1.3
7	<i>trans</i> -[Coen ₂ Cl ₂] ⁺	0.19

^a References for syntheses of salts of complex ion are: 1, A. Werner, *Lieb. Ann.*, 386, 103 (1912); 2 and 6, J. C. Bailar and D. F. Peppard, *J. Am. Chem. Soc.*, 62, 105 (1940); 3 and 7, J. C. Bailar, *Inorg. Syn.*, 2, 222 (1946); 4, see ref. 11. Replacement of first chlorine in 1 was too fast to measure by our techniques. 2, *cis*-dichloro-*trans*-diammine. 6, *trans*-dichloro.

relative amounts of these present initially.¹³ This calculation was carried out and it was found that the slow reacting component made up only 51% of the mixture and the rate constants for fast and slow reacting components, respectively, were 7×10^{-3} and 1.5×10^{-5} min.⁻¹. Such an observation may be accounted for if either (1) the material under investigation is a mixture of two geometric isomers of [CotetraenCl]Cl₂ or (2) it is a mixture of [Cotetraen-Cl]Cl₂ and [CotetraenCl₂]Cl. Professor Jonassen has recently told us that the tetraethylenepentamine supplied to us is still contaminated with an isomeric, tertiary pentamine. Since we have observed that chloro complexes containing the tertiary amine, β, β', β'' -triaminotriethylamine, react several times faster than analogous complexes containing the isomeric triethylenetetramine, we believe that the slower reacting component is the desired tetraethylenepentamine complex and the fast reacting component is the tertiary pentamine complex. The great difference in rates (factor of 500) is, however, unexpected. The rate

(13) H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, 71, 1845 (1949)

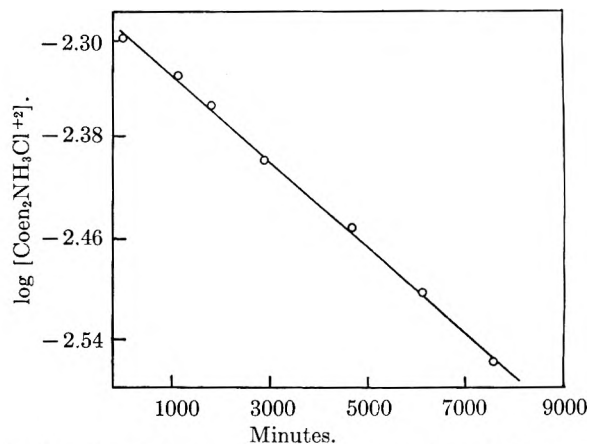


Fig. 2.—Plot of titration data for the rate of acid hydrolysis of *cis*-[Coen₂NH₃Cl]⁺².

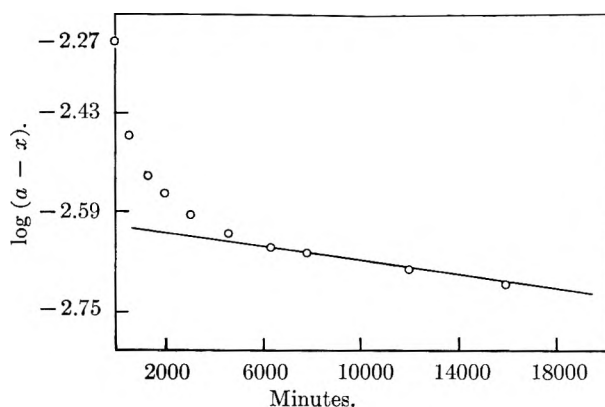


Fig. 3.—Plot of rate of chloride ion formation for a mixture believed to be [CotetraenCl₂]Cl and [CotetraenCl]Cl₂. Rate constant reported for [CotetraenCl]Cl₂ was calculated from straight line shown here.

value given in Table II must be regarded as tentative, therefore, for the tetraen complex.

TABLE II

RATES OF ACID HYDROLYSIS OF SOME CHLOROPENTAMMINE COBALT(III) COMPLEXES AT 35° AND pH 1

No. ^a	Complex	$k \times 10^4$ (min. ⁻¹)
8	[Co(NH ₃) ₅ Cl] ⁺²	4.0
9	<i>cis</i> -[Coen ₂ NH ₃ Cl] ⁺²	0.85
10	<i>cis</i> -[Cotrien NH ₃ Cl] ⁺²	.40
11	[Coen(dien)Cl] ⁺²	.31
12	[CotetraenCl] ⁺²	.15 ^b

^a References for syntheses of salts of above complex ions are: 8, H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1909, p. 173; 9, S. M. Jorgensen, *J. prakt. Chem.*, 41, 454 (1890); 10, 11 and 12, this paper. ^b See text for significance of this value.

Discussion

This investigation was carried out in an attempt to obtain some information on the molecularity of the acid hydrolysis of these hexavalent complexes. It was believed that if the reactions involve a direct attack by water, then as the central atom becomes less accessible with increased chelation there should be a marked decrease in rate of reaction. In general a decrease in rate was ob-

served to accompany an increase in chelation. However, these differences were not large and it also was not possible to make these changes without the simultaneous change of some other parameters which might affect the rates of reaction. Therefore it is believed the results obtained can be explained either on the basis of a dissociation (S_N1) or a displacement (S_N2) mechanism. The discussion which follows deals with three factors (1) inductive, (2) charge distribution, (3) steric, that change in the three series of complexes investigated and their probable effect on the rates of acid hydrolysis.

That the inductive effect of the coordinated nitrogens in these complex ions differs is obvious. It is not readily obvious what to use as a measure of this effect. Data are available on the acid dissociation constants of the following monoprotonated onium ions: $pK_{NH_4^+}$, 9.28¹⁴; pK_{enH^+} , 9.93¹⁵; pK_{dienH^+} , 9.98¹⁶; pK_{trienH^+} , 9.92.¹⁷ These results suggest that ammonia would have a different inductive effect and the polyamines would all be approximately the same. It follows therefore that if the inductive effect is the predominant factor in control of the rates of these reactions then for any given series of complex ions which contain no ammonia (cations No. 3 and 4 or No. 11 and 12) the rates of reaction should be essentially the same and this should also be true for complexes with the same number of coordinated ammonias (Nos. 9 and 10). The data in Tables I and II show that for these three cases there is in each instance approximately a twofold difference in rate and the slower rate is always associated with the complex chelated to the greater extent. Furthermore one would expect a greater difference in rate between cations 2 and 3 than between 3 and 4 or similarly between 10 and 11 than 9 and 10. Again the experimental observations do not bear this out. It would appear therefore that such small changes of inductive effect do not greatly alter the rates of acid hydrolysis of these complexes.

In all of the cases studied the largest differences in rate for a given series of compounds were always observed between the completely aminated complex and those which contained no coordinated ammonia. If these differences are attributed primarily to the lesser inductive effect of ammonia compared to the polyamines, it follows that the more rapid reactions of the ammonia complexes are not in accord with a dissociation mechanism. The greater the inductive effect of the coordinated ligands the greater the electron density on the central cobalt which would suggest there should be a greater tendency for the Co-Cl bond to break. It is not possible to say what effect this would be expected to have upon the rates for a displacement process because in such a case one must consider two competing tendencies. In addition to the greater ease with which the Co-Cl bond can be broken as the electron density on the cobalt in-

creases, it is also true that such a cobalt would have a smaller attraction for the negative end of the attacking water dipole.

The second factor which is expected to play an important role in changes in rates of reaction of these complexes is that of effective distribution of positive charge. Pauling¹⁸ has applied his "postulate of the essential electrical neutrality of atoms" to explain the greater stability of the transition metal ion hydrates over the corresponding etherates. This he explains on the basis of the greater ionic character of the O-H bond over that of the O-C bond. This permits a distribution of the positive charge of the central ion to the peripheral hydrogens of the hydrate complex, whereas no such charge distribution is possible for the etherates. Chatt and Wilkins¹⁹ have employed the same argument to account for the instability of the trialkylamine complexes compared to the corresponding ammonia complexes. It follows therefore that the positive charge of the complex ions under investigation is primarily transferred to the acid hydrogens (N-H) and this transfer is enhanced by an increasing number of such hydrogens.

Acid hydrolysis reactions wherein a negative ligand is replaced by water always result in the formation of a complex with a larger positive charge. This increase in positive charge is expected to take place more readily with the complexes that can more effectively distribute the additional charge, *i.e.*, complex ions having the larger number of acid hydrogens. In a consideration of differences in rates of reaction it is necessary to make a comparison not with the final product but instead between the ground state of the starting compounds and the transition state. For the reactions studied the transition state, regardless of whether the reaction mechanism is S_N1 or S_N2 , should have a larger positive charge than that of the initial state. Since the increased positive charge is most readily accommodated by the complex with the largest number of acid hydrogens, it is believed this would result in a lower activation energy and consequently a more rapid reaction. That there is a rather good linear correlation between the logarithms of the rates of acid hydrolysis and the number of N-H bonds in a complex is shown in Fig. 4. Another way of saying much the same thing is that the largest gain in energy is experienced by the compound with the greatest number of acid hydrogens due to the increased energy of solvation.²⁰ Thus strong solvation of the complex ion is an additional means of spreading the positive charge over a larger radius. This again will be more important for the transition state than for the ground state.

Finally changes in the steric effect are expected to alter the rates of these reactions. The ideal situation, which at best can only be approached but never entirely achieved, would be one in which all other factors that may affect the rate of reaction are maintained constant while the steric hindrance is gradually increased to render the central atoms

(14) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 122.

(15) R. K. Murmann, M.S. Thesis, Northwestern University, 1951.

(16) J. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

(17) J. Prue and G. Schwarzenbach, *ibid.*, **33**, 974 (1950).

(18) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(19) J. Chatt and R. G. Wilkins, *ibid.*, 4300 (1952).

(20) R. G. Pearson and F. V. William, *J. Am. Chem. Soc.*, **76**, 258 (1954).

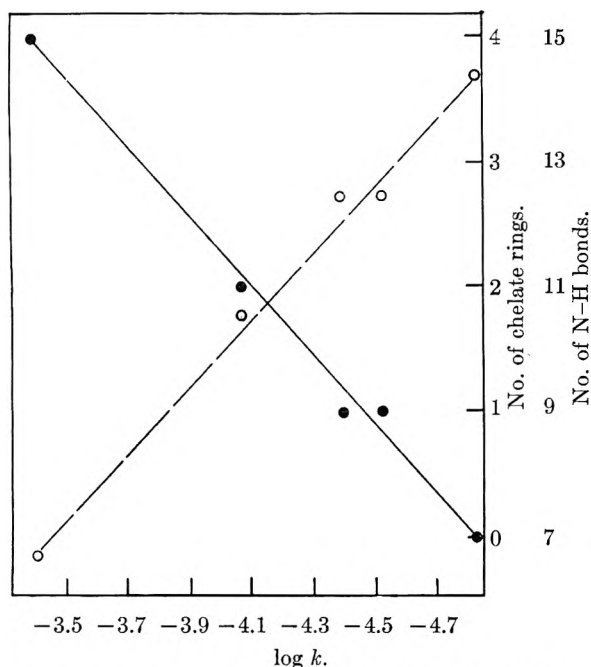


Fig. 4.—Plot of $\log k$ for acid hydrolysis of $[\text{CoA}_5\text{Cl}]^{+2}$ vs. no. of chelate rings (O) and no. of N-H bonds (●).

less susceptible to attack. Kinetic studies on the acid hydrolysis of such an ideal series of complexes would definitely furnish some information on whether or not a direct attack by water is involved in the transition state. Although the three series of complexes investigated here are by no means ideal in this respect, it is of interest that there is a decrease in rate of acid hydrolysis with increase in

chelation. Since the central cobalt becomes less available for attack by water as the amount of chelation becomes greater, the observed decrease in rate would suggest an $\text{S}_{\text{N}}2$ mechanism. However if one considers the molecular models it would appear that the cobalt is virtually completely shielded in complexes 11 and 12. The fact that these two complexes react only slightly slower than the less hindered ions in this series is perhaps the most direct piece of evidence in opposition to an $\text{S}_{\text{N}}2$ process.

The observed effect of chelation on the rates of reaction can be accounted for on the basis of a dissociation mechanism providing an assumption is made that the pentacovalent intermediate tends to have a symmetrical configuration.²¹ Since the energy required to rearrange a highly chelated complex is probably greater than that to rearrange a less complicated ion, the less complicated ion should react more readily. That there is a fairly good linear correlation between the logarithms of the rates of acid hydrolysis and the number of chelate rings is also shown in Fig. 4.

In conclusion it should be repeated that the results reported here can be explained either on the basis of an $\text{S}_{\text{N}}1$ or an $\text{S}_{\text{N}}2$ mechanism. However it is suggested that the rates of reaction for an $\text{S}_{\text{N}}2$ mechanism of the more highly hindered complex (11 and 12) should be appreciably less than were observed. In view of this, it is believed that these results are in agreement with an earlier report where it was concluded that the acid hydrolyses of some cobalt(III) complexes proceed by a dissociation mechanism.⁷

(21) D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953).

THE EFFECT OF LIGAND ISOMERISM ON THE STABILITY OF METAL CHELATE COMPOUNDS¹

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The relative stabilities of metal chelates of isomeric ligands are classified in three groups: (1) compounds which behave as predicted from known principles of metal chelate formation; (2) compounds which have lowered stability as the result of steric hindrance; and (3) compounds for which stability differences are less readily explained. In the third category may be found such effects as substitution on the donor atom, differences in the arrangement of chelate rings, and mutual repulsions of groups attached to an alicyclic ring.

With the discovery by Ley³ of the differences in stability of the copper(II)- α -alanine and β -alanine chelates, it became evident that stereoisomerism would play an important part in determining the stability of metal chelate compounds. Within recent years sufficient stability constant data have accumulated to make possible comparisons of metal ion affinities of isomeric ligands on a quantitative basis. In certain cases, however, it is still neces-

sary to use non-quantitative comparisons, such as the formation or non-formation of the chelate compound.

The strong influence of structure on stability of metal chelate compounds results from steric requirements on the part of both reactants—the metal and the ligand—further accentuated by the labile nature of the metal coordination bonds.

Normal Behavior

Among the characteristics of the ligand which are generally recognized to influence stability are: (1) basicity of the ligand; (2) resonance effects; (3) the number of metal chelate rings per ligand; and (4) the size of the chelate ring. In cases

(1) Presented before the 125th Meeting of the American Chemical Society, Symposium on Inorganic Isomerism, Division of Physical and Inorganic Chemistry, March 29, 1954.

(2) Chemical Institute, University of Zurich, Zurich, Switzerland (1954–1955).

(3) H. Ley, *Z. Elektrochem.*, **10**, 954 (1904).

TABLE I
 STABILITIES OF METAL CHELATES OF VARIOUS ISOMERIC LIGANDS

No.	Name	Ligand				Metal ion	Log formation constant				Ref.
		pk_1	pk_2	pk_3	pk_4		K_1^a	K_{12}^c	K_2^b		
1	2-Methyl-3,5-heptanedione	14.0				Ce(III)	9.86		9.03	<i>d</i>	
2	2,2-Dimethyl-3,5-hexanedione	14.2				Ce(III)	9.94		9.19	<i>d</i>	
3	3-Chlorosalicylaldehyde	7.8				Cu(II)		10.6		<i>e</i>	
4	5-Chlorosalicylaldehyde	8.6				Cu(II)		11.4		<i>e</i>	
5	3-Nitrosalicylaldehyde	6.0				Cu(II)		8.2		<i>e</i>	
6	4-Nitrosalicylaldehyde	7.4				Cu(II)		9.2		<i>e</i>	
7	2-Hydroxy-1-naphthaldehyde	8.4				Cu(II)		14.0		<i>e</i>	
8	2-Hydroxy-3-naphthaldehyde	9.9				Cu(II)		11.6		<i>e</i>	
9	1,2-Diaminocyclohexane-N,N'-tetraacetic acid	2.4	3.5	6.1	11.7	Ca(II)	12.5			<i>f</i>	
						Mg(II)	10.3				
10	1,3-Diaminocyclohexane-N,N'-tetraacetic acid	1.7	2.5	8.6	10.9	Ca(II)	4.77			<i>f</i>	
						Mg(II)	4.64				
11	1,4-Diaminocyclohexane-N,N'-tetraacetic acid	2.0	2.5	9.0	10.9	Ca(II)	4.19			<i>f</i>	
						Mg(II)	4.30				
12	1,2-Diaminopropane	7.0	9.8			Cu(II)	10.6		9.1	<i>g</i>	
13	1,3-Diaminopropane	9.0	10.7			Cu(II)	9.8		7.1	<i>h</i>	
14	α -Alanine	9.9				Cu(II)	8.5		6.5	<i>i</i>	
15	β -Alanine	10.2				Cu(II)	7.2		5.6	<i>h</i>	

^a $K_1 = (\text{MKe})/(\text{M})(\text{Ke})$, where M is the metal ion, and Ke is the fully-dissociated ligand. ^b $K_2 = (\text{MKe}_2)/(\text{MKe})(\text{Ke})$. ^c $K_{12} = K_1K_2$. ^d L. G. Van Uitert and W. C. Fernelius, *J. Am. Chem. Soc.*, **75**, 3862 (1953). ^e M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945). ^f G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **32**, 1682 (1949). ^g G. A. Carlson, J. P. McReynolds and F. H. Verhoek, *J. Am. Chem. Soc.*, **67**, 1334 (1945). ^h H. Irving, E. I. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949). ⁱ Ref. 4, pp. 525, 526.

where isomerism results in a stability difference which can be recognized as following the accepted pattern for one or more of these effects, the behavior will be considered normal. Since the nature of these effects has been generally described elsewhere,⁴ it will suffice to discuss only a few such examples in order to establish a basis for the consideration of deviations from normal behavior.

Basicity of the Ligand.—The isomeric β -diketones listed in Table I show slight differences in stability which are seen to lie in the same direction as corresponding differences in basicity (*i.e.*, pk values). When the formation constants of these and related compounds are plotted *vs.* pk values, straight lines are obtained, indicating a linear correlation of the type usually observed in such cases. For the chelate compounds containing two moles of ligand per metal ion, one might raise the question of steric repulsion between ligands. However, since the same linear correlation holds for the 2:1 chelates, this possibility seems to be eliminated.

The chloro- and nitrosalicylaldehyde ring-substitution isomers show a similar correlation with basicity. Apparently the interactions of the chloro and nitro groups with the ring affect the affinity of the ligand for copper and hydrogen ions in the same manner.

Resonance Effect.—There are very few examples of clear-cut resonance effects in chelate compounds which are not complicated by steric or other constitutional factors. The first, and still the most striking, example is the large difference in stability of the copper chelates of 2-hydroxy-1-naphthaldehyde and 2-hydroxy-3-naphthaldehyde. The resonating ring system characteristic of copper(II)- β -diketone chelates contributes to the stability, and

any interference with the resonance would affect the stability constant. Since the 1,2-bond in naphthalene has a greater degree of double-bond character than does the 2,3-bond, there would be less resonance interference with the metal chelate ring formed from 2-hydroxy-1-naphthaldehyde. It is interesting to note that the effect is great enough to reverse the influence of relative basicities of the two ligands. Alternatively, it may be stated that the resonance effect influences the affinity for copper and hydrogen ions differently, and that the basicity toward hydrogen ions is differently affected by the resonating systems than is the basicity toward copper ions.

Number of Rings.—The position isomerism of the 1,2-, 1,3- and 1,4-diaminocyclohexanetetraacetate ions has a profound effect on the affinities for calcium(II) and magnesium(II) ions. Schwarzenbach⁵ has pointed out that only the 1,2-isomer can form a hexadentate (or possibly pentadentate) chelate similar to the ethylenediaminetetraacetate alkaline earth chelates. Because of the greater spacing of the nitrogen atoms in the 1,3- and 1,4-isomers, these ligands can only form weak tridentate chelates. In this series of isomers, therefore, differences in affinity for metal ion can be correlated with the differences in the number of chelate rings that can form with a particular metal ion.

Size of Chelate Ring.—The isomeric propylenediamine and alanine chelates listed in Table I differ in that one pair of compounds involves 5-membered chelate rings, while the other contains 6 rings. As has been observed for a wide variety of aliphatic chelate rings, the five-membered ring is the more stable. In the case of aromatic ligands, or of chelates with conjugated linkages, the 6-ring is usually more stable. This difference

(4) A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, Chapter 4.

(5) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **32**, 1682 (1949).

TABLE II
 STABILITIES OF ISOMERIC DIAMINE CHELATES

Ligand Formula	pK_1	pK_2	Copper(II)		$\log K_1$	Nickel(II)		Ref.
			$\log K_1$	$\log K_2$		$\log K_1$	$\log K_2$	
$\text{H}_2\text{NCH}_2\text{CH}_2\text{N} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$	6.6	9.5	9.2	6.8	a
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_3$	7.6	10.6	10.2	8.4	6.8	5.3	..	b
$\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NHCH}_3$	7.3	10.1	9.7	6.6	6.7	3.8	..	a
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$	7.5	10.3	10.0	8.2	6.6	5.2	2.0	b
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$	7.7	10.6	9.1	7.4	5.2	3.5	..	b
$\text{H}_2\text{NCH}_2\text{CH}_2\text{N} \begin{array}{l} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_2\text{CH}_3 \end{array}$	7.1	10.0	8.2	5.5	a
$\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	7.5	10.3	9.9	8.3	6.7	5.6	2.2	b

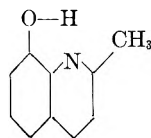
^a H. Irving, Paper No. 4, "A Discussion of Coördination Chemistry," Butterwick Research Laboratories, I.C.I., Sept. 21-22, 1950. ^b Same as ref. 12.

in behavior is due to the wider bond angles, and in some cases the resonance requirement of an even number of members, in the latter compounds.

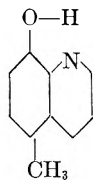
Steric Effects

With very few exceptions the recognized examples of steric influences on stability are based on qualitative observations which usually involve formation or non-formation of the metal derivative.

Substituted Oxines.—Probably the best-known example of steric inhibition of chelation is the difference in behavior of the isomeric 2-methyl- and 5-methyloxines observed by Merritt and Walker.⁶ The 2-methyl derivative does not precipitate Al(III), whereas the 5-methyl derivative



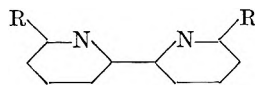
Ia



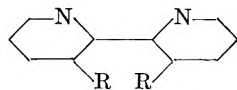
Ib

produces the normal 3,1 chelate as does oxine itself. Irving and co-workers⁷ prepared the 2-, 5-, 6- and 7-methyl derivatives and found that precipitation of aluminum(III) occurs with all but the 2-isomer. Through the examination of models, they concluded that mutual repulsions between ligands could result in a weakening of the Al-donor bonds for the 2-isomer, but not for the other compounds.

Inhibition of metal chelate formation reported by Burstall for the 6,6'-disubstituted dipyridyls (IIa) is probably due to a similar kind of steric repulsion



IIa



IIb

between two or more ligands about a metal ion. It is interesting that the isomeric 3,3'-disubstituted dipyridyls (IIb) reported by Cagle and Smith⁸

(6) L. L. Merritt, Jr., and J. K. Walker, *Ind. Eng. Chem., Anal. Ed.*, **16**, 387 (1944).

(7) H. Irving, E. J. Butler and M. F. Ring, *J. Chem. Soc.*, 1489 (1949).

(8) F. W. Cagle and G. F. Smith, *J. Am. Chem. Soc.*, **69**, 1860 (1947).

also show steric inhibition of metal chelate formation. In this case, however, the repulsions cannot occur between ligands. The only possible interpretation here is that the alkyl groups prevent the ligand from assuming a planar configuration and hence interfere with resonance stability in the ligand and introduce strain in the metal-donor bonds.

There are numerous other examples of steric effects of the types described above. The 2,2'-dimethyldipyrrylmethenes described by Mellor and Lockwood⁹ and inhibition of chelates containing two ligands per metal ion in the 2,2'-diquinolines,¹⁰ *o*-phenanthrolines,⁷ and N-alkylethylenediamines⁷ are examples of mutual steric repulsions between ligands. The inhibition of chelate formation in acetylacetonates containing branched chains at the 3-position¹¹ is probably due to steric inhibition of resonance through interference with the planarity of the acetylacetonate ring.

Specific Effects

The most complex and in many cases the most interesting effects of isomerism on stability may be found in the examples which cannot be placed in any of the above classifications. The following discussion is an analysis of such instances for which stability data are available, and an attempt to explain the results on the basis of present theories.

In Table II are listed a number of isomeric diamines which differ mainly in the number of alkyl groups attached to nitrogen.

For the isomeric dimethyl- and ethylethylenediamines it seems that whatever the steric influences of the different arrangement of alkyl groups, the effect on k_1 of the 1:1 chelates of copper(II) and Ni(II) is generally the same as for the addition of one hydrogen ion. In other words the chelate stabilities follow the basicities for the first association. In the second step the differences in stability become quite pronounced since the steric repulsion between ligands becomes important. From the data given, it appears that an ethyl group has less effect than two methyl groups, however

(9) D. P. Mellor and W. H. Lockwood, *J. Proc. Roy. Soc. N. S. Wales*, **14**, 141 (1940).

(10) A. P. Smirnov, *Helv. Chim. Acta*, **4**, 802 (1921).

(11) G. T. Morgan, *J. Chem. Soc.*, 127, 2611 (1925).

TABLE III

Ligand		pK_1	pK_2	pK_3	pK_4	$\log K_{Mg}$	Ref.
$\begin{array}{c} \text{HOOCCH}_2\text{CH}_2 \\ \diagdown \\ \text{NCH}_2\text{CH}_2\text{N} \\ \diagup \\ \text{CH}_2\text{CH}_2\text{COOH} \end{array}$		3.0	3.8	6.6	9.8	6.9 (30°)	a
$\begin{array}{c} \text{HOOCCH}_2 \\ \diagdown \\ \text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N} \\ \diagup \\ \text{CH}_2\text{COOH} \end{array}$		1.9	2.7	9.1	10.4	3.4 (20°)	b
$\begin{array}{c} \text{HOOCCH}_2 \\ \diagdown \\ \text{H}_2\text{NCH}_2\text{CH}_2\text{N} \\ \diagup \\ \text{CH}_2\text{COOH} \end{array}$..	5.6	11.0	..	4.5 (20°)	c
$\text{HOOCCH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{COOH}$		6.4	9.5	3.7 (30°)	a

^a S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 6228 (1952). ^b G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948). ^c G. Schwarzenbach, Federal Institute of Technology, Zurich, Switzerland, private communication.

distributed. Basolo¹² has pointed out that the structures of the 2:1 chelates of copper(II) and nickel(II) are probably analogous, regardless of differences in coordination number.

In the next four compounds listed in Table II relative effects of isopropyl and *n*-propyl groups, and of two ethyl and a *n*-butyl group are compared. It seems that chain branching, whether it occurs on the nitrogen atom or on the adjacent carbon atom, greatly reduces the stability of the chelate relative to that containing the same number of carbon atoms in the form of a single *n*-alkyl group. The fact that this effect occurs in opposition to the relative basicities serves to accentuate the difference. Since the effect occurs for the first formation constant, it must involve an unfavorable entropy factor connected with ease of formation of the metal chelate. The differences in stability become accentuated with the addition of the second ligand, but this must certainly also involve differences in the steric repulsions between ligands. Basolo has offered an alternative explanation for the greater stability of the chelates containing *n*-alkyl groups in the possibility of a shielding of the central metal ion from the solvent molecules.

In Table III are listed two pairs of isomeric aminopolycarboxylic acids and the corresponding formation constants of the 1:1 magnesium chelates.

The first two differ from ethylenediaminetetraacetic acid by two methylene groups. In the first compound there are two propionic acid groups in the place of two of the acetic acid groups; while in the second, the ethylenediamine bridge is lengthened by two additional carbon atoms. The effect on the stability of the magnesium chelate is profound, the stability of the latter being very much smaller. This indicates that the ethylene bridge between the nitrogens is required for strong complexing of alkaline earth ions. The coordination of the first compound, ethylenediamine diacetic dipropionic acid, with magnesium ion involves at least the two basic nitrogen atoms and the two acetate groups, and may also involve the propionate groups. The magnesium chelate of the second compound probably involves only one nitrogen atom and the two attached acetate groups.

The second pair of compounds in Table III in-

volves the symmetric and unsymmetric arrangement of two acetate groups on ethylenediamine. There seems to be little difference in stability; the unsymmetrical compound has a somewhat higher stability constant, which correlates with higher basicity. It is interesting, however, that in view of the low affinity of free amino groups for alkaline earth ions, the unsymmetrical compound is probably tridentate, with only the iminodiacetate groups coordinated with the metal ion. On the other hand, symmetrical ethylenediaminetetraacetic acid must act as a tetradentate ligand.

A suggestion of the possible reason for this apparent anomaly may be seen in the structures and relative stabilities of the zinc chelates of triaminotriethylamine and of triethylenetetramine given in Fig. 1. It is apparent that both struc-

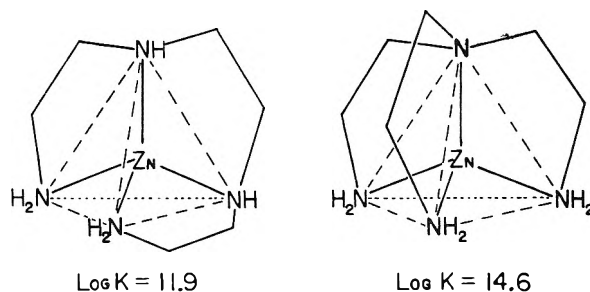


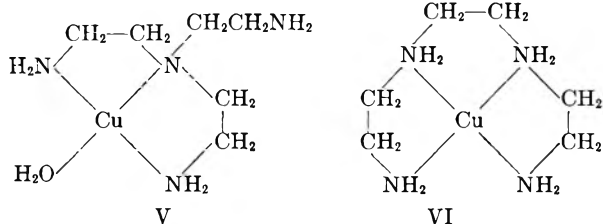
Fig. 1.—Probable structures and chelate stability constants of (a) diethylenetriamine-Zn(II); and (b) triaminotriethylamine-Zn(II).

tures have similar bonding, the same size, charge, and involve approximately the same degree of shielding from the solvent. Hence the differences in stability must be due to differences in the initial states of the solvated ligands. It is reasonable to conclude that triethylenetetramine has the greater freedom of movement and also is possibly more greatly solvated.¹³ Hence its initial free energy is lower than that of its isomer as the result of greater entropy and lower enthalpy. Thus the first factor and sometimes the second, will be reflected in abnormally low stability constants for metal chelates that must be formed by the coiling of a long-chain linear ligand.

(13) It is suggested that the linear polyamine exists mainly in the extended form, and is consequently more strongly bound to the solvent through hydrogen bonds.

(12) F. Basolo and R. K. Murman, *J. Am. Chem. Soc.*, **74**, 5243 (1952).

This generalization seems to be contradicted by the relative stabilities of the corresponding copper chelates, which have the log values of 18.8 and 20.6 for triaminotriethylamine¹⁴ and triethylenetetramine,¹⁵ respectively. If it is remembered that the copper valences are square-planar, however, it is seen that the anomaly is resolved in view of the fact that the former must be tridentate (formula V) while the latter is tetradentate (formula VI).



In Fig. 2 are given the possible structures of the isomeric cadmium(II) chelates of iminodiacetic

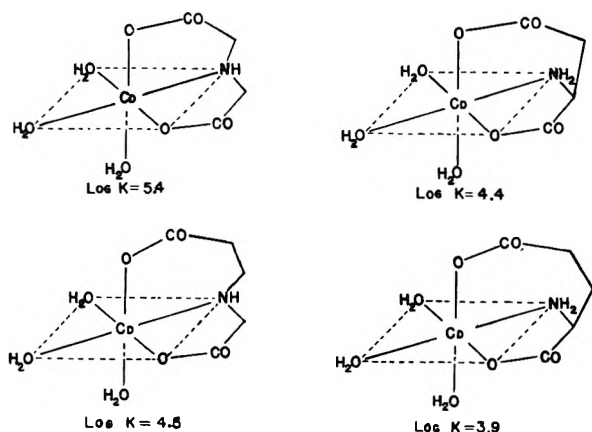


Fig. 2.—Possible structures of cadmium(II) iminodiacetate and iminopropionateacetate, and the isomeric aspartate and glutamate.

and aspartic acids, and of iminoaceticpropionic and glutamic acids. If both pairs of chelates are

(14) J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 995 (1950).

(15) G. Schwarzenbach, *ibid.*, **33**, 974 (1950)

assumed to have tridentate structures, then the members of each pair differ mainly in the way the chelate rings are arranged. It is possible, however, that the aspartate and glutamate ions are only bidentate toward the cadmium ion. In either case the chelates of the latter two compounds are weaker than those of the corresponding isomer.

The relative stabilities of metal chelates of *cis*- and *trans*-geometric isomers would be particularly interesting. Up to the present time no data on this subject have been reported in the literature. Recently, however, the *cis*- and *trans*-1,2-diaminocyclohexanes have been prepared¹⁶ by a stereospecific procedure, and the stabilities of the corresponding 1:1 copper chelates have been determined potentiometrically. The interesting result is that the stabilities of the isomeric chelates are nearly equivalent, and somewhat higher than that of ethylenediamine. An examination of molecular models reveals that both isomers can form a planar 5-membered chelate ring without strain, as does ethylenediamine. The corresponding structures, indicated in Figure 3, differ only

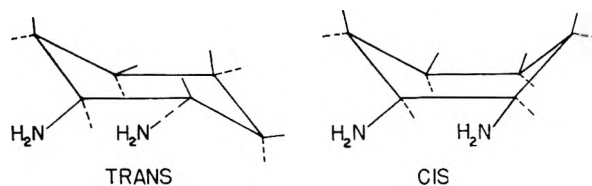


Fig. 3.—Configuration of *trans*- and *cis*-1,2-diaminocyclohexane with carbon-nitrogen bonds coplanar.

in that the cyclohexane ring of the *trans* diamine must have the chair configuration, whereas the *cis* chelate must exist in the boat form. There is also the possibility of forming a strained chelate ring from equatorial and polar *cis* amino groups with the cyclohexane ring in the more stable chair form. In either case, one would expect the Cu(II) chelate of *trans* 1,2-diaminocyclohexane to be more stable than that of the *cis* isomer. On the other hand one would expect the *cis*-1,2-diaminocyclopentane chelates to be always more stable than the corresponding *trans* isomers.

(16) F. Craven and A. E. Martell, unpublished work.

LOW PRESSURE ADSORPTION OF HEPTANE ON FERRIC OXIDE

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Received March 17, 1954

The adsorption isotherms of heptane on ferric oxide have been measured at three temperatures and at equilibrium pressures ranging from 0.05 to 70 μ . A detailed investigation was made of the experimental conditions required to obtain precise and reproducible results. No first-order phase transition was observed; it is possible to attribute such apparent transitions previously reported to an experimental artifact as well as to the very slow rates of adsorption at low pressures. The Brunauer, Emmett and Teller relations were shown to be valid for relative pressures down to 3×10^{-4} . This is in line with the high heats of adsorption observed. The thermodynamic functions for the adsorbed film have been calculated at two mean temperatures. A maximum in the heat content and entropy functions occurs at a surface coverage of approximately 0.2; at this same coverage a minimum occurs in the differential and integral entropy functions. An explanation is offered for these effects.

Introduction

Problems involving interaction between liquids and the surfaces of solids are of considerable interest to us. We are primarily concerned with the energetics of this interaction. One obvious method of attack involves a study of the adsorption of a vapor on the solid and the calculation of the thermodynamic functions for this adsorption process.

The thermodynamic functions for adsorption may be determined in two different ways: (1) An isotherm is determined and these data combined with those obtained calorimetrically, *e.g.*, heats of immersion or specific heats¹; (2) isotherms are determined at several different temperatures.² It is necessary in both methods to compute ϕ , the spreading pressure or decrease in free surface energy, as a function of equilibrium pressure of the vapor. In this computation, which employs the Gibbs adsorption equation,³ it is necessary that the adsorption isotherm be known precisely to a pressure sufficiently low so that Henry's law behavior is observed. We are concerned with liquids whose vapor pressures are on the order of 40 mm. at temperatures suitable for adsorption measurements; we are thus forced to such measurements at equilibrium pressures in the micron and submicron regions.

Adsorption experiments in this pressure region are difficult and it is not surprising that there has been some disagreement between results obtained by different workers. One such low pressure system, that of heptane on ferric oxide, has been investigated by several groups. It thus seemed desirable to use the heptane-ferric oxide system as a model on which a technique could be developed and the effect of experimental variables determined.

The adsorption of heptane on ferric oxide, according to Jura, Loeser, Basford and Harkins,⁴ is marked by a first-order two-dimensional phase transition below 30°. These results have been quoted to support theoretical arguments.⁵ Smith⁶ was unable to

confirm the work of Jura, *et al.* During the course of this investigation, Young, Beebe and Bienes⁷ reported results in qualitative agreement with those of Smith. Both Smith and Young, *et al.*, were concerned about the attainment of adsorption equilibria at low pressures; they point out it was likely that equilibrium was not attained in the earlier work of Jura, *et al.*

It is clear that the results of adsorption measurements at low pressures are markedly affected by variations in experimental techniques. For this reason, details of the present investigation are given below in quite complete form.

Experimental

Materials.—The ferric oxide was supplied by L. N. Smith of Pomona College and was identical with the material used in his work.⁶ The specific surface area as determined here by the application of the BET equation to the nitrogen isotherm at 77.3°K. was 6.82 square meters per gram; the area per nitrogen molecule in the monolayer was taken as 16.2 square ångströms. Helium which was used to measure the dead space was obtained from the Matheson Company in a Pyrex bulb fitted with a break-off. A sample of *n*-heptane certified to contain less than 0.1 mole per cent. impurity was obtained from the National Bureau of Standards. The heptane was distilled *in vacuo* into a tube containing baked-out calcium hydride and allowed to remain there for one week. The hydrocarbon was then subjected to several bulb-to-bulb distillations on the vacuum line and then degassed in the usual way. The degassing was considered complete when the pressure over the solid at liquid nitrogen temperature with the pumps cut off was less than 2×10^{-7} mm. (air equivalent) after several freezing and thawing cycles.

Apparatus.—A diagram of the adsorption system is given in Fig. 1. Valves A, B and C were mercury float valves.

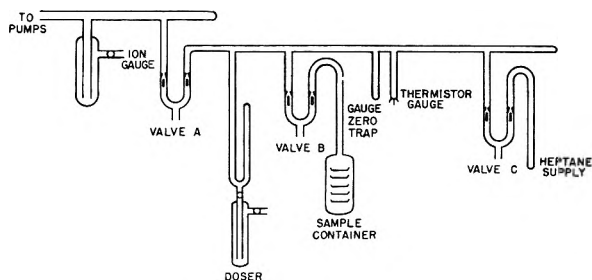


Fig. 1.—Adsorption apparatus for low pressure measurements.

The doser consisted of a U-tube connected to a mercury reservoir; the volume in the closed arm of the tube was known as a function of the height of mercury. Pressure differences were read to 0.05 mm. with a cathetometer. With this doser, it was possible to meter out heptane incre-

(1) J. A. Morrison, J. M. Los and L. E. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951); L. E. Drain and J. A. Morrison, *ibid.*, **48**, 840 (1952); **49**, 654 (1953), G. Jura and T. L. Hill, *J. Am. Chem. Soc.*, **74**, 1598 (1952).

(2) T. L. Hill, P. H. Emmett and L. G. Joyner, *ibid.*, **73**, 5102 (1951).

(3) See, for example, G. Jura and W. D. Harkins, *ibid.*, **66**, 1356 (1944).

(4) G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **14**, 117 (1946).

(5) See, for example, T. L. Hill in "Advances in Catalysis, IV," Academic Press, Inc., New York, N. Y., 1952, p. 221.

(6) L. N. Smith, *J. Am. Chem. Soc.*, **74**, 3477 (1952).

(7) D. M. Young, R. A. Beebe and H. Bienes, *Trans. Faraday Soc.*, **49**, 1086 (1953).

ments on the order of 0.2 cc. STP with an accuracy of 1%; doser pressures were always held to less than 20 mm.

Pressure Measurement.—Pressures were measured with a Western Electric D176255 thermistor gage and a slight modification of the off-balance bridge circuit described by Dushman.⁸ The gage was calibrated against two McLeod gages of overlapping range. The McLeods were made with precision-bore tubing, and for each point on the calibration curve were read at a minimum of three different compression ratios. A cathetometer was used and the maximum pressure in the gage was held to less than 20 mm. For a given initial pressure, the readings thus obtained were in agreement to better than 0.5%. Before each measurement with the thermistor gage, the bridge was rezeroed. This was accomplished by closing valve B and placing liquid nitrogen around the gage zero trap; the off-balance meter was then zeroed by an adjustment of the bridge potentiometer.

Adsorption Bulb.—Preliminary experiments indicated that, with a cylindrical adsorption bulb 20 mm. i.d. and containing 10 g. of solid, pressure over the solid was still decreasing appreciably after a contact time of 144 hours at pressures in the neighborhood of one micron. It thus seemed impossible to attain equilibrium in this conventional apparatus. Recourse was had to the tray type of adsorption bulb described by Jura and Criddle.⁹ The large dead space thus introduced into the system was of little consequence at the low pressures encountered.

Temperature Control.—The adsorption bulb was contained in a constant temperature bath controlled by a mercury thermoregulator through a thyatron relay. The temperature variation was less than 0.01°. Temperatures were read with a mercury-in-glass thermometer calibrated by the National Bureau of Standards; the corrections are known to 0.1°. It was noted in preliminary experiments that the temperature of the ferric oxide was altered sufficiently by radiation from the 100-watt bulb used as the bath heater to cause the heptane pressure to cycle in phase with the heater. The adsorption bulb was therefore covered with several layers of aluminum foil.

Degassing.—We define the leak rate as the rate of pressure increase in millimeters of mercury per hour measured five hours after the pumps had been cut off. Leak rates were measured both with the thermistor gage (TG), which was untrapped, and with an ion gage (IG) trapped with liquid nitrogen; pressure readings obtained with the TG were in heptane equivalents, and those with the IG in air equivalents. It should be noted that the IG readings were undoubtedly lower than the pressures in the system, owing to the cleaning-up action in the gage.

The leak rate in the thoroughly torched-out system with the ferric oxide cut off was 1×10^{-7} with the IG, and not measurable with the TG; after 48 hours with the pumps cut off, the TG reading was less than 5×10^{-6} mm. No increase in pressure was noted when the mercury in the float valves was run up and down. Valves A and B were then opened and the ferric oxide degassed at room temperature for 48 hours and at 450° for 18 hours. The mercury was then run up in valves A and B and the pumps cut off. No increase in pressure was noted when the mercury in valve A was run up and down. When the mercury was run down in valve B, however, with A closed and the solid at room temperature, a pressure of 3 microns was observed on the TG. This pressure increased when valve B was closed and then again opened. After six such operations, the pressure remained constant at 20 μ . It should be noted that this is a measure of the equilibrium pressure with respect to the adsorption of the contaminant on the solid. With the pumps cut off, valve A was then opened; the IG pressure was still in the 10^{-7} range, indicating that the contaminant had a very small vapor pressure at liquid nitrogen temperature.

The system was again evacuated with the sample tube at 450°. During this process, valve B and the mercury it contained were thoroughly torched-out. After 18 hours, the sample was allowed to cool with valve A closed. When the mercury in valve B was run up and then down, the measured TG pressure was 1×10^{-6} mm.; after 10 such operations, the pressure remained constant at 4×10^{-6} mm.

The sample was again baked out *in vacuo*, and valve B and its mercury torched-out repeatedly. After 18 hours, the

sample was allowed to cool. No detectable pressure was observed as measured with the TG when the mercury was run up and down in valve B. The significance of these findings with respect to apparent first-order transitions is discussed below. It is obvious that mercury vapor at a pressure of one micron remained as a contaminant in the system. It is generally assumed¹⁰ that the adsorption of mercury vapor is negligible; whether this assumption is correct is not known. The thermistor gage was calibrated against heptane in the presence of mercury vapor.

Adsorption Equilibrium.—With the solid in a cylindrical adsorption bulb, the pressure in one experiment decreased from 2.4 to 2.1 μ after 72 hours and to 1.9 μ in 144 hours. These findings are in essential agreement with those reported by Young and Beebe.⁷ With the tray system, the rates were much greater. It was decided to accept as equilibrium pressures those that remained unchanged for 16 hours. In the submicron range, several days were required to meet this requirement, while at higher pressures a few hours were sufficient; *i.e.*, no pressure change was noted during the following 16 hours.

Experimental Procedure.—Since previous measurements had indicated a large heat of adsorption, it was decided to measure isosteres directly, rather than to pick isosteric values off the isotherms; this procedure led to a more precise evaluation of the isosteric heats. In the pressure range investigated, the amount of vapor in the dead space turned out to be negligible with respect to the amount adsorbed. A dose of heptane vapor was metered out and admitted to the sample bulb with the constant temperature bath at 29.55°. After equilibrium had been attained, the bath temperature was lowered to 23.10° and then finally to 16.55°. In several cases, the temperature was brought back to 29.55° without the addition of more heptane; the equilibrium pressure was found to check the previous value within experimental error.

Calculations

Langmuir and BET Calculations.—At equilibrium pressures, p , very small with respect to the saturation pressure, p_0 , the Langmuir and the Brunauer, Emmett and Teller equations become identical and of the form

$$p/v = k_1 p + k_2$$

or in the BET terminology

$$\frac{p}{vp_0} = \frac{c-1}{v_m c} \frac{p}{p_0} + \frac{1}{v_m c}$$

in which v is the amount of vapor adsorbed at the pressure p ; c , a constant related to the heat of adsorption in the monolayer; and v_m , the monolayer capacity. BET plots for the three temperatures investigated are given in Fig. 2. It will be noted that the straight lines begin at p/p_0 equal to 3×10^{-4} or at surface coverages of approximately 40%. Values of p_0 for the three temperatures were calculated from the data given by Rossini, *et al.*¹¹ If the nitrogen surface area of 6.82 square meters per gram be taken as correct, some parameters for the adsorption of heptane on ferric oxide may be calculated, and are given in Table I.

TABLE I
BET PARAMETERS

Temp., °C.	v_m , cc. (STP)	Area per heptane molecule in the monolayer (sq. Å.)	c	$E_1 - E_L$, kcal./mole
29.55	0.3666	69.2	2070	13.4
23.10	.3864	65.7	2210	13.5
16.55	.4014	63.2	2470	13.3

(8) S. Dushman, "Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 330.

(9) G. Jura and D. Criddle, *This Journal*, **55**, 163 (1951).

(10) See S. Brunauer, "Physical Adsorption," Princeton Univ. Press, Princeton, N. J., 1943, p. 31.

(11) Rossini, *et al.*, Natl. Bur. Standards Circ. C451, 123 (1947).

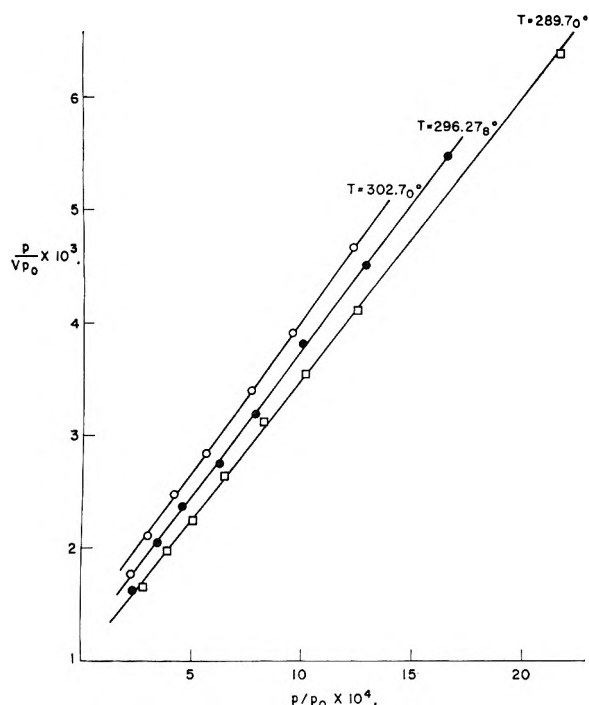


Fig. 2.—Brunauer, Emmett and Teller plots for heptane on ferric oxide.

Thermodynamic Functions.—In general, we will follow the procedure of Hill, Emmett and Joyner²; we employ their calculations and their notation. The spreading pressure or decrease in surface free energy, ϕ , is calculated by means of the Gibbs adsorption equation. The spreading pressure, in ergs per square centimeter, is given by the relation

$$\phi = \frac{RT}{V\Sigma} \int_0^p \frac{v}{p} dp$$

where V is the molar gas volume, Σ is the specific surface area, and v is expressed in cc. at STP adsorbed per gram of solid. From the lowest point determined experimentally, the isotherm was extrapolated linearly to zero pressure. The integral $(v/p)dp$ was then evaluated graphically as a function of p with the aid of Simpson's rule. It should be noted that the uncertainty in ϕ for the lower pressures is the limiting factor in the accuracy of the later derived thermodynamic functions.

From the isosteric heat calculations, v is known as a function of \bar{x} , the mean relative pressure, for the two mean temperatures. If at a given mean temperature the monolayer capacity is taken as the mean of the values for the two experimental temperatures, then the monolayer capacity v/v_m , or θ , is known as a function of \bar{x} . For a given ϕ or ϕ/T , the monolayer capacity is then calculated from the corresponding value of \bar{x} . Several of the calculation crosschecks described by Hill, Emmett and Joyner were utilized; the agreement was good.

Results

The isotherms are plotted in Fig. 3. Plots of the differential and integral entropies as a function of surface coverage are given in Fig. 4 for \bar{T} equal to 299.44°K. and \bar{T} equal to 292.94°K. Plots of the

heat and energy functions are given for the two mean temperatures in Figs. 5 and 6.

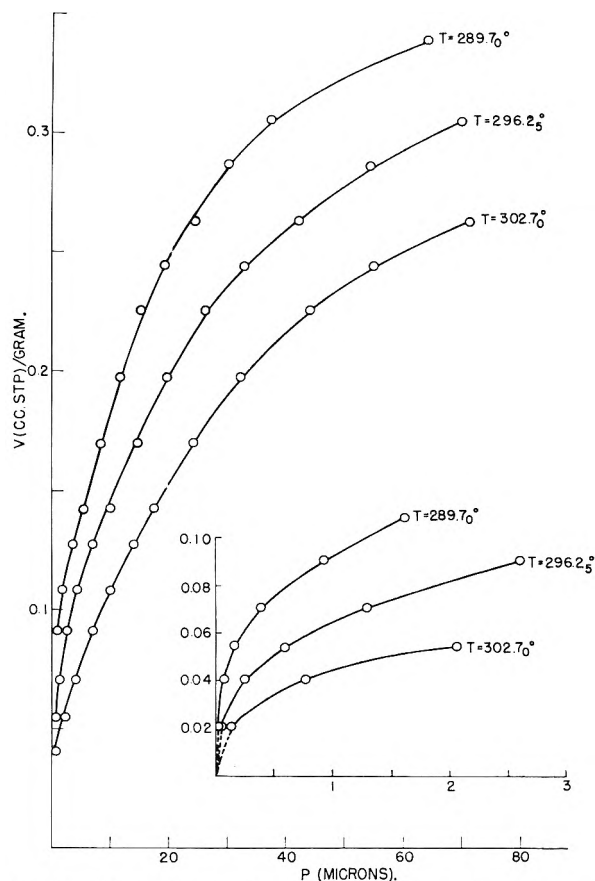


Fig. 3.—Adsorption isotherms of heptane on ferric oxide.

Discussion

Range of Validity of the BET Equation.—It is generally stated that the BET equation no longer fits adsorption data below relative pressures of 0.05. The failure of the equation is attributed to the fact that the theory does not take into account the heterogeneity of the surface; *i.e.*, the heat of adsorption in the first layer is assumed independent of surface coverage. In the present work, the BET expression was found to fit the data down to a relative pressure of 3×10^{-4} , or for surface coverages greater than 0.4. For greater surface coverages, the isosteric heats indicated that the surface was quite homogeneous in the energy sense. It is to be expected that for systems with a high heat of adsorption or large "c" the monolayer point will be attained at quite low relative pressures; if the heats of adsorption become relatively independent of surface coverage at θ equal to 0.5, then the BET equation should be valid at relative pressures considerably smaller than 0.05. The region in which the experimental data fit the BET equation might better be expressed in terms of surface coverage rather than relative pressure; in this manner, the effect of heat of adsorption is implicitly included.

The value for the heat of adsorption calculated from the BET "c," 13.5 kcal. per mole, was in excellent agreement with the isosteric heats for adsorption on the relatively homogeneous portion of the surface, 14.5 kcal. per mole.

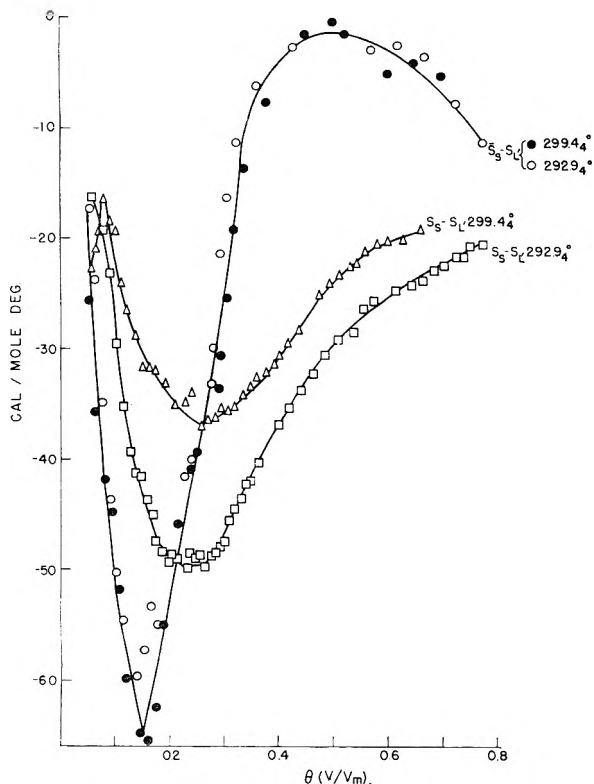


Fig. 4.—Differential and integral entropies of adsorption of heptane on ferric oxide.

First-order Transition.—The ferric oxide used in this work was not identical with the material discussed by Jura, *et al.* It is quite clear, however, that equilibrium was not attained in the experiments reported by these investigators.

It is possible to attribute the apparent first-order transition to an experimental artifact introduced by the float-valve effect described above. Thus, one might expect that in the low pressure region the extent of heptane adsorption would be decreased in the presence of a contaminant occupying the most active sites on the surface. Actually, the pressure measured would be the sum of the pressures of the heptane and contaminant. If the pressure of the contaminant is large compared with that of the heptane, then the total pressure would increase with each float-valve manipulation until a saturation value was reached. Then, as the heptane pressure becomes measurable, the total pressure would increase. It would be possible to obtain an apparent first-order transition in this manner.

The present state of knowledge permits the following conclusion. The existence of first-order transitions for adsorbed films on solids is doubtful. The weight of the evidence favors the view that the transitions that have been observed are not real but are due to some experimental artifact. A crucial experiment would involve careful measurements with a variety of techniques on the identical solid for which a first-order transition had been observed by the method of Jura and his collaborators.

Thermodynamic Functions.—Our principal purpose in this investigation was to work out a suitable experimental procedure. We do not, at this time, wish to discuss in detail various implications arising

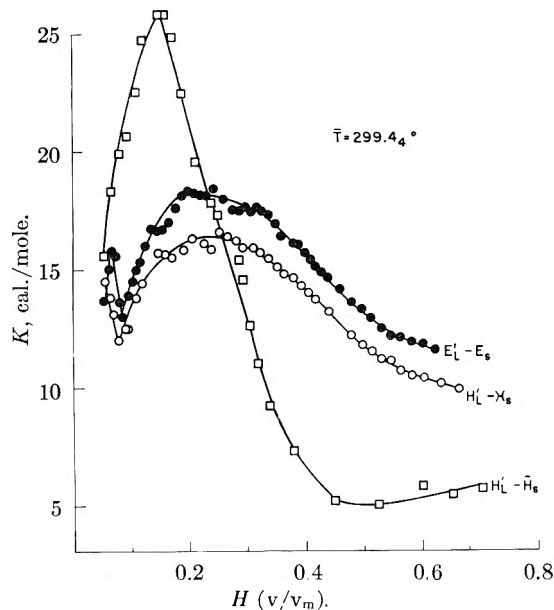


Fig. 5.—Differential and integral heats of adsorption of heptane on ferric oxide; $\bar{T} = 299.4^\circ\text{K}$.

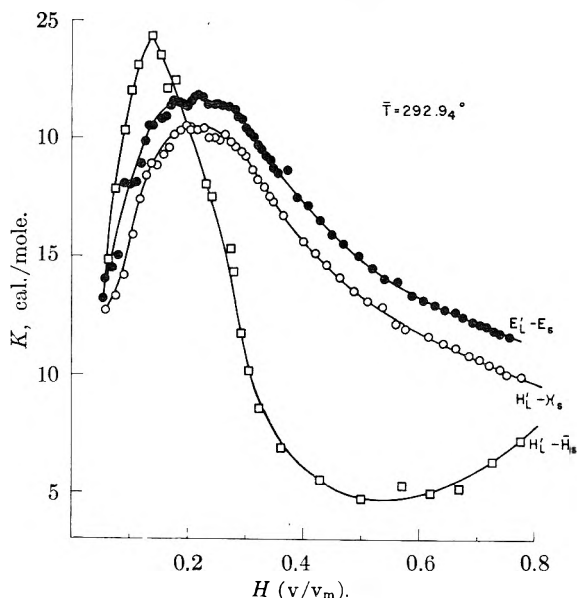


Fig. 6.—Differential and integral heats of adsorption of heptane on ferric oxide; $\bar{T} = 292.9^\circ\text{K}$.

from the behavior of the thermodynamic functions. One feature, however, does merit some comment in this paper.

The various maxima and minima noted in the thermodynamic functions are real; they could not arise owing to experimental error and appear for both sets of temperatures. It is tempting to interpret these maxima and minima in terms of a pseudo monolayer effect at surface coverages of approximately 0.2. Similar maxima and minima are noted in the thermodynamic functions at the true monolayer. It might be pointed out that no maxima in the variation of ϕ , the free energy function, are obtained.

Let us consider a situation in which the site distribution in energy is such that the surface is homogeneous energy-wise to coverages of approxi-

mately 0.2; the energy per site then drops off rapidly with coverage to a coverage of 0.4. Let the high energy sites be distributed over the surface in patches large compared with a heptane molecule. The surface would then be a composite, and we might expect the existence of what appear to be two monolayer points in terms of the entropy and a cooperative effect in the heats. Such a model would explain the results observed in this investigation;

heats observed at low surface coverages are comparable with the heats observed for hydrocarbons on carbon blacks by Beebe, Polley, Smith and Wendell¹² of 4 kcal. per mole of CH₂ groups. At the maximum in the isosteric heat curves, the heat per CH₂ (and CH₃) groups for heptane on ferric oxide is 4.5 kcal. per mole.

(12) R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, *J. Am. Chem. Soc.*, **69**, 2291 (1947).

HYDROGEN OVERVOLTAGE (CATHODIC POTENTIAL) ON TITANIUM IN ACIDIC AND BASIC SOLUTIONS¹

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Cathodic potential, or hydrogen overpotential, measurements on titanium electrodes at various current densities (in milliamp./cm.²) in the presence of air were made by the direct method in HF, HCl, HBr, H₂SO₄, CF₃COOH, CH₃COOH, NaOH and KOH, using different concentrations of these electrolytes at room temperature, 24–32°. The overpotential values became more negative with increasing current density. The relationship between these two quantities was a linear one in HF, and a logarithmic, or Tafel's relationship, in all other cases. It was shown that the first relation applies, if the titanium electrode dissolves in the electrolyte with hydrogen evolution. By replacing air with hydrogen, the straight lines obtained in HF were shifted 0.01 to 0.02 volt, toward more negative values. The *a'* and *b'* constants of the linear relation as well as the *a* and *b* constants of the Tafel curves changed with concentration of the electrolytes. The *b* values in volts decreased from -0.119 in 10 *N* H₂SO₄ to -0.241 in 0.02 *N* acid; in 0.5 *N* acid a *b* value of -0.175 was obtained, which is close to the average *b* value of pure metals. In general the hydrogen overpotential of titanium becomes more negative with the decreasing hydrogen ion concentration of the electrolyte, reaching a value of -1.34 volts in a 0.1 *N* KOH solution for *i* = 1 ma./cm.². The purity of titanium has some influence on the overpotential values of the metal.

Introduction

Very few literature references² are to be found concerning hydrogen overvoltage or overpotential on titanium.³ It has been shown that hydrogen overpotential on titanium increases with current density and can be substantially augmented by adding soluble fluorides to the acids.⁴

The hydrogen overpotential on a given cathodic metal at a certain current density is usually defined as the difference between the potential of this metal cathode at which hydrogen is being evolved and the potential of the reversible hydrogen electrode in the same solution (*definition I*).⁵ The use of the hydrogen electrode in the same solution is not often desirable because of possible uncontrolled changes of the potential of the electrode. It is much more advantageous to use the 1 *N* hydrogen electrode (with hydrogen ion activity equal to one) for all the cathodic potential measurements. Thus the data listed below represent potential (or overpotential) measurements on titanium, at which hydrogen is cathodically evolved, against the *normal hydrogen electrode (definition II)* of overpotential). At known hydrogen ion activities of the electrolyte,

overpotential values were also calculated according to definition I.

The sign given to the cathodic potential measurements is in accordance with that adopted by the Electrochemical Society, and which is in use in England and on the European Continent.

The Method, the Materials and the Experimental Procedure.—The "direct" method^{5,6} was chosen for this investigation, because this method is much simpler than the "indirect" method, and gives results which, according to many authoritative views,^{5,7} are equally accurate and reliable.

The over-all arrangement of the equipment for overpotential measurements consisted of (1) an electrolytic cell made of a polyethylene beaker containing a titanium cathode, a 2 × 2 cm. platinum anode, and a stirrer making 375 revolutions per minute, (2) a 1 *N* calomel electrode as a reference electrode and a KCl salt bridge, (3) a potentiometer with a sensitive external galvanometer, (4) a milliammeter for measuring the current passing the cell and several other necessary accessories.

The titanium cathode, cut from a piece of high purity titanium, had a surface area of 1.8 × 0.85 cm., and was mounted on a piece of glass tubing covered with a layer of pyseal wax to protect the glass from attack by hydrofluoric acid.

The end of a Luggin capillary was pressed horizontally against the titanium electrode, in such a way as to prevent shielding of the metal by the tip itself.

The potential of the titanium cathode was measured against the 1 *N* calomel electrode in the cell

Ti // electrolyte / 3.5 *N* KCl, salt bridge / 1 *N* KCl, Hg₂-Cl₂ // Hg

(1) Extract from a thesis submitted by S. T. Shih in partial fulfillment of the requirements for the Ph.D. degree at the Graduate School of the University of Missouri. The thesis is based on a portion of work carried out by S. T. Shih at the Missouri School of Mines and Metallurgy for the Wright Air Development Center under Contract No. AF 33(616)-75.

(2) R. A. Schaefer and W. King, *Plating*, **39**, 487, 627, 769 (1952).

(3) A. Thiel and W. Hammerschmidt, *Z. anorg. Chem.*, **132**, 15, 23 (1924).

(4) M. E. Straumanis and C. B. Gill, *J. Electrochem. Soc.*, **101**, 10, 13 (1954).

(5) J. O'M. Bockris, *Chem. Revs.*, **43**, 525 (1948).

(6) M. E. Straumanis, in G. M. Schwab, "Handbuch der Katalyse," Vol. VI, Springer-Verlag, Wien, 1945, pp. 132, 137-143.

(7) See e.g., A. L. Ferguson, *Trans. Electrochem. Soc.*, **76**, 113 (1939). Ferguson also enunciated his opinion at the meeting of the Electrochem. Soc. in Philadelphia on May 6, 1952, which was that the direct and indirect methods, if applied correctly, would give approximately equal results.

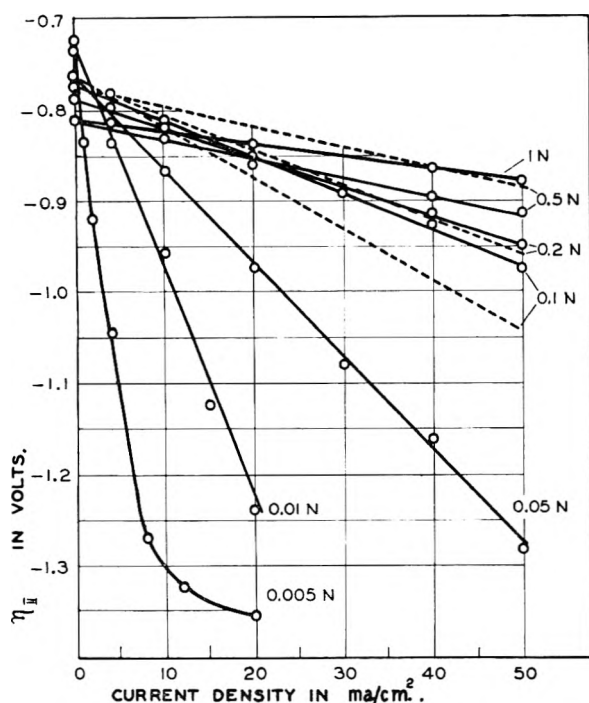


Fig. 1.—Cathodic potentials (η_{II}) of pure titanium vs. current density in hydrofluoric acid in presence of air. Each point represents the average of two runs; dashed lines, cathodic potentials (η_{II}) of less pure Remington Arms Ti under the same conditions; hydrogen scale.

and was reduced to the potential of the 1 *N* hydrogen electrode, by adding +0.280 volt to the negative value obtained by the measurement of the cell at 25°.

Potential variations of the 1 *N* calomel electrode³ due to temperature fluctuations were disregarded.

All of the materials used were of C.P. grade. The hydrofluoric acid was an analyzed reagent. The titanium was of two kinds: a relatively impure Remington Arms titanium of approximately 97%⁹ purity in the form of a sheet .6 mm. thick, and a high purity iodide titanium,¹⁰ 99.99% produced by the Foote Mineral Company in the form of a crystal bar.

The titanium cathodes were attacked by the hydrofluoric acid during the experiments. To remove the roughness caused by previous runs, the titanium was polished through No. 00 emery paper, and then immersed in 1 *N* hydrofluoric acid for about 1 minute, followed by quick rinsing in distilled water.

The titanium cathode and platinum anode were mounted on the same frame at a definite distance apart. "Apparent" cathodic current densities were used; no "roughness" factor was introduced.

A few potential readings were taken on the titanium electrode before current was passed. Then the circuit was closed and after a few minutes of stabilization a series of readings was made with increasing current up to a maximum, and then, in some experiments, readings were made with decreasing current. However, in most instances, the occurrence of hysteresis phenomena was observed.

While hydrofluoric acid readily attacks titanium,^{9,11} all other acids dissolve the metal either slowly or not at all.¹¹ A difference in the cathodic behavior of titanium should be expected, as in hydrofluoric acid it shows all the features of a very active metal, while in other acids it behaves as a noble metal.

Experimental Results

1. Hydrofluoric Acid.—The measurements were carried out in 0.005, 0.01, 0.05, 0.1, 0.2, 0.5 and 1 *N*

(8) See S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1946, p. 941.

(9) M. E. Straumanis and P. C. Chen, *J. Electrochem. Soc.*, **98**, 234, 236 (1951).

(10) So named industrially because it is purified by thermal decomposition of titanium iodide.

(11) M. E. Straumanis and P. C. Chen, *Corrosion*, **7**, 229 (1951).

acids of checked concentrations.¹² Higher concentrations of the acid were not used because the attack on the titanium electrode was then too rapid.

The results obtained with pure iodide titanium electrodes are summarized in Fig. 1.

Instead of the usual logarithmic Tafel equation,¹³ there is a linear relation between hydrogen overpotential η_{II} (according to definition II) and current density i

$$\eta_{II} = a' + b'i \quad (1)$$

where b' and a' are constants. Even if definition I is applied for the calculation of overpotential values, eq. 1 will retain its validity, only the intercept a' will be shifted in the positive direction, more for the diluted acids and less for the more concentrated acids. The concentration dependence of the overvoltage values as expressed by the slope constant b' will also be retained. The first point of each of the straight lines, which fits well to them, is $\epsilon' = a'$ if $i = 0$. In the case of a logarithmic relationship, it is impossible to plot this first point at $i = 0$, and it cannot be included in the system of lines (see Fig. 3). The deviation of the experimental points from the average value lines of Fig. 1 was between ± 0.8 to 1.6, or about 2%; this deviation being less at lower concentrations of the acid.

A dark grayish black film, with a deepest color in about an 0.2 *N* acid,⁹ was formed on the surface of the titanium electrode during the course of the experiments.

The same straight line relationship was also observed if a less pure metal (Remington Arms titanium) was used for the cathodic material as shown by the dashed lines on Fig. 1. However, the potentials at zero current density (a' constants) were closer together than in the case of iodide titanium, in agreement with previous potential measurements.⁹

Oxygen acts as a depolarizer and shifts the potential of a working cathode in the positive direction, especially if the current density is low.¹⁴ To check this point for titanium, another series of experiments was performed in an H-shaped cell, with purified hydrogen being bubbled through it.

It was found that the overvoltage on pure titanium in hydrofluoric acid in a hydrogen atmosphere is only by 0.01 to 0.02 volt more negative than in air. The admission of air simply shifts the overvoltage-current density line nearly parallel to itself in the less negative direction, hence there is no change in the b' constant. Similar measurements previously made with a cadmium cathode in 0.1 *N* sulfuric acid gave the same result.¹⁵

Thus, air as well as oxygen developed on the anode in sulfuric acid, has only a slight influence on the hydrogen overpotential in agreement with Hickling and Salt.^{14b} Consequently, all further experiments were made in air, which was much more convenient, and higher current densities could be applied.

(12) E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1952, p. 99.

(13) J. Tafel, *Z. physik. Chem.*, **50**, 641 (1905).

(14) (a) M. Straumanis, *Korrosion u. Metallschutz*, **12**, 148 (1936);

(b) A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, **37**, 319 (1941).

(15) M. Straumanis and N. Brakšs, *Z. physik. Chem.*, **185**, 37 (1939).

2. **Hydrochloric and Hydrobromic Acids.**—In plotting the cathodic potential of titanium in these two acids against the log of current density, straight lines resulted in agreement with Tafel's relationship¹³

$$\eta_{II} = a + b \log i \quad (2)$$

Fig. 2 shows that the a constant, or the intercept of the Tafel lines on the potential axis, changes with concentration, becoming more negative with the dilution of the acid, while the b constant, or the slope of the lines, changes very little. The break in the straight line in 4 N hydrochloric acid could also be interpreted as a curve indicating a deviation from eq. 2 in favor of eq. 1. The reproducibility of the parallel runs was even better than in hydrofluoric acid.

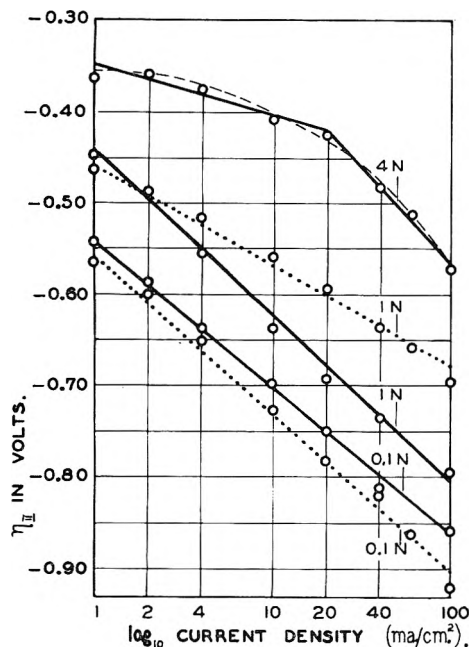


Fig. 2.— η_{II} on pure titanium vs. log of current density in hydrochloric (solid lines) and hydrobromic acids (dotted lines); hydrogen scale.

In tracing back the variation of the hydrogen overvoltage with decreasing current density a potential of as much as +0.9 volt in some experiments was finally measured when the current was shut off. A similar phenomenon was noticed by Schlain and Smatko.¹⁶ As chlorine or bromine was developed on the platinum anode during the electrolysis of HCl or HBr, it is assumed that a small amount of platinum went into solution creating conditions similar to those of the experiments of Schlain. However, the same experiments repeated with a pure spectroscopic carbon anode produced the same cathodic effect, and besides, no platinum lines were detected in the thin grayish film on titanium by spectroscopic analysis. Hence, the problem of passivation was left unsolved, and because of this uncertainty, the potential measurements in the three halogen acids were discontinued.

3. **Sulfuric Acid.**—The cathodic potentials of titanium in this acid as plotted against $\log i$, produce

straight lines in accordance with Tafel's law. Both the a and b constants of the equation vary with the concentration of sulfuric acid (Fig. 3).

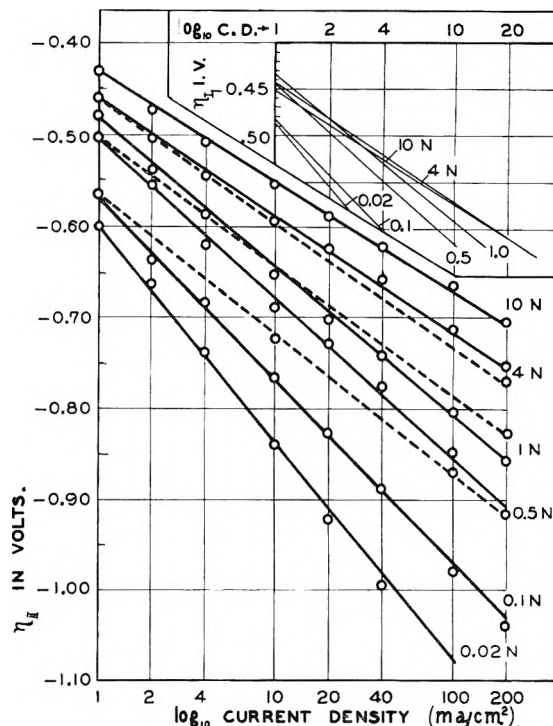


Fig. 3.— η_{II} of pure Ti vs. log of current density in sulfuric acid. Dashed lines (without experimental points on them), η_{II} for less pure Remington Arms Ti; inset, hydrogen overpotential η_I (definition I) on pure Ti; the potential of the hydrogen electrode was reduced to that in the acid used.

In a few experiments the measurement of cathodic potentials was traced back with decreasing current density. Although some hysteresis was observed, the results agreed generally with those obtained with increasing current density. The residual potential observed in hydrochloric and hydrobromic acid when the current was shut off, was not noticed in sulfuric acid; nor was any visible film formed on the titanium in this acid.

As the activity coefficients of different concentrations of sulfuric acid are known,¹⁷ the hydrogen overpotential η_I according to definition I was calculated. The straight lines shown in the inset of Fig. 3 demonstrate that the dependency of the a constant on the concentration still persists, but with a scatter of only one third of the previous instance. The b constant remains, of course, the same in both cases, showing a dependency on the concentration of the acid.

Experiments with less pure Remington Arms titanium showed no significant difference (dashed lines on Fig. 3), except that the change of the slope (b constant) with concentration was less pronounced, and that a visible dark film was formed on the surface of the electrode during the experiment, while the pure iodide titanium was only slightly tarnished.

4. **Acetic and Trifluoroacetic Acid.**—In acetic acid, as a weak acid, the measurements were limited

(16) D. Schlain and J. S. Smatko, *J. Electrochem. Soc.*, **99**, 417 (1952); also D. Schlain, U. S. Department of Interior, Bureau of Mines Report of Investigation 4965, 1953.

(17) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935); also B. E. Conway, "Electrochemical Data," Elsevier Publ. Co., New York, N. Y., 1952, p. 91.

to current densities below 30 to 40 ma./cm.². The measured potentials follow the Tafel law, and the concentration of the acid seems to have no marked effect either on the a nor on the b constant.

Trifluoroacetic acid (CF₃COOH), on the other hand, shows good conductivity but a break was noticed around 40 ma./cm.².

5. Sodium and Potassium Hydroxide Solutions.

—Tafel's relationship holds quite well in 0.1 and 1 *N* potassium hydroxide, and in 0.1 *N* sodium hydroxide solutions. The intercept on the potential axis (the a constant) becomes less negative, while the slope (b constant) tends to be less steep with increasing concentration. The potentials are quite negative: -1.35 volts at a current density of 1 ma./cm.², down to -1.77 volts at 100 ma./cm.² in 0.1 *N* sodium hydroxide solution.

Discussion of Results

The Straight Lines and the Logarithmic Relationships.—Butler and Armstrong and others¹⁸ derived an equation showing the straight line relationship being correct for small currents.^{18–20} Schuldiner found this relationship on bright platinum at low current densities.²¹ But as far as is known by the authors, nobody has reported on the one relation (eq. 1) to be valid in one solution, and the other one (eq. 2) in other solutions over a considerable range of current densities for the same cathodic metal.

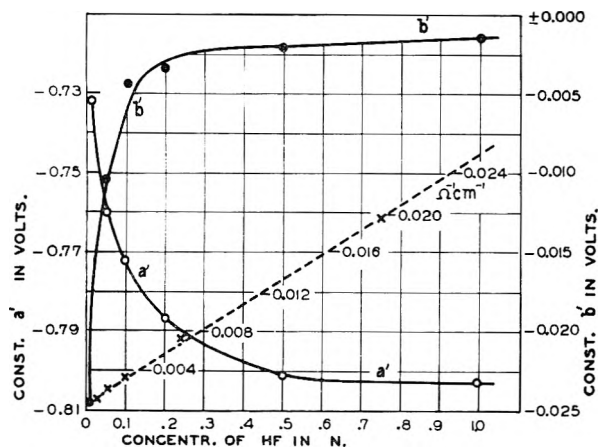


Fig. 4.— a' (left side) and b' (right side) vs. concentration of HF, iodide titanium cathode; broken lines, conductivity of the acid vs. concentration.

The experimental results obtained in the work with titanium lead to the conclusion that the straight line relationship (eq. 1) takes place if the cathodic metal, titanium, dissolves with hydrogen evolution in the acid (HF, Fig. 1), and the logarithmic one (eq. 2) if it does *not* dissolve in the electrolyte, but behaves as a noble metal (in HCl, HBr, H₂SO₄, CH₃COOH, Figs. 2 and 3).

This conclusion is further supported by the following facts.

(18) J. A. V. Butler and G. Armstrong, *J. Chem. Soc.*, 743 (1934).

(19) P. Dolin, B. Ersher and A. Frumkin, *Acta Physicochim. U.R.S.S.*, **13**, 779 (1940).

(20) N. E. Khomutov, *Trudy Moskov. Khim. Tekhnol. Inst. im. D. I. Mendeleeva.*, **16**, 127 (1940).

(21) S. Schuldiner, *J. Electrochem. Soc.*, **99**, 488 (1952); **101**, 393 (1954).

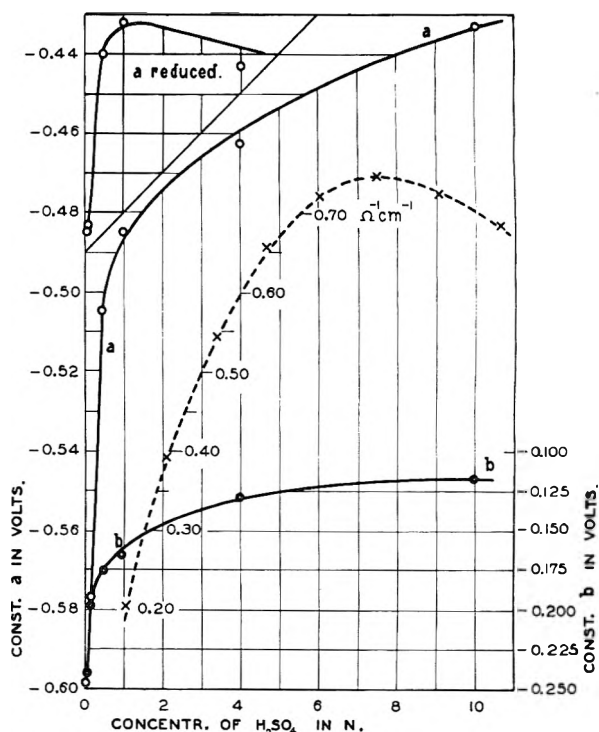


Fig. 5.— a (left side) and b (right side) vs. concentration of sulfuric acid. Overpotential definition II. Inset: a vs. concentration of sulfuric acid (definition 1). Iodide titanium cathode. Dashed lines, conductivity of sulfuric acid vs. concentration.

Logarithmic curves were formed instead of straight lines if the rate of dissolution could be sufficiently decreased by some means: such as by the addition of alkali fluorides,⁴ or by diluting the acid (0.005 *N* HF, Fig. 1), and *vice versa* (in 4 *N* HCl, Fig. 2).

This change from linear relationship to logarithmic is a gradual one accompanied by a decrease in the rate of dissolution, with the increase of fluoride concentration, and conversely.

Hydrogen Ion Concentration, and the a and b Constants.—Hydrogen ion concentration is listed by some authors as one of the factors influencing, more or less, the hydrogen overpotential.^{5,6,22,23} DeBéthune and Kimball found that at higher hydrogen ion concentrations the overvoltage decreases, that is, the cathodic potential becomes more positive.²⁴

Figure 4 shows the dependence of a' and b' on the concentration of hydrofluoric acid. The value of the slope constant b' depends on the units (here volts per ma./cm.²). The values of the a' constants, representing the potential of titanium at zero current may be influenced by the rate of dissolution of titanium. The rate was not measured.

Figure 5 shows the change of the a constant of the logarithmic equation 2 with the concentration of sulfuric acid (a is the cathodic potential on tita-

(22) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand, New York, N. Y., 1946, p. 1019.

(23) S. Levina and V. Zarinskii, *J. Phys. Chem. U.S.S.R.*, **9**, 621 (1937).

(24) A. J. DeBéthune and G. E. Kimball, *J. Chem. Phys.*, **13**, 53 (1945).

nium at 1 ma./cm.²).²⁵ The b constant (in volts) which is independent of the two overpotential definitions, and of the units, shows a clearly expressed trend, similar to that in hydrofluoric acid, with increasing concentration of the acid (Fig. 5). In comparing the conductivity curves for hydrofluoric acid and of sulfuric acid²⁶ with the b' and b curves (Figs. 4 and 5), it is evident that there is no simple relationship between these two constants and the conductivities of the acids used. This means that in addition to some ohmic overpotential, caused by the resistance r between the tip of the capillary and the surface, there are also other factors responsible for the formation and decline of b with increasing concentration of the electrolyte.²⁷ The average of the b factor in 0.5 N sulfuric acid is 0.175, which is in agreement with 0.17, the average value for the b factor of pure metals according to Bockris.²⁸ The extreme values of 0.12 and 0.24 are completely within the scope of b factors found for all other pure metallic electrodes.^{6,28}

As to the theoretical interpretation of hydrogen overpotential,^{5,29} it is worth mentioning that the catalytic theory of overpotential, originally developed by Bonhoeffer,³⁰ and recently upheld with some new examples by Cremer and Kerber, has gained wide recognition.³¹ Accordingly titanium, exhibiting no remarkable catalytic properties, shows a fairly high hydrogen overpotential (or a very negative cathodic potential). The fact that at the same time this metal absorbs hydrogen confirms the conclusion of Thiel that there is no such parallelism between solubility of hydrogen and overpotential³ as suggested by Nernst.³²

Conclusion

The hydrogen overpotential on titanium (cathodic potential) as shown by Figs. 1, 2 and 3 is fairly high. Knowing the a' and b' and the a and b constants (Figs. 4 and 5), the cathodic potential at any intermediate concentration and current density

(25) If it is desirable to express the current density in amp./cm.², the new a constant can be calculated from that one given by the simple equation

$$a_{\text{amps/cm}^2} = a_{\text{ma/cm}^2} - 3b$$

(26) Landolt-Börnstein, (Roth/Scheel), "Physikalisch-chemische Tabellen," Vol. 5, Auflage II, Verlag. Julius Springer, Berlin, 1923, pp. 1076-1077.

(27) C. A. Knorr, *Z. Elektrochem.*, **57**, 599 (1954).

(28) J. O'M. Bockris, *Chem. Revs.*, **43**, 525, 537 (1948).

(29) On overpotential theories see, e.g., J. O'M. Bockris, in J. A. V. Butler, "Electrical Phenomena on Interfaces," Methuen and Co., London, 1951, p. 155; also G. Kortum and J. O'M. Bockris, "Textbook of Electrochemistry," Vol. II, Elsevier Publ. Co., New York, N. Y., 1951, p. 420, 425.

(30) K. F. Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

(31) E. Cremer and R. Kerber, *Z. Elektrochem.*, **57**, 757 (1953).

(32) W. Nernst and F. Dolezalek, *ibid.*, **6**, 549 (1900).

up to 50 ma. in hydrofluoric and up to 200 ma./cm.² in sulfuric acid can be calculated.

A good measure of the magnitude of an overpotential value, in order to compare it with other values, is the a' (for $i = 0$) and a constant (for $i = 1$ ma./cm.²). In Table I some of these constants are listed.

TABLE I
 a' AND a CONSTANTS OF THE EQUATIONS 1 AND 2 OBTAINED AT TITANIUM IN SOME ACIDS AND BASES

Electrolyte	Concn.	a' or a in volts		Atm.
		a'	a	
HF	0.1	-0.774	...	Air
	0.2	-0.787	...	Air
	0.2	-0.799	...	H ₂
	0.5	-0.810	...	Air
	1.0	-0.812	...	Air
	1.0	-0.817	...	H ₂
HCl	0.1	...	-0.534	Air
HCl	1.0	...	-0.447	Air
HBr	0.1	...	-0.564	Air
HBr	1.0	...	-0.464	Air
H ₂ SO ₄	0.02	...	-0.601	Air
	0.1	...	-0.584	
	0.5	...	-0.503	
	1.0	...	-0.480	
CF ₃ COOH	1.0	...	-0.596	Air
CH ₃ COOH	1.0	...	-0.760	
KOH	0.1	...	-1.338	Air
KOH	1.0	...	-1.290	Air
NaOH	0.1	...	-1.351	Air
NaOH	1.0	...	-1.267	Air

In hydrofluoric acid the cathodic potential of titanium becomes more negative with the increasing concentrations of the acid. However, at higher current densities in hydrofluoric acid (Fig. 1), and in all other acids and bases the cathodic potential values of titanium (at 1 ma./cm.² and more) are shifted in the positive direction with increasing concentration of the electrolyte.

This behavior, without doubt, bears some relation to the ability of hydrofluoric acid to dissolve to a certain amount the oxide coating on the surface of titanium and to attack the metal. In the other reagents, which react only slowly or not at all with the coatings on the metal, the conditions for overpotential formation are different, as a consequence of which two different potential-current density relationships 1 and 2 are obtained.

Acknowledgment.—The authors are grateful to the Wright Air Development Center for continued support of this work and permission to publish the results obtained.

INFRARED SPECTRA OF POLYPEPTIDES AND RELATED COMPOUNDS. I

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Infrared absorption spectra of nine polypeptides have been measured in the frequency region from 5000 to 600 cm^{-1} . There have been observed many bands common to all these polypeptides, but some of the bands appearing between 1200 and 800 cm^{-1} were found to depend considerably on the sequence of amino acids in the polypeptide. It was concluded that in silk fibroin glycine and alanine residues are arranged alternately, although some authors prefer the at-random arrangement to the periodic arrangement.

Many papers have been published on the infrared spectra of polypeptides and proteins.^{1,2} There are, however, many problems remaining to be solved as to the interpretation of the spectra in terms of the structure of polypeptides. Concerning these problems we have published several papers on the structure of molecules with one and two peptide bonds, (N-methylacetamide,³ acetyl amino acid, N-methylamides,⁴ etc.).

As Professor Noguchi of Kanazawa University kindly placed various samples of synthetic polypeptides at our disposal, we could extend our structural studies and could obtain some interesting results concerning the sequence of amino acid residues in polypeptides. The results will be reported in this and the following communications.

Experimental

Noguchi found a new method of synthesis⁵ of polypeptides by the polymerization of carbothiophenylamino acids or carbothiophenyloligo peptides. The first seven samples shown in Table I were prepared by him by this method. In addition to these the last two samples shown in the same table were used in the present measurement.

TABLE I
SAMPLES USED IN THE INFRARED MEASUREMENT

Sample	Mol. wt.
Polyglycine	135,200
Poly-DL-alanine	22,400
Copolymer of glycine and DL-alanine (1:1)	11,500
Polyglycyl-DL-alanine	34,800
Poly-DL-phenylalanine	59,400
Poly- β -alanine	43,500
Poly-glycyl-DL-phenylalanine	30,600
Silk fibroin (crystalline part), see ref. 17
Poly- ϵ -capramide film

The infrared spectra were recorded at 20° in the frequency region from 5000 to 600 cm^{-1} by the Baird spectrophotometer with NaCl optics. Except for poly- ϵ -capramide film the samples were measured in Nujol mull.

Results and Discussions

The results of infrared measurements are shown in Figs. 1-4. The dotted lines indicate the absorption of Nujol bands overlapping the bands of the sample under investigation. Figure 1 contains the absorption curves of N-methylacetamide in the liquid state, and acetylglycine N-methylamide,

(1) G. B. B. M. Sutherland, *Advances in Protein Chem.*, **7**, 291 (1952).

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, Chapter 12.

(3) S. Mizushima, T. Shimanouchi, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba and O. Fujioka, *J. Am. Chem. Soc.*, **72**, 3490 (1950).

(4) S. Mizushima, T. Shimanouchi, M. Tsuboi, *et al.*, *ibid.*, **73**, 1330 (1951); **74**, 270, 4639 (1952); **75**, 1863 (1953).

(5) J. Noguchi, *J. Chem. Soc. Japan*, **74**, 961 (1953); J. Noguchi and T. Hayakawa, *J. Am. Chem. Soc.*, **76**, 2846 (1954).

acetylglycylglycine N-methylamide⁶ and polyglycine in powder form. At the top of the figure is given the assignment of the bands of N-methylacetamide to various vibrational modes.

Figure 2 shows the absorption curves of poly-DL-alanine and poly-DL-phenylalanine, Fig. 3 those of poly- β -alanine and poly- ϵ -capramide and Fig. 4 those of glycine-DL-alanine copolymer (1:1), polyglycyl-DL-alanine (periodic), crystalline part of silk fibroin and polyglycyl-DL-phenylalanine (periodic). It will be seen from these figures that there are several bands common to all polypeptides measured in this experiment. These appear at 3300, 3080, 1640, 1550, 1480-1340, 1280-1230 and 725 cm^{-1} . On the other hand the bands observed in the range from 1200 to 800 cm^{-1} are characteristic of the structure of each polypeptide and, as shown below, we can derive some interesting conclusions from the frequency values of their peaks.

I. Absorption Bands Common to All Polypeptides Measured in This Experiment. (a) **The Band at 3300 cm^{-1} .**—This arises from the NH stretching vibration of the peptide bond in the planar *trans* form which is involved in the hydro-

gen bonds, $-\text{NH} \dots \text{O}=\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{N}-\text{H} \dots \text{O}=\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$,

in the chain type polymer. The details have been reported.^{4,7}

On the higher frequency side of this band there was sometimes observed a shoulder peak due to the adsorbed water which naturally disappears on dehydration. For example, poly- ϵ -capramide under 0.01 atmosphere of water vapor showed the water band at 3500 cm^{-1} which disappeared on dehydration over concentrated sulfuric acid.⁸ On the other hand the sample of poly- β -alanine used in this experiment had bound water which could not be removed on dehydration over concentrated sulfuric acid.⁹ For the disappearance of the water band it was necessary to heat the sample for ten hours at 135° in the dry air over phosphorus pentoxide.

(b) **The Band at 3080 cm^{-1} .**—This is also assigned to the bonded NH stretching vibration.^{7,10} The intensity ratio of this band to that at 3300 cm^{-1} depends on the nature of the polypeptide.

(c) **The Bands at 3000-2800 cm^{-1} .**—They arise from the CH stretching vibrations.

(6) The sample was prepared by T. Sugita in our Laboratory.

(7) M. Tsuboi, *Bull. Chem. Soc. Japan*, **22**, 215, 255 (1949).

(8) M. Tsuboi, *ibid.*, **25**, 160 (1952).

(9) The measurement was made with Perkin-Elmer Infrared Spectrophotometer Model 112, with LiF prism.

(10) S. Mizushima, T. Shimanouchi and M. Tsuboi, *Nature*, **166**, 406 (1950); M. Tsuboi, *Bull. Chem. Soc. Japan*, **25**, 385 (1952).

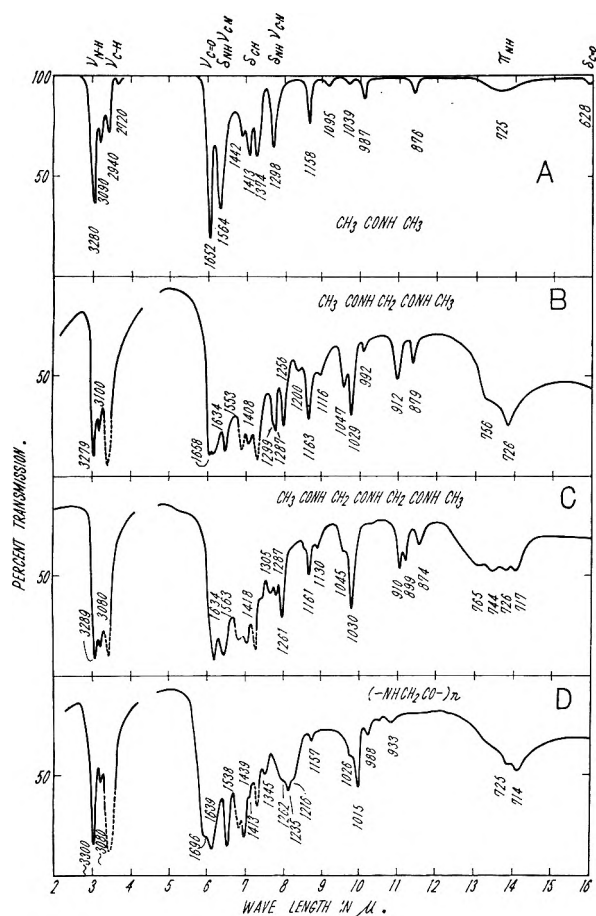


Fig. 1.—Infrared absorption curves of N-methylacetamide (A), acetylglycine N-methylamide (B), acetylglucylglycine N-methylamide (C) and polyglycine (D). Dotted lines indicate the absorptions due to Nujol in which the samples are suspended (ν , stretching; δ , deformation; π , out of plane vibrations).

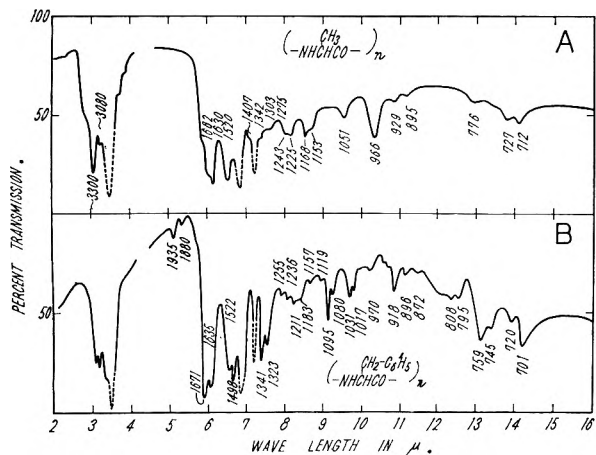


Fig. 2.—Infrared absorption curves of poly-DL-alanine (A) and poly-DL-phenylalanine (B).

(d) **The Band at 1640 Cm^{-1} .**—This is assigned to the C=O stretching vibration.

(e) **The Band at 1550 Cm^{-1} .**—This is characteristic of the peptide $-\text{NH}-\text{CO}-$ bond which is involved in $\text{N}-\text{H} \cdots \text{O}=\text{C}$ hydrogen bonding and in which the N-H and C=O bonds are in the *trans* position with respect to each other. This band has been assigned either to the N-H deformation vi-

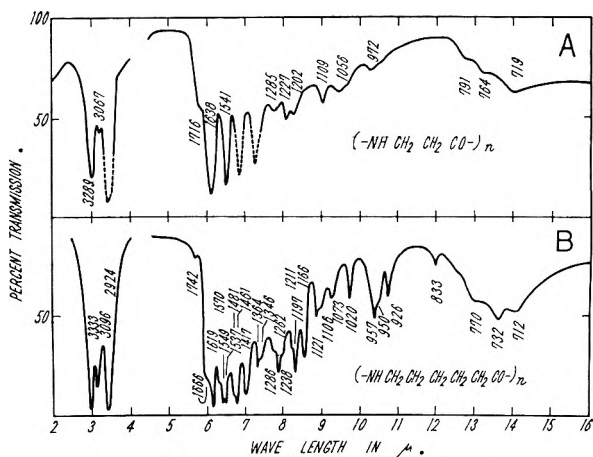


Fig. 3.—Infrared absorption curves of poly- β -alanine (A) and poly- ϵ -capramide (B).

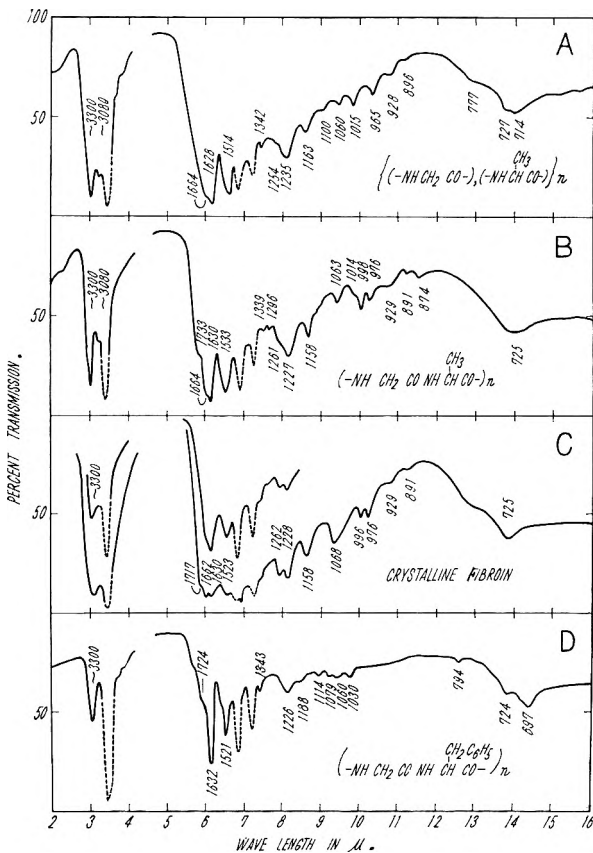


Fig. 4.—Infrared absorption curves of glycine-DL-alanine at random copolymer (1:1) A; poly-glycyl-DL-alanine (periodic) B; crystalline fibroin C; and poly-glycyl-DL-phenylalanine D.

bration¹¹ or to the C-N stretching vibration.¹² It has been shown by Fraser and Price¹³ and by Miyazawa, *et al.*,¹⁴ that the two vibrations contribute considerably to this band.

(f) **The Bands at 1480-1340 Cm^{-1} .**—These are assigned to the various C-H deformation vibrations.

(11) R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

(12) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangle, "Infrared Determination of Organic Structure," D. Van Nostrand Co., New York, N. Y.

(13) R. D. B. Fraser and W. C. Price, *Nature*, **170**, 490 (1952).

(14) T. Miyazawa, *et al.*, to be published.

(g) **The Twin Bands at 1280 and 1230 cm^{-1} .**—Most of the polypeptides show these bands. From the comparison of the four absorption curves in Fig. 1 the twin bands can be concluded to correspond to the 1290 cm^{-1} band of N-methylacetamide, assigned to the vibration contributed by both the NH in-plane deformation and C-N stretching motions.¹⁴ It is not probable to assign these bands to the NH_3^+ vibration of the side chain.

In Fig. 5 are reproduced the absorption curves in this frequency region. It will be seen that the intensity ratio of these two bands is different in different polypeptides.

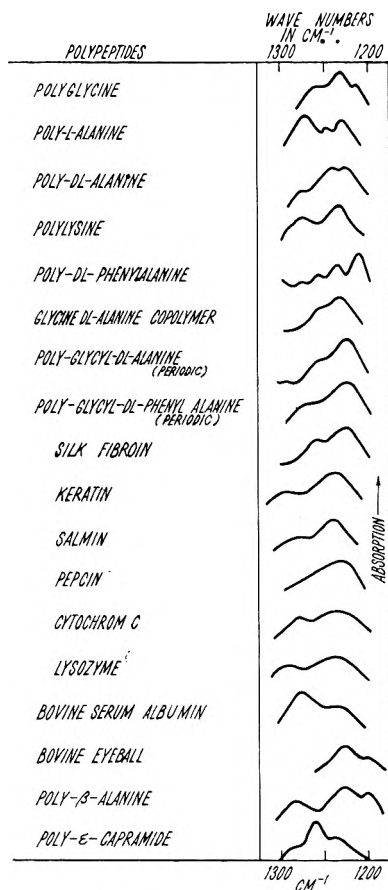


Fig. 5.—The 1200~1300 cm^{-1} region absorptions of polypeptides.

(h) **The Band at 725 cm^{-1} .**—This arises from N-H out of plane deformation vibration.¹⁵

II. The Band at 1015 cm^{-1} Characteristic of the Glycylglycine Residue.—As referred to above the spectra observed in the region from 1200 to 800 cm^{-1} are characteristic of the structure of polypeptides and, therefore, the interpretation of the absorption bands in this region is very important. Among others that of the band at 1015 cm^{-1} is clear-cut. This band is concluded to arise from the glycylglycine structure from the following reasons: (1) This band is very strong and sharp for polyglycine and is not observed at all for such polymers as poly- β -alanine and poly-DL-alanine which do not contain glycine residues. (2) Even in polymers containing glycine residues this band es-

caped detection for those in which no two glycine residues adjoin each other. (3) This band is observed for glycine-alanine copolymers in which the two residues are arranged at random and which, therefore, contain glycylglycine structures.

This conclusion is compatible with the experimental results of Blout and Linsley who observed a strong band at $1015 \pm 10 \text{ cm}^{-1}$ for glycylglycine, oligopeptides with glycine residues only and polyglycine.¹⁶

In Table II are shown the bands of various substances observed in the frequency region, $1015 \pm 20 \text{ cm}^{-1}$. It will be seen that acetylglycine N-methylamide and acetylglycylglycine N-methylamide also show a sharp and strong band at 1030 cm^{-1} similar to the 1015 band referred to above (see also Fig. 1, B,C). Such a band does not appear at all for acetylnorleucine N-methylamide and acetylvaline N-methylamide.

III. Sequence of Aminoacid Residues in Polypeptides.—The appearance or otherwise of the band at 1015 cm^{-1} referred to above is a good criterion upon which we can test the existence of two consecutive glycine residues in the polypeptide. In addition to this there have been observed some other bands which seem to depend upon the sequence of amino acid residues.

The lines shown in Fig. 6 denote the positions and intensities of bands observed in the region from 1200 to 800 cm^{-1} . It is seen that the spectrum of glycine-alanine at random copolymer (1:1) are almost the superposition of those of polyglycine and polyalanine, including the band at 1015 cm^{-1} of polyglycine and that at 965 cm^{-1} of polyalanine. The latter may be characteristic of the alanylalanine structure just as the former is characteristic of the glycylglycine structure.

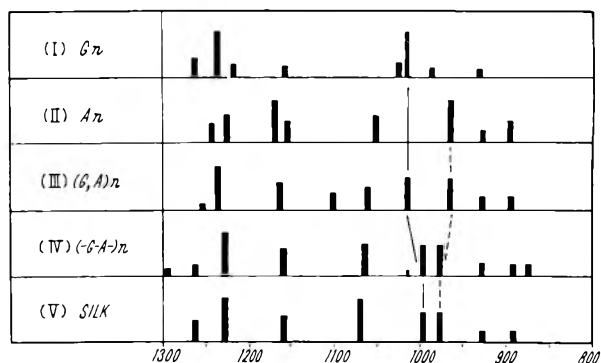


Fig. 6.—The 800~1300 cm^{-1} region absorptions of polyglycine (G_n), poly-DL-alanine (A_n), glycine-DL-alanine at random copolymer (1:1) ($(G,A)_n$), poly-glycyl-DL-alanine (periodic) ($(G-A)_n$), and silk fibroin.¹⁷

By contrast in glycine-alanine periodic polymer in which the two different residues are arranged alternately along the polymer chain, the two bands at 1015 and 965 cm^{-1} are not observed at all and the two strong bands appear at 998 and 975 cm^{-1} . There has been observed no other significant difference between the spectra of the at-random copolymer and periodic polymer.

In connection with this, the spectrum of "the crys-

(15) H. K. Kessler and G. B. M. Sutherland, *J. Chem. Phys.*, **21**, 570 (1953).

(16) E. R. Blout and S. C. Linsley, *J. Am. Chem. Soc.*, **74**, 1946 (1952).

TABLE II
THE BANDS IN THE REGION $1015 \pm 20 \text{ CM.}^{-1}$

Comps.	Formula	CM. ⁻¹	Intensity
N-Methylacetamide	$\text{CH}_3\text{CONHCH}_3$	None
Carbothiophenylglycine	$\text{C}_6\text{H}_5\text{SCONHCH}_2\text{COOH}$	{ 1012 1003	Medium Weak
Glycylglycine	$\text{NH}_3^+\text{CH}_2\text{CONHCH}_2\text{COO}^-$	1015	Strong ¹⁶
Triglycine ~ Hexaglycine	$+\text{NH}_3\text{CH}_2\text{CO}(\text{NHCH}_2\text{CO})_{1-4}\text{NHCH}_2\text{COO}^-$	1015	Strong ¹⁶
Acetylglycine-N-methylamide	$\text{CH}_3\text{CONHCH}_2\text{CONHCH}_3$	1029	Strong
Acetylglycylglycine N-methylamide	$\text{CH}_3\text{CONHCH}_2\text{CONHCH}_2\text{CONHCH}_3$	1030	Strong
Polyglycine	$(-\text{NHCH}_2\text{CO}-)_n$	1015	Strong
Carbothiophenyl-DL-alanine	$\text{C}_6\text{H}_5\text{SCONHCH}(\text{CH}_3)\text{COOH}$	1023	Medium
Poly-DL-alanine	$(-\text{NHCHCO}-)_n$	None
Carbothiophenyl-β-alanine	$\text{C}_6\text{H}_5\text{SCONHCH}_2\text{CH}_2\text{COOH}$	1023	Weak
Poly-β-alanine	$(-\text{NHCH}_2\text{CH}_2\text{CO}-)_n$	None
Carbothiophenyl-glycyl-DL-alanine	$\text{C}_6\text{H}_5\text{SCONHCH}_2\text{CONHCH}(\text{CH}_3)\text{COOH}$	{ 1022 994	Weak Weak
Poly-glycyl-DL-alanine (periodic)	$(-\text{NHCH}_2\text{CONHCH}(\text{CH}_3)\text{CO}-)_n$	998	Medium
Glycine DL-alanine copolymer (1:1) (at random)	$\left\{ \begin{array}{c} \text{CH}_3 \\ \\ (-\text{NHCH}_2\text{CO}-)(-\text{NHCHCO}-) \end{array} \right\}_n$	1015	Medium

talline residue of silk fibroin¹⁷ is interesting. This shows strong bands at 996 and 976 cm.^{-1} but no bands at 1015 and 965 cm.^{-1} . We can, therefore, conclude that in the crystalline part of silk fibroin the glycine and alanine residues are arranged alternately just as in periodic polymer and not as in at-

(17) S. Akabori, K. Satake and K. Narita (*Proc. Japan Acad.*, **25**, 206 (1949)) showed that silk fibroin underwent gradual degradation in dilute hydrogen peroxide at room temperatures, in the presence of a small amount of ferrous sulfate as catalyzer, leaving insoluble residue, 35% in weight of the original silk fibroin, which was found to be a high polymer consisting mainly of glycine and alanine (1:1). This residue was called by them the "crystalline residue" and was considered by them to correspond to Meyer's crystalline part of silk fibroin because it showed sharp Debye-Scherrer rings similar to those shown by the original silk fibroin. The sample used in the present experiment is this crystalline residue of silk fibroin.

random copolymer. This is in agreement with the model of silk fibroin proposed by Meyer, *et al.*,¹⁸ but not with that corresponding to the at-random copolymers of glycine and alanine.

Acknowledgment.—The authors wish to thank Professor J. Noguchi of Kanazawa University for the samples of many synthetic polypeptides used in this experiment. They are also indebted to Professor S. Akabori of Osaka University and Professor K. Narita of Ochanomizu University for the sample of crystalline residue of silk fibroin and to Dr. K. Hoshino and Dr. H. Yumoto of Toyo Rayon Company for poly-ε-capramide film.

(18) K. H. Meyer, M. Fuld and C. Klemm, *Helv. Chim. Acta*, **23**, 1441 (1940).

LIGHT SCATTERING BY AQUEOUS SOLUTIONS OF SODIUM LAURYL SULFATE¹

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Measurements of turbidity of pure sodium dodecyl sulfate in water and in salt solutions are reported. Their interpretation is briefly discussed and leads to several conclusions: The molecular weight of the micelles varies from 23,000 to over 35,000 as the concentration of salt increases. The effective charge of a micelle, calculated for the first time from light scattering, remains constant at about 14. The turbidity in water at high detergent concentration can be predicted on the basis of very simple assumptions suggesting that the micellar charge and size may not change radically in this region. Traces of lauryl alcohol induce the formation of micelles below the C.M.C. At still lower concentrations they give rise to large turbidities which may be used to detect the presence of lauryl alcohol and also to determine its solubility. Finally, some of the previous light scattering results are reviewed and reinterpreted.

Light scattering measurements of solutions of association colloids are a very powerful tool for

(1) Presented in part at the J. W. McBain Memorial Symposium of the Division of Colloid Chemistry at the Chicago Meeting of the American Chemical Society, September, 1953.

(2) Colgate-Palmolive Peet Company Postdoctoral Fellow, 1952-1953.

probing their nature. As has been shown by Debye,^{3,4} they provide information about the weight of micelles and as we shall show, also about micellar charge, and about the presence of certain impurities.

(3) P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 573 (1949).

(4) P. Debye, *THIS JOURNAL*, **53**, 1 (1949).

The present study concerns light scattering by solutions of sodium lauryl sulfate (NaLS) in water and in the presence of salt and the interpretation of these and related results.

Experimental

Turbidity Measurements.—These were determined in a commercial apparatus (Phoenix Precision Instrument Company, Philadelphia, Pa.) similar to the one described by Brice, *et al.*⁵ Minor modifications were made in the slit system to reduce stray light. The apparatus was calibrated against an opal glass diffusor as a primary reference standard. The opal glass was examined on a General Electrical photometer by Dr. K. J. Palmer of the Western Regional Laboratory, U. S. Department of Agriculture, and its diffuse transmittance was found to agree within 0.7% with the value given by the manufacturer. Redistilled benzene was employed as a secondary standard, the observed Rayleigh ratio at λ 4360 being 48.5 in good agreement with previously determined values, *viz.*, 48.4, 48.4 and 48.3.⁵ In the case of the detergent solutions the green line of mercury (λ 5460) was used throughout.

The measurements were usually carried out at room temperature, *viz.*, $22 \pm 1^\circ$. The temperature coefficient of the turbidity was found to be approximately 1% per degree centigrade.

Refractive Increment Determinations.—These were determined on a differential refractometer similar to the one described by Brice, *et al.*,⁶ with a green line of mercury (λ 5470) at 25° . The refractive increment $(n_1 - n_0)/c$ was found to be effectively independent of temperature within the range 20 – 30° , of detergent concentration up to 4% and of sodium chloride concentration up to 0.4 molar. Its value was 0.115.

Materials.—The sodium lauryl (dodecyl) sulfate and lauryl alcohol used in this investigation were highly purified specimens which have been described elsewhere.⁷

Preparation of Solutions.—Stock solutions were prepared on a weight/volume basis and diluted volumetrically. Distilled water or sodium chloride solutions in distilled water were used as the solvent. For each solvent at least two independent stock solutions and dilution series were prepared.

The solutions were clarified by filtration through an "ultrafine" Pyrex sintered glass filter directly into the optical cell. Suction filtration was found satisfactory provided vacuum grease or o-rings were used and hydrocarbon vapors scrupulously excluded. To ensure a reasonable rate of filtration (~ 1 cc./minute) the filters were frequently cleaned with hot nitric acid and then washed with distilled water until the filtrate was optically clear.

Water was considered clear when its turbidity (τ_0) was 2.0×10^{-6} cm.⁻¹, this value including any stray light in the apparatus. The same value was obtained when aluminum hydroxide was precipitated in the water and removed by filtration through a fine sintered Pyrex filter.

Measurements at 90° in semi-octagonal cells were used throughout this work. Asymmetry measurements were meaningless because of the presence of a strong stray reflection at 45° . After completion of this work, Dr. E. K. Mysels found that by painting the outside of the cell with black paint (except for the space required for entry and exit of light) this reflection could be substantially eliminated and the dissymmetry determined precisely. She found that water and NaLS solutions give no measurable dissymmetry ($< 2\%$) when filtered as described and was able to recheck the turbidity values described in this paper to within 1% using a different sample of NaLS, distilled water from several sources and several "ultrafine" filters.

The accuracy of the calculated values of the molecular weight and the effective charge of the micelle depends upon a number of factors.

(1) The absolute standardization of the light scattering photometer: The precision with which this instrument may be calibrated is of the order of $\pm 1\%$ but the uncertainty associated⁵ with the use of opal glass as an "absolute standard" reduces the over-all accuracy to $\pm 5\%$.

(2) The precision of measurement of the turbidity: The relative turbidities of the solution can be determined to within $\pm 1\%$ but difficulties of clarification reduce the reproducibility to about 2%.

(3) The accuracy of the extrapolation of the Debye function (see below): The slope and intercept of this function is sensitive to both the solvent correction term τ_0 and to the value of the cmc. This uncertainty has been discussed elsewhere⁷ and in the present work its effect on the calculation of the molecular weight and the effective charge has been reduced to a minimum by using the best available values of the cmc,⁷ with a corresponding small correction in τ_0 .

(4) The accuracy with which the refractive increment can be determined: This is estimated at $\pm 0.5\%$ and involves an uncertainty of 1% in the computation of the Einstein constant H (see below).

Taking into account these various sources of error the absolute accuracy with which the molecular weight can be determined is estimated at $\pm 10\%$. Relatively, however, the molecular weight values are considerably more certain ($\sim \pm 2\%$). The effective charge is calculated relative to the molecular weight and hence errors involved in the absolute calibration of the instrument are eliminated. The accuracy with which the effective charge can be determined is markedly dependent on the slope of the Debye function and is estimated to vary between about 5% in aqueous solution and 60% in 0.4 *M* NaCl.

Results and Discussion

The Molecular Weight of the Micelles.—The molecular weight is generally determined from light scattering data by extrapolating the function $Hc/(\tau - \tau_0)$ to zero concentration, the intercept being equal to $1/M$. H is a constant taking into account refractive index and geometrical factors and in the present case equals 1.45×10^{-6} . For micelles of association colloids such as NaLS, Debye^{3,4} has substituted the expression $H(c - cmc)/(\tau - \tau_0)$. This is based on the assumption that $(c - cmc)$ represents the concentration of the micelles and that these behave as independent colloidal ions.⁸ Below the cmc, the amount of light scattered is independent of the detergent concentration and this constant value is equated to the solvent blank (τ_0).

Figure 1 illustrates the linear nature of the Debye function at low micelle concentrations. The values of the molecular weight (M) calculated from the reciprocal of the extrapolated values of Fig. 1, are given in Table I.

The molecular weight increases upon addition of salt, first rapidly and then more slowly. As a function of the total concentration of the sodium gegenions at the C.M.C. the increase seems definitely less than linear on a log-log graph as shown in Fig. 2. Debye^{3,4} has noted previously that salts increase the micellar weight of some cationic detergents. When his values are plotted on this type of graph, it becomes apparent, as shown in Fig. 2, that the slopes are of the same order (~ 0.2) for sodium lauryl sulfate and the quaternary alkylammonium bromides but some three times larger (0.65) for dodecylamine hydrochloride. It is possible that hydrolysis is a contributing factor in the latter case. The tendency toward a limiting molecular weight at high salt concentrations in the case of sodium lauryl sulfate suggests a saturation of the electrical double layer under these conditions.

The earliest estimate of the weight of the NaLS micelle is probably that of Miller and Anderson,⁹

(5) B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

(6) B. A. Brice and M. Halwer, *ibid.*, **41**, 1033 (1951).

(7) R. J. Williams, J. N. Phillips and K. J. Mysels, *Trans. Faraday Soc.*, in press.

(8) K. J. Mysels, *This Journal*, **58**, 303 (1954).

(9) G. L. Miller and K. J. I. Anderson, *J. Biol. Chem.*, **144**, 475 (1942).

TABLE I

NaCl, mole/l.	C.M.C. ^a mg./100 cc.	Mol. wt. × 10 ³	<i>n</i>	<i>B</i> ^b × 10 ⁴	<i>p</i> ^c	Best mol. wt. ^d × 10 ³	<i>n</i>
0	234	23.0 ± 0.1	80	245.4 ± 0.5	14.5	23.05	80
.02	112.5	27.0 ± .6	94	47.3 ± 1.5	12.8	27.3	95.5
.03	90.2	28.8 ± .4	100	29.8 ± 0.3	12.8	28.65	99
.1	42.2	32.4 ± .3	112.5	8.4 ± 0.5	13.4 ± 1	32.3	112
.2	26.2	33.9 ± .4	118	6.3 ± 1.0	17.0 ± 2	34.2	119
.4	16.6	36.2 ± .4	126	2.8 ± 1.7	17.0 ± 10	35.7	124

^a Best line of ref. 4. ^b Slope of Debye's plot. ^c Effective charge, electrons per micelle. ^d From smooth line through mol. wt.

who combined diffusion and sedimentation rate measurement to obtain a value of 12,500. They studied, however, a highly impure commercial mixture of salts with sodium sulfate derived from coconut oil and with "other sulfur compounds" in 0.2 *M* lithium chloride. Their micelles therefore were those of the lithium and not of the sodium salts and are certainly not comparable to ours.

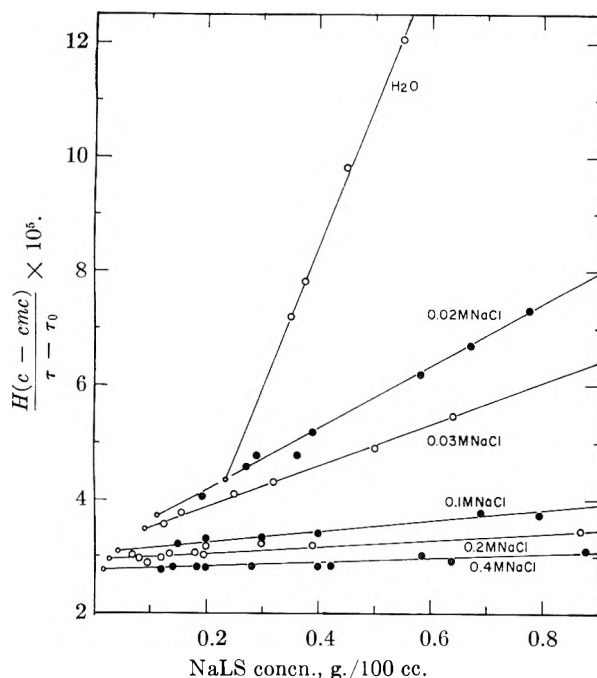


Fig. 1.—Light scattering by dilute solutions of sodium lauryl sulfate in water and salt solutions.

Hakala¹⁰ using the same procedure on a much purer material arrived at a value of about 22,000 for micelles of 0.5–1.2% NaLS in 0.05–0.2 *M* NaCl. This is some 30% lower than our values.

Granath¹¹ again by sedimentation rate and diffusion has recently obtained the values shown in Fig. 2 in NaBr and Na₂CO₃ solutions. The results agree with ours in 0.2 *N* salt but increase much faster with concentration of salt.

Mattoon, Stearns and Harkins¹² used X-ray diffraction data on a 20% solution of NaLS to obtain 16,000. This determination in addition to the admitted uncertainty of interpretation of the X-ray I-halo deals with such a concentrated solution that comparison with our data seems meaningless.

(10) N. V. Hakala, Ph.D. Thesis, University of Wisconsin, 1943.

(11) C. Granath, *Acta Chem. Scand.*, **7**, 297 (1953).

(12) R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **16**, 644 (1948).

Philippoff¹³ by an incompletely published method of interpreting osmotic and conductivity data obtained the value 23,600 in water which is in remarkably close (2%) agreement with our results.

Recently Stigter¹⁴ developed a novel interpretation of precise conductivity measurements¹⁵ on the same NaLS which we used and arrived at about 13,000 for the micellar weight in water.

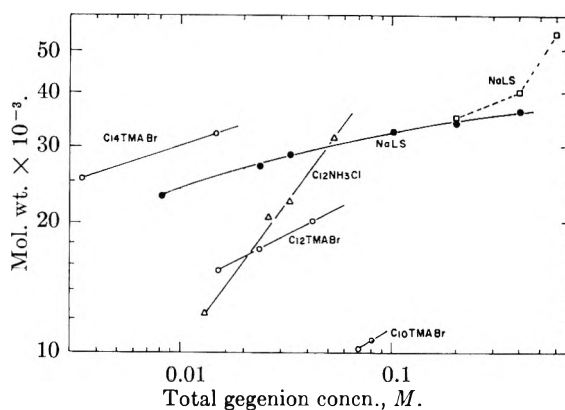


Fig. 2.—Effect of added salts on micellar weights: ●, sodium lauryl sulfate in NaCl, this work; □, same, sedimentation rate and diffusion in Na₂CO₃ and KBr¹³; ○, alkyl trimethylammonium bromides in KBr³; △, dodecylamine hydrochloride in NaCl.³

Self-diffusion measurements on this same NaLS can be interpreted to be in agreement with our results as discussed elsewhere.¹⁶

The Effective Charge of the Micelles.—It has been shown recently that the charge of colloidal electrolytes can be calculated from the slope *B* of the *Hc/τ* versus *c* curve¹⁷ and a simplified treatment of this theory has been presented by one of us. Ideal behavior of all species is assumed in the derivation so that the charge *p* thus obtained is only an effective charge. It is given by

$$p = M\sqrt{2Bx}$$

where *B* is the slope at infinite dilution of the colloidal ion, *i.e.*, in the case of association colloids at the cmc.^{9,7} and *x* is the concentration of simple salt at that point (in the present case this equals the concentration of added salt plus the cmc.). If the usual convention of expressing concentrations in g./cc. is observed, the *x* must be expressed in equiv./cc.

(13) W. Philippoff, *Faraday Soc. Disc.*, **11**, 96 (1951).

(14) D. Stigter, *Rec. trav. chim.*, in press.

(15) Unpublished data of C. I. Dulin from this Laboratory.

(16) D. Stigter, R. J. Williams and K. J. Mysels, *THIS JOURNAL*, **59**, 330 (1955).

(17) J. T. Edsall, H. Edelhoeh, R. Lontie and P. R. Morison, *J. Am. Chem. Soc.*, **72**, 4641 (1950).

Table I and Fig. 3 show the charges of NaLS as calculated from our results. Debye did not interpret his light scattering data in terms of charge effects attributing the high slope to non-ideality and to solvent effects.³ The effective charges calculated from Debye's data are shown by dashed lines in Fig. 3.

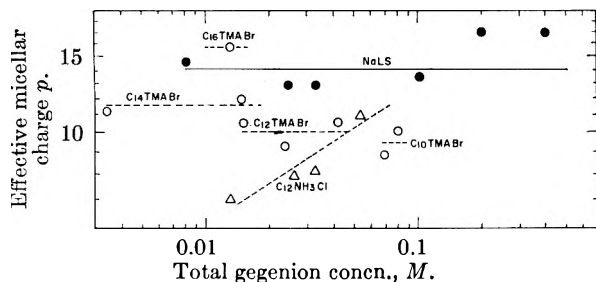


Fig. 3.—Effect of added salts on the micellar charge p : ●, sodium lauryl sulfate in NaCl, this work; ○, alkyl trimethylammonium bromides in KBr³; △, dodecylamine hydrochloride in NaCl.³

The values scatter considerably but seem to show no definite trend with salt concentration with the exception again of dodecylamine. The values seem to increase somewhat with molecular weight for the homologous alkyl trimethylammonium salts.

The effective charge p of about 14 which we thus find for NaLS cannot be readily compared with other values because it refers to the equivalent charge under ideal conditions. It is considerably less than the native charge on the micelle (80–120) and lower than the true value at the shear surface (23–36) calculated¹⁸ from the electrophoretic mobility.

On the other hand, it is very close to the value of 15 deduced by Philippoff¹³ by his combination of osmotic and conductivity results. Our value of p is the same as the charge calculated by Hutchinson¹⁹ on the assumptions that the mobility decreases with the cube root of the degree of association and that the micelle contains 80 LS⁻ ions. These agreements suggest that the non-ideality is the same for light scattering as it is for conductivity, at least in this case.

Effects at Higher Concentration of NaLS.—Figure 4 shows that at higher concentrations the Debye plot curves upward for solutions containing salt, *i.e.*, the turbidity increase is less than expected. This effect is not very large and is in the opposite direction from what would be anticipated from charge effects or from polydispersity. It may be due to a slightly increasing order as the micelles crowd each other.

In the absence of added salt the Debye plot curves radically in the opposite direction at the same concentrations and then becomes almost horizontal as shown in Fig. 5. This curvature is in the direction expected from the charge effects and the experimental points fit remarkably well the line which is a calculated extension of the straight line of Fig. 1. The calculation is based on very simple assumptions about the system and the theory of charge effects in light scattering which assumes that fluctuations in micelle concentration

occur under conditions of electroneutrality while simple ions maintain an equilibrium distribution given by Donnan's condition so that⁹

$$\frac{Hc}{\tau} = \frac{1}{M} \left[1 + \frac{p}{1 + (2xM/cp)} \right]$$

We assume that the weight M and effective charge p of the micelle remain constant. If the concentration x of simple electrolyte is assumed to be constant and equal to the cmc, the calculated curvature is much sharper than shown by the experimental points.

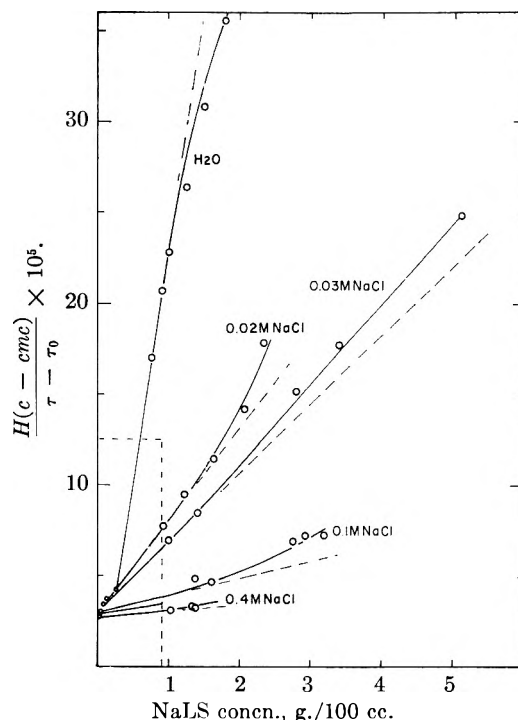


Fig. 4.—Light scattering by more concentrated sodium lauryl sulfate solutions in water and salt solutions.

However, if a solubility product type of relation is assumed, namely

$$[LS^-]^n [Na^+]^{n-p} = (cmc.)^{2n-p}$$

where n is the number of LS⁻ ions per micelle, and the usual material balances introduced, the line of Fig. 5 is obtained. The values of n (80) and p (14.5) are obtained from the intercept and slope at the cmc. The whole curvature is predicted. The agreement extends till about 8% or almost 0.3 *N* NaLS. This agreement might be taken as an indication that our assumptions may be not very far from reality and that any deviations tend to compensate each other.

The Presence of Lauryl Alcohol.—As stated earlier, our standard procedure was to clarify, by filtration, each solution after dilution and prior to turbidity determination. When treated in this way, NaLS, both pure and containing some lauryl alcohol (LOH), shows no measurable turbidity below the cmc. If an alternate procedure is followed and a clarified concentrated solution is gradually diluted with clarified water, pure NaLS still yields the same result. The presence of a part per thousand of LOH in the NaLS changes the picture radically, however, as shown in Fig. 6. A very high and

(18) D. Stigter and K. J. Mysels, *THIS JOURNAL*, **59**, 45 (1955).

(19) E. Hutchinson, *J. Coll. Sci.*, **9**, 191 (1954).

sharp peak appears below the C.M.C. The height of this peak increases with the proportion of LOH. Fig. 7 shows the result obtained with NaLS containing 1% of LOH.

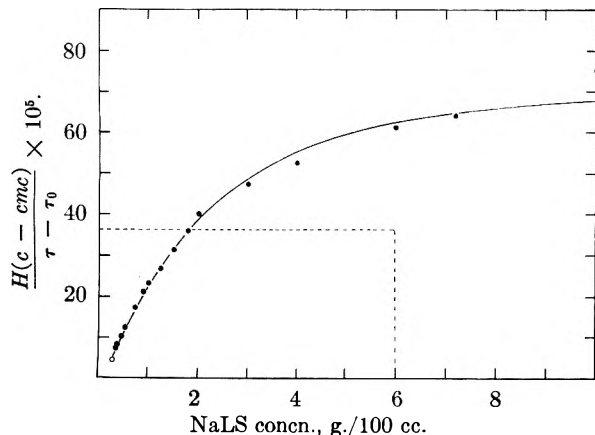


Fig. 5.—Light scattering by more concentrated solutions of sodium lauryl sulfate in water. The line is calculated from initial value and slope.

Above the C.M.C. the alcohol is fully solubilized by the micelles of the sulfate. That the micelles are not altered significantly by the small amount of alcohol is shown by the unchanged turbidity recorded in Fig. 6 above the C.M.C. Below the C.M.C. however in the absence of micelles a new, finely divided phase is formed which scatters light very strongly and causes the peak. This phase is probably not the pure alcohol but the LOH·2NaLS alcoholate characterized by Epstein, *et al.*²⁰ The light scattered by this dispersion fluctuates rapidly by a few per cent. but the average value is quite reproducible and constant. Over 24 hours it increases about 10%, which suggests a slow growth of particles. Filtration removes the dispersed matter completely so that it does not appear in our usual method of clarification.

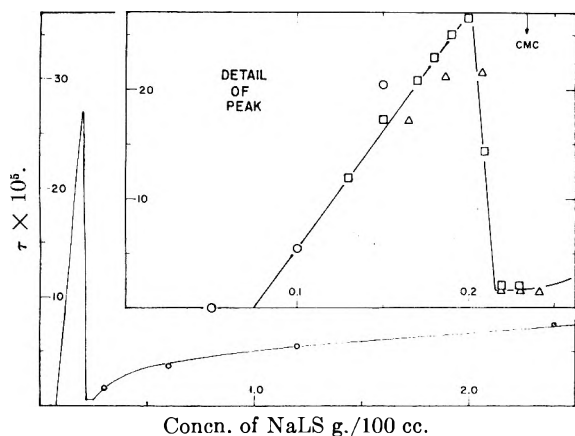


Fig. 6.—The effect of 0.145% of lauryl alcohol in sodium lauryl sulfate upon the turbidity of aqueous solutions. Solid line above the C.M.C. from values obtained in the absence of alcohol.

Below the peak the turbidity decreases rapidly as the dispersion is diluted and disappears completely at a finite concentration as shown by the

detail of Fig. 6. Obviously the turbidity is lowered by both simple dilution and by the dissolving of the alcoholate in water. The intercept gives a solubility of 6×10^{-6} mole per liter which is about a quarter of the value obtained by extrapolating from the solubilities of C₅-C₈ alcohols.²¹ This would of course be expected if the dispersed phase is the alcoholate and not the alcohol.

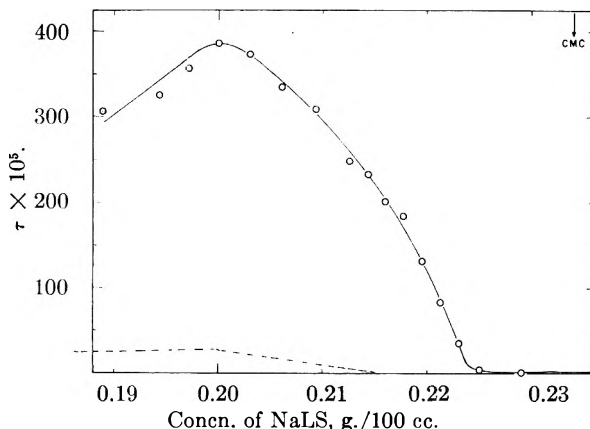


Fig. 7.—The effect of 1.03% of lauryl alcohol in sodium lauryl sulfate upon the turbidity of aqueous solutions. The dotted line shows the peak of Fig. 6 on the same scale.

The height of the peak is at least roughly proportional to the amount of alcohol present. Obviously it could be made into a sensitive quantitative method for determining LOH in NaLS and for other similar systems but we have not developed the necessary standardization. The lower limit for the appearance of the peak is given by the solubility of the alcohol in water. If the solution below the C.M.C. contains so little alcohol that it all dissolves the dispersion is not formed and no peak is observed. From the solubility computed above, this corresponds to 0.05% lauryl alcohol in the NaLS. In fact, we have found that addition of 0.03% of alcohol to our NaLS gives no perceptible peak and conclude therefore that the alcohol content of our NaLS must be of the order of 0.01% or less.

With increasing concentration the turbidity decreases very rapidly from the peak as the alcoholate becomes solubilized. The peak itself corresponds to the point where this process just overtakes the normal increase of turbidity with concentration. The peak occurs at 0.200% in both solutions which is 0.034% below the C.M.C. of NaLS; hence formation of micelles is induced by the presence of LOH at a concentration at which their formation is not otherwise perceptible. Sufficient micellization is induced to solubilize all the alcoholate when the concentration reaches 0.215 and 0.225% NaLS, respectively, which is still much below the normal C.M.C. It may be noted that for the higher alcohol concentration, even if *all* the NaLS between 0.200 and 0.225% were micellized, there would be only 11 LS⁻ ions per mole of alcoholate, or 13 per mole of alcohol, in the induced micelles. In reality the proportion must be much lower.

Thus the system LOH-NaLS shows the same

(20) M. B. Epstein, A. Wilson, C. W. Jakob, L. E. Conroy and J. Ross, *THIS JOURNAL*, **58**, 860 (1954).

(21) A. Seidell, "Solubilities of Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1941.

effects of induced micellization which Mukerjee²² found to account for the behavior of the pinacyanol-NaLS system. This shows that polar non-electrolytes can influence micellization in the same way as certain solubilized electrolytes.

(22) P. Mukerjee and K. J. Mysels, presented at 127th ACS Meeting, New York, September, 1954; *J. Am. Chem. Soc.*, in press.

Acknowledgment.—We are grateful to Dr. Estella K. Mysels and Dr. K. J. Palmer for their help, to the Colgate Palmolive Peet Company for the fellowship which made this work possible and to the Office of Naval Research for making available the pure sodium lauryl sulfate prepared by Dr. R. J. Williams through Project 356-254.

MICELLAR SELF DIFFUSION OF SODIUM LAURYL SULFATE¹

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The recently developed porous disc method has been used to determine the self-diffusion coefficient of micelles formed by sodium dodecyl sulfate in water and in salt solutions, using a water-insoluble dye to tag the micelles. A strong concentration dependence of the self-diffusion coefficient in water has been found. The presence of salt greatly reduces this concentration effect. Extrapolation to the critical micelle concentration leads to an estimate of the size of the micelles. Assuming a spherical shape, comparison with known molecular weights permits an estimate of hydration. A monomolecular layer of water of hydration accounts best for the results.

Data derived from light scattering measurements of soap solutions are currently interpreted in terms of the molecular weight of the *unhydrated* micelle. The rate of micellar diffusion on the other hand is related to the size and shape of the *hydrated* micelle. One may hope therefore that information regarding the extent of hydration (and possible asymmetry) of the micelles may be obtained by comparing the light scattering and self-diffusion of the micelles.

Accordingly, we have obtained new data for the self-diffusion of micelles of sodium lauryl sulfate (NaLS) in water and in dilute aqueous sodium chloride solutions, using the porous disc method which was developed to permit accurate self-diffusion measurements and has been recently described.² The micelles were tagged³ with Orange OT (1-*o*-tolyl-azo- β -naphthol). The principle of the method is to measure the rate of diffusion of the tracer in solutions of NaLS and sodium chloride which are uniform in concentration and immobilized by sintered glass throughout the diffusion column. As reported elsewhere, the same NaLS has been used to determine the molecular weight of micelles of NaLS by light scattering,⁴ the critical micelle concentration (C.M.C.) by several methods,⁵ and the electrophoretic mobility of micelles.⁶

In the present paper we shall report the experimental results, discuss their accuracy and consider possible interpretations.

Experimental

Materials.—The pure NaLS and the Orange OT have been described previously.⁵

Apparatus and Procedure.—The main apparatus and procedure have been described previously.² All measurements were made at 25° in the air thermostat. The only important change in procedure was the use of a "coarse"

fritted glass cell in addition to the previously described "medium" ones. Coarse sintered glass cannot be fused externally without excessive restriction of some pores which makes quantitative filling and washing impractical. (Later samples of "medium" glass also proved unsatisfactory.) We therefore embedded the fritted cylinder in polymethylacrylate plastic (Lucite) by a procedure used for geological cores.⁷ The discs, with integral Lucite rings, proved easy to handle and showed no dye uptake. Because of much faster drainage, quantitative washing and filling required 3 volumes of liquid. Reproducible recovery of the liquid between the two discs by procedures used with "medium" discs was found not to be feasible. However, a thin, dry, "coarse" fritted glass disc placed on top of the lower disc imbibed all the free liquid in a perfectly reproducible manner.

A previously unnoticed difficulty was encountered. Widely scattered, low results were occasionally obtained. This was traced to accidental entrapment of an air bubble between the discs during assembly with consequent obstruction of the diffusion path. Care in putting enough liquid on top of the lower disc and slow lowering of the upper one onto it eliminated this difficulty almost completely. Data which were thus vitiated have been discarded.

Preparation and Analysis of Tracer Solutions.—Solutions of NaLS were prepared on a weight per volume basis. To obtain a tracer solution 30 ml. of stock solution was shaken with a few milligrams of dye for some hours at room temperature in a glass bottle fitted with a screw cap lined with Teflon. The colored solution was filtered through a No. 41 Whatman filter paper to remove the bulk of the excess dye, the funnel being covered to prevent evaporation of water. Any fine particles remaining in the filtrate were dissolved by adding 10 ml. more solution and shaking for a further 6–12 hours. In this way a clear, undersaturated solution of dye was obtained.

The concentration of dye was measured with a Beckman ultraviolet spectrophotometer using 10-mm. cells and a wave length of 498 m μ , any turbidity being corrected for by subtracting 1.4 times the optical density at 625 m μ (where Orange OT does not absorb). It was found helpful to acidify the dye solutions with hydrochloric acid immediately before measuring the optical density, as in alkaline and neutral solutions the absorption is slightly less and the measurements become erratic due to possible pH changes during the run.

Computations.—The ratio R of transport across the plane of separation of the discs at a time t to the transport at equilibrium can be shown⁸ to depend only on t and the

(1) Presented in part at the J. W. McBain Memorial Symposium of the Division of Colloid Chemistry at the September, 1953, A.C.S. Meeting in Chicago.

(2) K. J. Mysels and D. Stigter, *THIS JOURNAL*, **57**, 104 (1953).

(3) For a justification of this use of the term see H. W. Hoyer, K. J. Mysels and D. Stigter, *ibid.*, **58**, 385 (1954), footnote 5.

(4) J. N. Phillips and K. J. Mysels, *ibid.*, **59**, 325 (1955).

(5) R. J. Williams, J. N. Phillips and K. J. Mysels, *Trans. Faraday Soc.*, in press.

(6) D. Stigter and K. J. Mysels, *THIS JOURNAL*, **59**, 45 (1955).

(7) W. E. Showalter, *J. Petr. Techn.*, **2**, 8 (Dec., 1950, Sec. 1).

(8) Mimeographed First Technical Report ONR Project No. NR054-254 available from K. J. Mysels or the Library of the University of Southern California or the Library of Congress.

diffusion coefficient D , provided D is independent of concentration and the concentrations are originally uniform on each side of the plane. These conditions are obviously satisfied in our tracer experiments. Thus, if the same R is obtained at times t_1 and t_2 for two substances, then

$$t_1 D_1 = t_2 D_2$$

In practice the cells were calibrated by measuring the diffusion of sodium chloride between 0.2 and 0.7 M solutions between which concentrations the value of D is approximately constant and equal to 1.474×10^{-6} cm.² per sec.⁹ A plot of R against $t^{1/2}$ for sodium chloride was thus obtained for each set of discs.¹⁰ The value of R was then determined for a sodium lauryl sulfate solution after an arbitrary time t_2 ; t_1 was read from the calibration graph and hence D_2 calculated.

To obtain R it is necessary to know the total amount of tracer present at the beginning of the run. This was calculated from the total dye content found at the end of the run, taking into account the amount present in the small volume Δ of upper disc solution used in making the boundary. This procedure gave more consistent results than calculating the initial total from volume and optical density measurements. The value of Δ used was obtained from the material balance of the more precise calibration runs and differed slightly between operators.

The absolute calibration of the cells depends upon sodium chloride solutions. A relative calibration can be obtained, however, from any measured system. Upon reviewing some 50 tracer results obtained on the basis of the sodium chloride calibration with five cells used, we found definite discrepancies between cells. The maximum difference was 2.7%, which seems just beyond the limits of accuracy of the sodium chloride calibration. The results were therefore recalculated on the basis of giving equal weight to all the tracer and to all the calibration experiments (the latter are less numerous but somewhat more precise) for establishing relative cell constants and weighting the number and precision of the calibration runs for establishing the absolute values. The maximum correction thus introduced amounted to 0.95%, the average correction to 0.50%.

Validity of the Method

Several aspects of the accuracy of this method^{2,8} and the validity of the use of neutral, water-insoluble dyes as tracers^{2,6} have been discussed previously. We shall consider only the question of surface effects and of the contribution of the unsolubilized (free) dye.

Surface Effects.—In our measurements diffusion proceeds in the presence of the large surface of the sintered glass. If any tracer dye is adsorbed by the glass, the results are obviously vitiated, whether the adsorbed dye is immobilized or diffuses along the surface.

In an attempt to apply the method to a *cationic* detergent (lauryltrimethylammonium chloride, courtesy of Armour and Co. Research Laboratory) with Orange OT tracer, we found that during the filling operation as much as 50% of the dye was adsorbed by the glass. The probable mechanism of this adsorption is that the dye is solubilized between a double layer of adsorbed detergent. The first layer is adsorbed at very low concentration with polar heads on the glass and hydrocarbon tails directed outward to give a hydrophobic surface. The second layer is adsorbed onto the first at higher concentrations, near the C.M.C. where the detergent solutions again wet glass, and has the polar heads directed outward. This double layer over

the surface of the glass is equivalent to a giant McBain lamellar micelle and can obviously show solubilizing effects. This may be properly called "surface solubilization" and should be investigated further.

In the case of anionic detergents we have not found any evidence of rapid adsorption of dye by the glass surface within the 1% limit of our precision. Furthermore, comparison of the diffusion coefficients obtained from the more frequently used cells of "medium" sintered glass with those from the "coarse" glass cells showed no significant variation. (A solution of 2% sodium lauryl sulfate in 0.1 M sodium chloride gave $D = 0.851 \pm 0.005$ and $0.855 \pm 0.013 \times 10^{-6}$ cm.²/sec. in "medium" and "coarse" cells, respectively.) The average radii of capillaries in the two sets were 3 and 25 μ , respectively, as determined for us by mercury injection by Mr. Irving Fatt of California Research Corporation, so that the two surface-to-volume ratios were in the ratio of at least 8 and probably close to 60.

Hence the effect of surface is negligible in the system presently studied but may lead to gross errors in others, particularly with cationic detergents.

Transport of Free Dye.—If all the tracer dye molecules are solubilized by the micelles, the observed coefficient of tracer diffusion D_{tr} is equal to that of micellar diffusion D_m . However, a finite, though very small, dye concentration is always maintained in the aqueous part of the system because of the water-solubility of the dye and its diffusion coefficient in water D_w is relatively large. It has already been shown that this may lead to a high value of D if a dye such as Oil Blue, appreciably soluble in water, is used as a tracer.²

A quantitative estimate of this effect may be obtained if it is assumed that the partition equilibrium is independent of the total concentration of the dye and is established rapidly compared with the rate of diffusion, so that a constant fraction K of the total tracer is present in the water at all levels of the diffusion column. By a reasoning analogous to that used for electrophoresis⁶ we find

$$D_{tr} = D_m [1 + K(D_w/D_m - 1)]$$

If to a first approximation we can treat both species involved as spheres, the ratio D_w/D_m is inversely proportional to the cube root of their molecular weights. In our case the molecular weight of the dye is 261 and that of the micelle is about 30,000, hence $D_w/D_m = 5$ is the correct order of magnitude. Thus

$$D_{tr} = D_m (1 + 4K) \quad (1)$$

An estimate of the constant K can be derived from colorimetric measurements.⁵ Solutions of NaLS below the C.M.C. when saturated with Orange OT have an optical density not greater than 0.002 for a 1-cm. light path. Above the C.M.C. the optical density of a saturated solution is about 6 ($c - cmc$) where c and cmc are in grams per 100 ml. of solution. Hence

$$\frac{\text{tracer in water}}{\text{tracer in micelles}} = \frac{0.002}{6(c - cmc)} = \frac{K}{1 - K} \approx K$$

Since in this work the lowest $c - cmc$ was 0.108 g. per 100 ml. of solution, equation 1 indicates that under these extreme conditions the difference $D_{tr} -$

(9) R. H. Stokes, *J. Am. Chem. Soc.*, **72**, 763 (1950).

(10) A more convenient method is to plot $R - b \cdot t^{1/2}$ against R , where b is the slope of the straight section of the R vs. $t^{1/2}$ curve, as this enables a more expanded ordinate scale to be used over the entire range of useful values of R .

D_m is not higher than 1.2%. At higher NaLS concentrations the difference decreases rapidly. An appropriate correction for this small methodical error has been applied to our observed values.

Results

Table I summarizes our results. Each figure is the average of two to six determinations.

Figure 1 shows the marked effect of concentration of NaLS upon the self diffusion coefficient and that this effect is greatest in pure water and decreases markedly upon addition of salt. Accurate extrapolation to the C.M.C. on this graph is impossible. We have found empirically, however,

TABLE I
MICELLAR SELF DIFFUSION COEFFICIENT OF SODIUM LAURYL
SULFATE AT 25°, $\text{Cm.}^2/\text{sec.} \times 10^6$

NaLS, g./100 ml.	NaCl, M		
	0	0.03	0.1
0.342	1.023
.350	...	0.946	...
.375	0.955
.500932	0.923
.609	.887
1.000	.832	.892	.914
2.000	.759	.837	.858
3.000	.680	.764	.819
5.000	.617

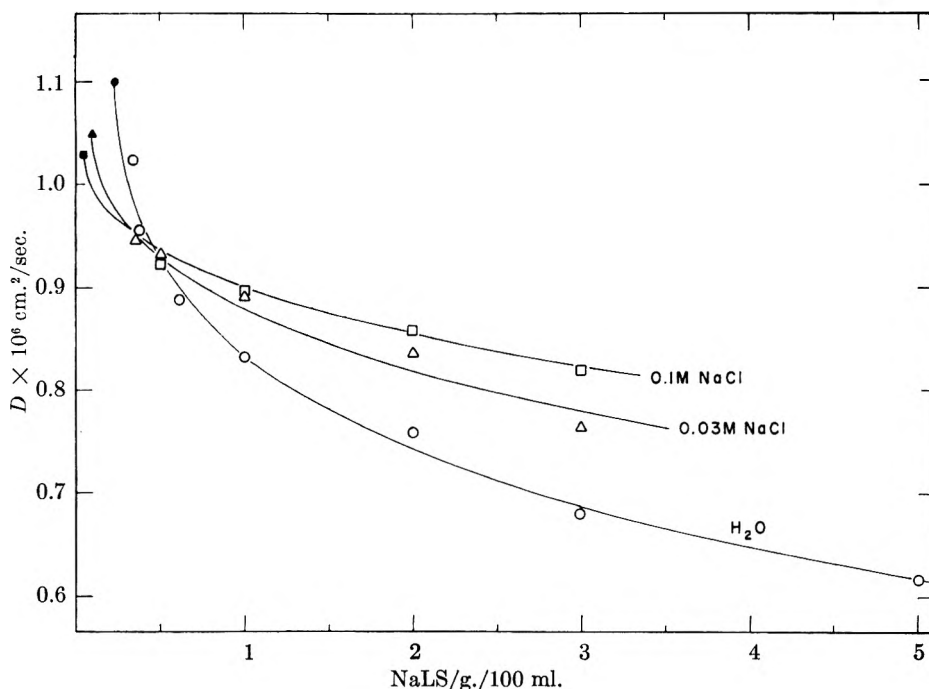


Fig. 1.—Micellar self-diffusion coefficient of sodium lauryl sulfate at 25° in water and in salt solutions. The curves correspond to straight lines of Fig. 2.

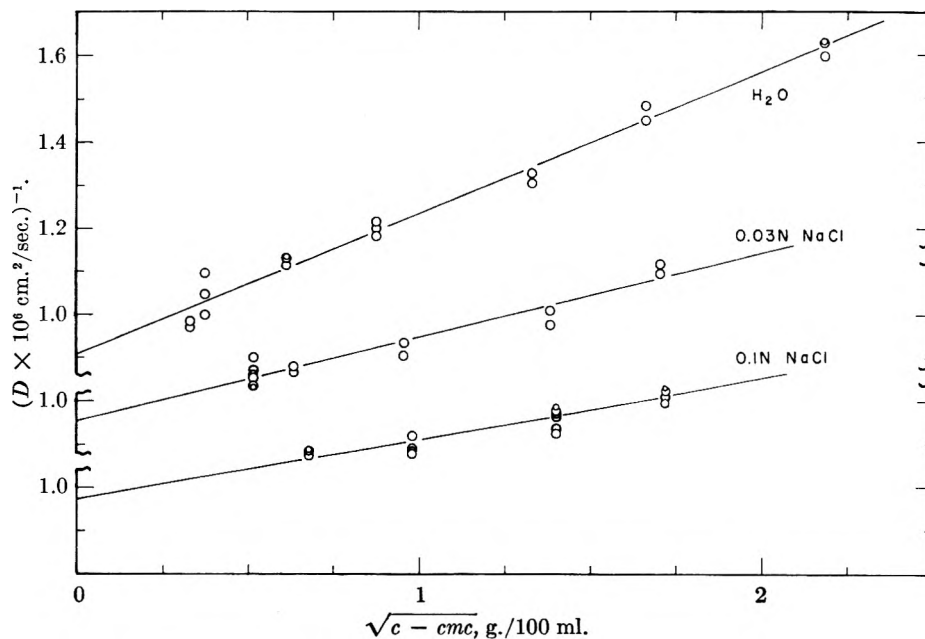


Fig. 2.—Extrapolation of the self diffusion coefficient of sodium lauryl sulfate to the C.M.C.

TABLE II

Solvent	C.M.C. ^a mg./100 cc.	Mol. wt. ^b × 10 ⁻³	$D_{cmc} \times 10^6$, cm. ² /sec.	$f^c \times 10^3$, dyne sec./cm.	f/f_0	$r, ^c$ Å.	Mol. wt. ^c × 10 ⁻³	
							Unhydrated	Hydrated ^d
H ₂ O	234.0	23.05	1.099	3.74	1.13	22.2	31.55	25.6
0.03 M NaCl	90.2	28.65	1.050	3.91	1.09	23.3	36.15	29.5
0.1 M NaCl	42.2	32.3	1.028	4.00	1.07	23.7	38.5	31.65

^a Best values of reference 5. ^b Light scattering values of reference 4. ^c Calculated from D_{cmc} . ^d Assuming monolayer hydration.

that the points lie close to straight lines on a plot of $1/D$ vs. $(c - cmc)^{1/2}$ as shown in Fig. 2. Here the individual measurements are also shown. The straight lines of Fig. 2 are drawn by the method of least squares and permit extrapolation to the C.M.-C. The limiting diffusion coefficients so obtained are shown in Table II. The straight lines of Fig. 2 are also transformed into the corresponding curves of Fig. 1.

The average deviation of individual points from their averages is 1.55%; it tends to decrease as the concentrations of salt and of NaLS increase because of the corresponding increased amount of solubilized dye. The average deviation of the points from the straight lines is 1.8% and shows the same trend.

Discussion

The hydrodynamic friction factor f of a particle can be related to its size and shape. For a sphere $f = 6\pi\eta r$ by Stokes' law. At infinite dilution for an uncharged particle in a pure solvent it is well known that

$$D = kT/f \quad (2)$$

In real solutions several other effects enter, however, and complicate the interpretation. Adamson¹¹ has recently reviewed various factors involved, especially the activity gradient, diffusion potential, electrophoretic and solvent concentration effects, and the reasons why these do not affect self-diffusion coefficients. We shall therefore consider only two factors which play a role in self diffusion.

(a) **Micellar Interaction.**—The presence of other micelles presumably interferes with the diffusion of any one. Qualitatively this is clear but we have at present no theory to predict even the order of magnitude of non-ideality of diffusion caused by interaction between large, highly charged particles.

The observed concentration dependence of D can be due either to a large growth of the micelle (some threefold between the C.M.C. and 3% concentration) or to the interaction with other micelles, or a combination of these causes. Light scattering,⁴ solubilization^{6,12} and conductivity measurements¹³ suggest that there is no drastic change in the size of these micelles through this range. Hence it is interaction that must be responsible for the curvature of lines of Fig. 1.

It is known^{4,14} that micelles tend to increase in size upon addition of salt. Hence D would be expected to decrease as the sodium chloride concentration increases. This we observe at the lowest

experimentally accessible concentration of NaLS when interaction is small. At higher concentration of NaLS, however, the opposite is found, so that the experimental lines cross at quite low concentrations as shown in Fig. 1.

This is the result expected if the change in D with NaLS concentration is attributed to intermicellar effects caused by their high charge. In the presence of salt, due to the swamping or screening by the small ions, the interaction should be reduced and the behavior more ideal, as is observed.

The non-ideal behavior in diffusion is somewhat similar to the non-ideality observed⁵ in light scattering by NaLS solutions: The change is greatest near the C.M.C. and the curve then flattens out. This resemblance can perhaps be explained by an intrinsic similarity of the two processes. The activated state determining the rate of self diffusion, must involve unequal concentrations of the diffusing specie in adjacent space elements, *i.e.*, concentration fluctuations. Light scattering, as is well known, is caused precisely by concentration fluctuations. Hence the same factors which reduce light scattering (and increase the HC/τ function) should also reduce the rate of diffusion. The light scattering effects are reasonably well understood either on the basis of Donnan equilibria among fluctuating volumes,^{6,15} or on the basis of a hard sphere model.¹⁶ No equivalent theory of diffusion seems to be available at present, but our data could apparently serve to test one when it appears. Figure 2 suggests that $1/D$ should vary with the square root of micelle concentration.

For the time being measurements at finite concentration cannot be interpreted further. Intermicellar influences have to vanish, however, with the concentration of micelles and the measured D values can be extrapolated empirically to infinite dilution of micelles, *i.e.*, to the C.M.C. as we define it.⁵

(b) **Relaxation Effect.**—The motion of an ion is retarded by its lagging ion atmosphere. This relaxation effect is not eliminated in self diffusion as has been shown by Gosting and Harned.¹⁷ It should increase with the charge and mobility of the diffusing particle, the thinness of the double layer, and the friction factors of the gegenions. Onsager¹⁸ has given a first approximation theory which seems to apply satisfactorily¹⁷ to extremely dilute solutions of monovalent ions. If this equation is applied to our system at the C.M.C., using known⁶ values of micellar mobility, one finds that the relaxation effect reduces the diffusion rate by over 90%. This obviously impossible result shows

(11) A. W. Adamson, *THIS JOURNAL*, **58**, 514 (1954).

(12) G. S. Hartley, *J. Chem. Soc.*, 1968 (1938); I. Kolthoff and W. Stricks, *THIS JOURNAL*, **52**, 915 (1948).

(13) D. Stigter, *Rec. trav. chim.*, **73**, 611 (1954); Thesis, Utrecht, 1954.

(14) P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, [4] 575 (1949).

(15) K. J. Mysels, *THIS JOURNAL*, **58**, 303 (1954).

(16) P. Doty and H. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).

(17) L. J. Gosting and H. S. Harned, *J. Am. Chem. Soc.*, **73**, 159 (1951).

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

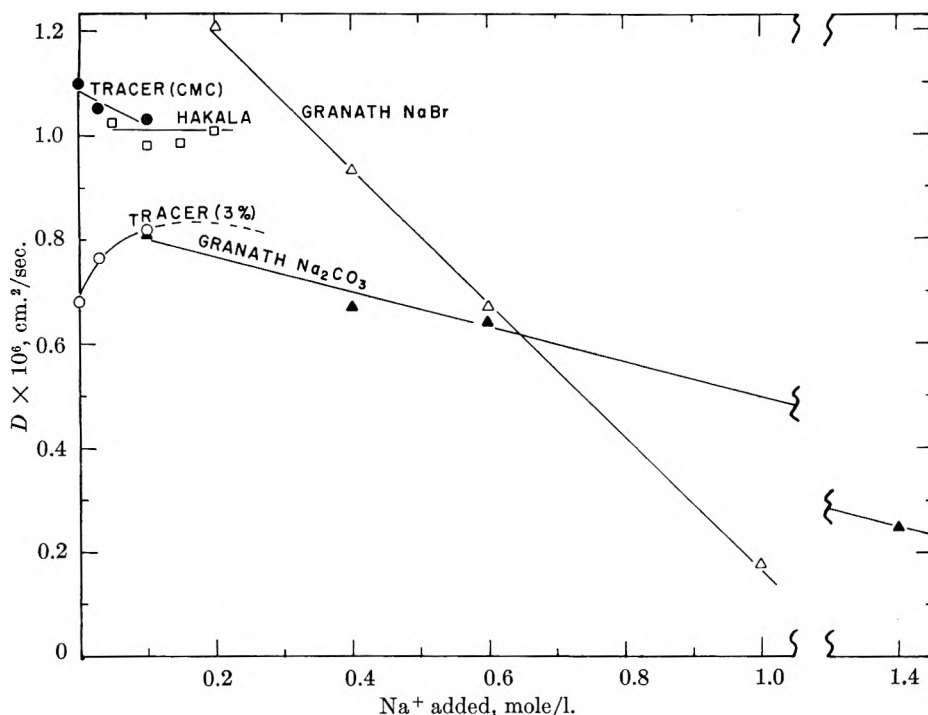


Fig. 3.—Comparison of diffusion and self diffusion results: ●○, self-diffusion, this work at C.M.C. and 3% NaLS; □, Hakala²¹ 0.3–1.5% in NaCl reduced from 20 to 25°; ▲△, Granath²² 0.4–1.2% in NaBr and Na₂CO₃ reduced from 30° to 25°.

the inadequacy of Onsager's theory in case of a large and highly charged particle.

In the absence of any other theory of the relaxation effect for the diffusion of colloidal electrolytes, we shall neglect this effect in our calculations. It may be worth noting, however, that according to the prevalent qualitative view, relaxation effects can only slow down the particle, hence their neglect can only make too large any size calculated from D .

Comparison with Diffusion Data

The integral and semi-differential¹⁹ diffusion coefficients of sodium lauryl sulfate have been measured on three occasions. Miller and Anderson²⁰ worked in the presence of a 20-fold or greater excess of Li⁺ ion so that their results pertain to the lithium rather than the sodium lauryl sulfate and their material was highly impure. Hakala²¹ used a much purer material in sodium chloride solutions and Granath²² made measurements in Na₂CO₃ and NaBr solutions. Optical methods were used in all cases and no significant variation either with concentration of NaLS or between integral and semi-differential diffusion coefficients was observed. Granath worked at 30°, the others at 20°. For purposes of comparison we have reduced the data to

(19) The diffusion coefficient is measured either between a concentration c and zero concentration or between two concentrations, c_1 and c_2 . The result when obtained by the former method is always called the integral diffusion coefficient, when by the latter sometimes integral, sometimes differential. It seems reasonable to reserve the term differential diffusion coefficient for the limit of D as c_1 and c_2 merge. We would like to suggest the term *semi-differential* for the result of measurements when c_1 and c_2 differ from each other and from zero.

(20) G. L. Miller and K. J. I. Anderson, *J. Biol. Chem.*, **144**, 475 (1942).

(21) N. V. Hakala, Thesis, Wisconsin, 1943; quoted in part in E. M. and E. B. Bevilacqua, M. M. Bender and J. W. Williams, *Ann. N. Y. Acad. Sci.*, **46**, 309 (1945).

(22) K. Granath, *Acta Chem. Scand.*, **7**, 297 (1953).

25° by correcting for the absolute temperature and for the viscosity of water, *i.e.*, factors of 0.881 and 1.144, respectively. These results, as well as some of ours, are summarized in Fig. 3. Granath's values show two surprising effects: one is exact linearity with added Na⁺ ion, the other the great effect of the negative ion. The latter is in the opposite direction from an ionic strength effect and is in contrast to the heretofore observed absence of any similarly-charged-ion effect on micellar weight¹⁴ and on the C.M.C.²³

Figure 3 shows that on the whole there seems to be no great discrepancy between self diffusion and diffusion values. Particularly Hakala's values and Granath's Na₂CO₃ values are in the same range as ours. This approximate agreement suggests that the activity effect, the electrophoretic effect and the contribution of unmicellized LS⁻ ions either compensate each other or are not enormous since these are the main factors which should cause self diffusion coefficients to differ from diffusion coefficients in these systems. On the other hand, this range of some 20% in D corresponds to some 75% in molecular weight.

The Size and Molecular Weight of the Micelle

After extrapolation to the C.M.C. and neglect of relaxation effects, the diffusion coefficient can be converted directly into the friction factor by equation 2. If the micelle is assumed to be spherical, Stokes' law yields the radius. The values which we obtain are shown in Table II. Then, if a density is assumed for the micelle, the molecular weight may be calculated.

Density measurements of solutions of NaLS by

(23) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

several authors^{22,24} make a value of 1.14 g./ml. quite probable for the density of micellized NaLS. If the micelle is assumed to be only NaLS, the corresponding molecular weights vary from 31,500 in water to 38,500 in 0.1 *M* sodium chloride as shown in Table I and by the open diamonds in Fig. 4. The corresponding molecular weights determined on other portions of the same sample by light scattering⁴ are shown in the table and by the solid line in Fig. 4. They are lower by some 25%. This corresponds to f/f_0 values of 1.13 to 1.07 and indicates either hydration or dissymmetry of the micelle or both.

An axial ratio of about 3.5 to 2.5 would give proper molecular weights. We prefer, however, to assume that hydration accounts for the whole effect because it is to be expected that the hydrophilic heads and adsorbed gegenions will be hydrated and that the micelle will be rough due to the presence of the polar heads⁶ and thus entrain some water within the roughness. Furthermore, the radii of micelles here considered do not exceed the length (23 Å.) of the extended LS⁻ chain so that dissymmetry is not required on structural grounds. If a hydration layer averaging one molecule of H₂O, *i.e.*, 1.5 Å., is assumed to surround the NaLS, the unhydrated molecular weight is lowered to 23,000

(24) K. Hess, W. Phillipoff and H. Kiesig, *Koll. Zeit.*, **88**, 40 (1939); N. V. Hakala, Thesis, Wisconsin, 1943.

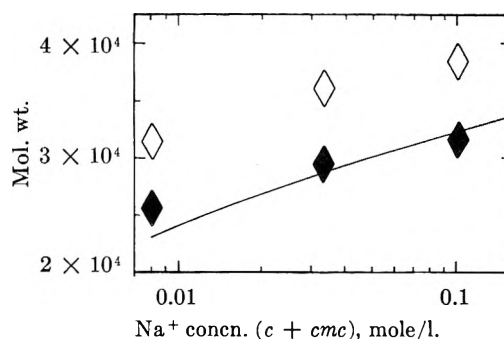


Fig. 4.—Molecular weights of micelles of lauryl sulfate in water and salt solution: solid line, light scattering values⁴; ◇, from diffusion assuming no hydration; ◆, from diffusion with monomolecular hydration.

to 32,300 as shown in Table II and by the black diamonds of Fig. 4. The agreement with light scattering (which determines, of course, the unhydrated weight) is probably as good as could be expected.

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AUTOPHOBIC LIQUIDS AND THE PROPERTIES OF THEIR ADSORBED FILMS

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A class of polar liquids has been found having the remarkable property of being unable to spread on their own adsorbed films. Many branched as well as unbranched polar compounds exhibit these properties on high energy surfaces as diverse as platinum, α -alumina and fused silica. A rectilinear relation exists between the cosine of the contact angle of each liquid and the surface tension. It is demonstrated that the "autophobic" property of such liquids is caused by the adsorption of an oriented monolayer of the liquid. When the resulting low energy surface has a critical surface tension below the surface tension of the liquid, non-spreading or "autophobicity" results. Studies of the effect of varying the baking temperature of α -alumina and silica on the contact angles of autophobic liquids revealed that considerable surface dehydration of α -alumina and vitreous silica surfaces takes place at 200°. The effect of such dehydration was to decrease the contact angles in every instance, the effect being greatest on α -alumina. It is concluded that the acids and alcohols studied were able to adsorb on silica and α -alumina through hydrogen bonding to the adsorbed water layer.

Introduction

In a recent report¹ a series of experiments were described which demonstrated that the low wettability of adsorbed monolayers is not restricted to those comprising adsorbed, straight chain, amphipathic molecules but can be caused by adsorbed molecules of a number of other structural types. In another study² many pure liquids including a wide variety of esters, ethers and hydrocarbons have been shown to exhibit finite and reproducible contact angles on high energy surfaces such as brass, steel, silica and α -alumina (sapphire). It was concluded from an examination of the spreading mechanisms and materials present that when an ester is non-spreading the behavior must be caused by the for-

mation of an adsorbed film of acid or alcohol which is released by hydrolysis *in situ*, *i.e.*, hydrolysis during adsorption at the liquid-solid interface. Furthermore, such non-spreading could be caused by adsorption of branched chain polar compounds like 2-ethylhexanoic acid and derivatives.

This paper reports the results of an investigation of the wetting and spreading behavior on high energy surfaces of pure, lower-boiling acids, amines and alcohols (both branched and unbranched). It is shown that many of these compounds have the property of being "autophobic" or unable to spread on their own adsorbed films. Also it is proved that acids and alcohols which would be released by hydrolysis "in situ" of many of the esters discussed in reference 2 are capable of forming monolayers which would be imperfectly wetted by the parent ester.

(1) H. W. Fox, E. F. Hare and W. A. Zisman, *J. Colloid Sci.*, **8**, 194 (1953).

(2) H. W. Fox, E. F. Hare and W. A. Zisman, to be published.

Materials and Procedures.—The solids used in this investigation included platinum, 18-8 stainless steel, drill rod steel, fused silica and synthetic sapphire (α - Al_2O_3). The polishing and cleaning techniques used to prepare the surfaces are described elsewhere.² In the footnotes to the tables are listed the sources of the polar liquids used. Where it was found necessary to redistill the liquid this has been indicated, and the boiling point and refractive index of the "cut" used are given. The stearic acid was an exceptionally pure compound (m. p. 69.5°) obtained from the Hormel Foundation; there was no unsaturation as shown by a zero iodine number. The source and purity of the various liquids used to characterize the wettability of the adsorbed monolayers have been described in previous papers in this series.³⁻⁵ Each liquid was percolated through appropriate adsorbents immediately before use. The contact angles measured were those of the liquid slowly advancing over the surface. All measurements were made in a constant temperature room at 20° and 50% relative humidity with great care taken to exclude organic vapors. The surface tensions of the alcohols at 20° were measured by the Sugden maximum bubble pressure method with the usual corrections.⁶ The surface tensions of the acids cited from the literature were chosen from those values determined by methods independent of the contact angle. The importance of this last restriction is conclusively demonstrated by the results of the present

study. The surface tensions used in this report are therefore considered the most reliable values available. A check of the surface tension of *n*-octanoic acid by maximum bubble pressure agreed with the literature value used in Table II.

Experimental Results

Early in this investigation it was noted that the contact angle between polar liquids and the surface of α -alumina varied erratically from one surface cleaning to the next. Since the variation was as much as twenty degrees and appeared random, chemical deterioration of the surfaces due to the action of the nitric-sulfuric acid cleaning solution was considered unlikely. Because such hydrophilic surfaces as α -alumina and silica were presumed to be readily hydrated, and because the acid cleaning operation was followed by rinsing the surface in distilled water and drying it at 120° for varying lengths of time up to 16 hours, it was suspected that uncontrolled dehydration of these surfaces was causing the difficulty.

To test this theory the α -alumina and silica surfaces, after being cleaned as described previously, were heated at 200° for 2.5 hours in a grease-free desiccator containing anhydrous CaCl_2 . They then were cooled in the desiccator to 20°, and the contact angles of drops of pure octanol-1 or *n*-octanoic acid were measured within a minute after exposure to the room air (R.H. = 50%). Octanol-1 and *n*-octanoic acid exhibited contact angles on the α -alumina of only 6 and 5°, respectively. These liquids had been found earlier to have contact angles of 42° on the unbaked α -alumina. The contact angle of *n*-octanoic acid on silica similarly decreased from an initial value of 33° to a final value of 24° due to the same treatment. When both surfaces were acid cleaned, the original high contact angles were observed again.

Hence, heating silica or α -alumina at 200° in the presence of a desiccant caused a marked lowering of the contact angles of the liquid acid and alcohol studied. It is concluded that the early variations in the contact angles were due to prolonged drying of the alumina at 120°. Both hydrophilic solids had evidently dehydrated sufficiently at 200° to increase the wettability by the polar organic liquids studied. The greater effect of dehydration on the contact angles exhibited by the polar liquids on α -alumina is good evidence that alumina adsorbs water much more weakly than silica. In order to eliminate the difficulty in obtaining reproducible contact angles on these surfaces in the air, they were dried at 120° for a maximum of 5 minutes after being rinsed free of nitric-sulfuric acid.

In Table I are given the observed slowly advancing contact angles of a number of pure alcohols and acids on the various clean surfaces studied. It will be noted that the contact angles for each of the acids and alcohols listed were equal on platinum and α -alumina. The contact angles of octanol-1 and *n*-octanoic acid were equal on stainless steel and drill rod steel. The fact that both of these steel surfaces were rougher than the platinum accounts for the contact angles being somewhat lower on steel. Considering surfaces of comparable roughness, it will be noted that the contact angles of octanol-1 and *n*-octanoic acid are the same on each surface except in the case of *n*-octanoic acid on silica. The

TABLE I

AUTOPHOBIC CONTACT ANGLES OF POLAR LIQUIDS ON HIGH-ENERGY SURFACES AT 20°

Liquid	Source	γ_{LVO} at 20°	Plati- num	18-8 stain- less steel	Drill rod steel	SiO_2	α - Al_2O_3
Alcohols							
Octanol-1	a	27.8	42°	35°	35°	42°	43°
Octanol-2	b	26.7	29°	14°	..	30°	26°
2-Ethyl-							
hexanol-1	c	26.7	20°	<5°	..	26°	19°
2-Butyl-							
pentanol-1	d	26.1	7°	20°	7°
Acids							
<i>n</i> -Octanoic	e	29.2	42°	34°	34°	32°	43°
2-ethyl-							
hexanoic	f	27.8	11°	<5°	..	17°	12°

^a Redistilled Eastman Kodak Co. "white label" grade; b.p. 89.5° at 10 mm., n_{D}^{20} 1.4290. ^b Redistilled Eastman Kodak Co. "white label" grade; b.p. 87.0° at 20 mm., n_{D}^{20} 1.4255. ^c Redistilled commercial preparation from du Pont; b.p. 79.5-80.0° at 20 mm., n_{D}^{20} 1.4310. ^d Eastman Kodak Co. "white label" grade used as received. ^e Redistilled Eastman Kodak Co. "white label" grade; b.p. 124.0° at 10 mm., n_{D}^{20} 1.4278. ^f Redistilled commercial preparation from Carbide and Carbon; b.p. 120° at 13 mm., n_{D}^{20} 1.4248.

TABLE II

AUTOPHOBIC CONTACT ANGLES OF *n*-ALKANOIC ACIDS AT 20°

Acid	Source	γ_{LVO} at 20°	Ref.	Av. contact angle on		
				Pt	Fused SiO_2	α - Al_2O_3
Nonanoic	a	29.5	d	46°	33°	45°
Octanoic	b	29.2	e	43°	32°	42°
Heptanoic	a	28.7	e	37°	28°	37°
Hexanoic	c	28.1	e	34°	26°	35°
Pentanoic	a	27.4	e	16°	17°	18°
Butanoic	a	26.8	e	Spread	<5°	<5°

^a Eastman Kodak Co. "white label" grade used as received. ^b Redistilled Eastman Kodak Co. "white label" grade; b.p. 124.0° at 10 mm., n_{D}^{20} 1.4278. ^c Redistilled Carbide and Carbon commercial preparation; b.p. 97-99° at 10 mm., n_{D}^{20} 1.4163. ^d D. G. Douglas and C. A. MacKay, *Canadian J. Research*, 24, 8 (1946). ^e D. C. Jones and L. Saunders, *J. Chem. Soc.*, 2944 (1951).

(3) H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, 5, 514 (1950).

(4) F. Schulman and W. A. Zisman, *ibid.*, 7, 465 (1952).

(5) E. F. Hare, E. G. Shafrin and W. A. Zisman, *THIS JOURNAL*, 58, 236 (1954).

(6) S. Sugden, "The Parachor and Valency," Knopf, New York, N. Y., 1930.

contact angle of the acid on silica is lower than on α -alumina and platinum. Octanol-1 exhibited identical contact angles on all three surfaces. Branching of the octanol caused lowering of the contact angle, although the effect was less pronounced on silica than on α -alumina and platinum. Branching of the octanoic acid likewise tended to lower the contact angle; in this case, the effect of branching was minimized on silica to such an extent that the contact angle of 2-ethylhexanoic acid was larger on silica than on α -alumina and platinum despite the fact that the behavior of the straight chain acids was in the opposite direction. Some of these generalizations will be given a fundamental interpretation in the discussion section of this report.

Contact angles of the n -alkanoic acids on clean platinum, silica and α -alumina were determined for n -butanoic through n -nonanoic acids and are presented in Table II. The cosine of the contact angle (θ) is a linear function of the surface tension (γ_{LV}) of the acid in Fig. 1. It was also found that $\cos \theta$ increased nearly rectilinearly with increasing chain length of the acid for each surface studied. Since the autophobic contact angles on alumina and platinum are equal within the experimental error, one straight line (curve A) fits both sets of data in Fig. 1. Acids above pentanoic exhibit lower contact angles on silica (see curve B) than on α -alumina or platinum as noted previously. Both butanoic and pentanoic acids exhibited the same contact angles on these three surfaces.

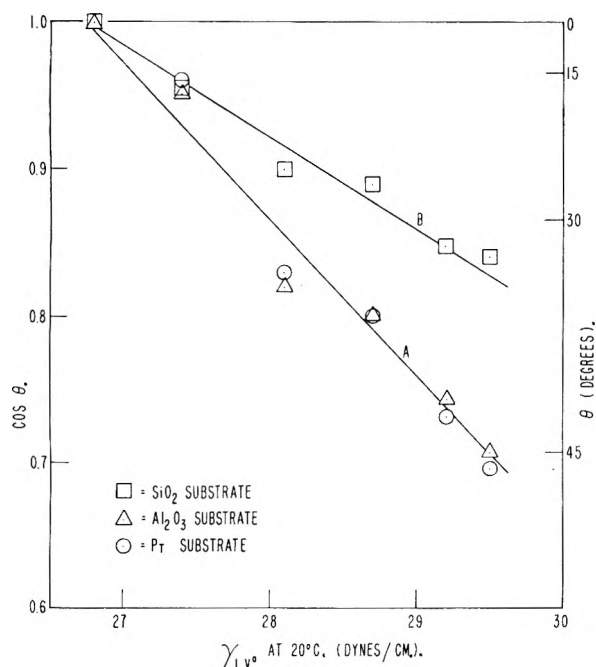


Fig. 1.—Autophobic contact angles of n -alkanoic acids.

Because 2-ethylhexanoic acid and 2-ethylhexanol have the highest degree of branching in the series of pure liquid isomers studied, it was of both theoretical and practical interest to characterize completely the wettability of the oriented monolayers resulting from contact with them. The contact angles of a group of representative liquids were

therefore examined on oriented monolayers of (a) 2-ethylhexanol, (b) 2-ethylhexanoic acid, and (c) 2-ethylhexylamine adsorbed on polished platinum; the results are given in Table III. Each monolayer was prepared by the "thermal gradient" technique.⁷ In order to minimize the solubility effects encountered with some of the liquids studied, it was found necessary to dissolve in each a maximum of 5% of the acid or alcohol of which the monolayer was composed. The amount of solute added was insufficient to affect significantly the surface tension of the test liquids. Only with tetradecane and hexadecane was it necessary to add the amine as solute in obtaining contact angles on a monolayer of 2-ethylhexylamine. Control experiments showed that the liquid polyethylenes and the A.P.I. hydrocarbons dissolved the adsorbed film too slowly to affect the contact angle measurements; therefore, no solute was required for these liquids.

Each liquid studied exhibited higher contact angles on the alcohol and amine monolayers than on the acid. Somewhat larger contact angles were found on the 2-ethylhexylamine monolayer prepared by the thermal gradient technique than the values reported in reference 1 where the monolayer was adsorbed from aqueous solution. It is believed this occurred because a somewhat closer packed monolayer was adsorbed in the former method. Cosines of the contact angles given in Table III have been plotted in Fig. 2 as a function of the surface tensions of the liquids.

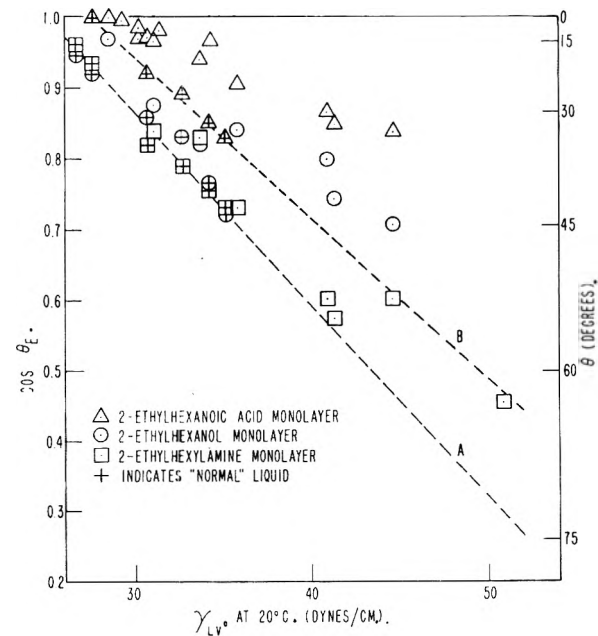


Fig. 2.—Spreading of liquids on monolayers of 2-ethylhexyl derivatives adsorbed on platinum.

As found in earlier work,³⁻⁵ the n -alkanes define a curve representing "normal" wetting behavior. Deviations from this line are in the direction of lower values of θ_E and are believed to result always from either solubility⁸ or association such as caused

(7) H. R. Baker, E. G. Shafrin and W. A. Zisman, *THIS JOURNAL*, **56**, 405 (1952).

(8) E. G. Shafrin and W. A. Zisman, *J. Coll. Sci.*, **7**, 166 (1952).

TABLE III

SPREADING OF SELECTED LIQUIDS ON ADSORBED MONO-LAYERS OF 2-ETHYLHEXYL DERIVATIVES AT 20°

Liquid	Av. contact angles on monolayers			
	γ_{LV}° at 20°	2-hexanol	2-hexylamine ^b	2-ethylhexanoic acid
Tetradecane	26.7	19°	16°	Spread
Hexadecane	27.6	24°	21°	2°
Decyl acetate	28.5	14°	..	2°
Bis-(<i>n</i> -butyl)-pyrotartrate	29.3	5°
Bis-(2-ethylhexyl)- β -methyl adipate	30.2	14°
1,6-Hexanediol bis-(2-ethylhexanoate) ^a	30.2	10°
Bis-(2-ethylhexyl) tetrahydrophthalate	30.7	14°
Polyethylene SS 906 ^a	30.7	31°	35°	23°
Bis-(2-ethylhexyl)-sebacate	31.1	29°	33°	15°
1,10-Decanediol bis-(2-ethylhexanoate) ^a	31.4	11°
1-Cyclohexyl-2-(cyclohexylmethyl)-pentadecane PSC 65 ^a	32.7	34°	38°	27°
<i>t</i> -Butylnaphthalene	33.7	35°	34°	20°
9- <i>n</i> -Dodecylperhydrophenanthrene PSC 141 ^a	34.2	40°	41°	32°
Bis-(2,2'-ethylbutoxyethyl) azelate	34.3	15°
1,1-Bis-(α -decalyl)-hendecane PSC 122 ^a	35.1	44°	43°	34°
Bis-(cyclohexaneethyl)- β -methyl adipate	35.8	33°	43°	25°
Tricresyl phosphate	40.9	37°	53°	30°
Bis-(2-phenylethyl)- β -methyl adipate	41.3	42°	55°	32°
α -Bromonaphthalene	44.6	45°	53°	33°
Methylene iodide	50.8	..	63°	..

^a The film forming material not added to liquid. ^b The film forming material was added only to tetradecane and hexadecane in the case of the amine monolayers.

by hydrogen bonding.^{9,10} The liquid polyethylenes and A.P.I. hydrocarbons behave nearly normally and have therefore been included in the same curve with the *n*-alkanes. It will be noted that the normal liquids lie on straight lines in Fig. 2. Contact angles of these normal liquids are the same on the alcohol and amine monolayers; hence, a single dashed line has been drawn in Fig. 2 to define the curve A for both layers. The analogous line (curve B) for the acids is above and parallel to that for the alcohol and amine, which means that the monolayer of acid has a looser packing of methyl groups than either the alcohol or the amine. It will be noted in Fig. 2 that an approximately straight line relation is defined for the acid monolayer by the non-normal liquids. Of the thirteen non-normal liquids, eleven are esters and therefore behave approximately as homologs; hence the observed linearity is understandable. This curve deviates markedly from curve B because the esters are powerful solvents for the monolayers. Alcohol monolayers are more soluble in the liquids studied than

(9) A. H. Ellison, H. W. Fox and W. A. Zisman, *THIS JOURNAL*, **57**, 622 (1953).

(10) A. H. Ellison and W. A. Zisman, *ibid.*, **58**, 503 (1954).

are the analogous amine monolayers, and therefore liquids other than hydrocarbons exhibit lower contact angles on the former. In no case is the solubility sufficient to cause a liquid to exhibit as small a contact angle on the alcohol as on the acid monolayer.

With this background of information it is possible to prove that hydrolytic products developed in an ester derived from 2-ethylhexanoic acid can form an adsorbed film on which the parent liquid (the ester) will not spread. The addition to pure 1,10-decanediol bis-(2-ethylhexanoate) of 5% by weight of pure 2-ethylhexanoic acid resulted in contact angles of 13° on both platinum and α -alumina and 9° on silica. When the diester was rigorously and freshly purified by selective adsorption, it exhibited a zero contact angle on each of these surfaces. This spreading property was not affected by the addition of 5% by weight of pure 1,10-decanediol. Now the contact angle of the pure ester on a close-packed monolayer of 2-ethylhexanoic acid adsorbed on platinum is listed in Table III as 11°. This agrees within the experimental error with the value of 13° obtained in the preceding experiment. It can be concluded that the non-spreading effect observed above was caused by an adsorbed monolayer of 2-ethylhexanoic acid. This demonstration is of value in understanding the non-spreading behavior of many esters; the implications are discussed in full elsewhere.²

Discussion

Pure liquid acids exhibited equal contact angles on clean platinum and α -alumina. This means that either the adsorption sites of the acids on α -alumina and platinum are equally spaced or that the type of adsorption involved does not require localized adsorption sites. Considering the data for platinum and α -alumina in Fig. 1, it is evident that the marked displacement from the straight line of the graphical point for hexanoic acid makes the purity of this acid suspect; the corrected contact angle for the pure acid can be estimated from the curve as 31° on both platinum and α -alumina. The behavior of hexanoic acid on silica again makes its purity suspect.

The rectilinear relationship of Fig. 1 for $\cos \theta$ vs. γ_{LV}° for the homologous group of acids is like similar graphs for homologous families of liquids on the many other low energy solids and monolayers investigated previously. However, in those studies the composition and packing of the organic surface was the same each time, while in the present investigation the molecular species in the low energy surface varies in chain length with the nature of the liquid applied to the surface. The straight lines of Fig. 1 can be explained by starting with the Young-Dupré equation

$$\gamma_{LV}^\circ \cos \theta = \gamma_S^\circ - \gamma_{SL} \quad (1)$$

In the homologous series of fatty acids of *N* carbon atoms per molecule γ_{LV}° is given by

$$\gamma_{LV}^\circ = k_1 + k_2 N \quad (2)$$

This is a good enough approximation over the range *N* = 4 to *N* = 9. Here $k_1 = 24.85$ dynes/

cm. and $k_2 = 0.52$. We can assume as a first approximation the linear relations

$$\gamma_{S^{\circ}} = a - bN \quad (3)$$

$$\gamma_{SL} = \alpha - \beta N \quad (4)$$

provided the surface packing of the adsorbed molecules does not become so loose that a significant proportion of $-\text{CH}_2-$ groups becomes exposed to contact with the wetting liquid. These are reasonable assumptions for the fatty acids having $N \geq 4$.¹¹ Hence

$$(k_1 + k_2N) \cos \theta = (a - bN) - (\alpha - \beta N) \\ = (a - \alpha) - (b - \beta)N \quad (5)$$

As $k_1 \gg k_2N$, it is approximately true that

$$\cos \theta = \frac{a - \alpha}{k_1} - \frac{b - \beta}{k_1} N \quad (6)$$

also

$$\cos \theta = \frac{a - \alpha}{k_1} + \frac{b - \beta}{k_2} - \frac{b - \beta}{k_1 k_2} \gamma_{LV^{\circ}} \quad (7)$$

Therefore, $\cos \theta$ is a linear decreasing function of $\gamma_{LV^{\circ}}$ whose intercept on the axis of ordinates is

$$\frac{a - \alpha}{k_1} + \frac{b - \beta}{k_2}$$

and whose slope is $(b - \beta)/k_1 k_2$.

This theory would lead one to expect that the contact angles exhibited by C_7 - C_9 alkanolic acids on a close-packed monolayer of stearic acid should be about the same values that would be predicted by Fig. 1 from the surface tensions of the respective liquid acids. To prove this point, clean platinum foil was placed in a saturated solution of stearic acid in hexadecane and a monolayer of acid was isolated on the foil upon retraction. Drops of liquid nonanoic, octanoic and heptanoic acids placed on the resulting coated surfaces exhibited contact angles of 47, 43 and 38°, respectively. A solution of 5% stearic acid in octanoic also gave a 43° contact angle on the stearic acid film. These are in good agreement with the autophobic contact angles of these acids on clean platinum as listed in Table II. It is, therefore, conclusively demonstrated that the n -alkanoic liquids adsorb layers of themselves which repel the bulk liquid; this is the justification for using the new term "autophobic" to describe such behavior. The n -acids from $n = 7$ to larger values all adsorb to form surfaces of methyl groups whose packing varies only slightly. This argument confirms the soundness of the assumed linear relations (3) and (4); this is valuable since there is no way known to measure $\gamma_{S^{\circ}}$ or γ_{SL} .

As will be noted in Table I, the autophobic contact angle of octanol-1 is the same on α -alumina and platinum; furthermore, it is equal to that of n -octanoic acid (see Table II). The equality of the contact angles of unbranched alcohols and acids on α -alumina and platinum can also be extended to include the branched compounds (see Table I). In general, the effect of branching alcohols or acids is to lower the autophobic contact angle, and the lowering becomes more pronounced with increased length of the branches. Our conclusion in the first

paragraph of the Discussion that the adsorption sites on α -alumina are either equally spaced or are not concerned in this type of adsorption can also be broadened to include all branched and unbranched carboxylic acids and alcohols.

According to Fig. 2 a "normal" liquid having a surface tension of 26.7 dynes/cm. should exhibit a contact angle of 19° on a 2-ethylhexanol monolayer. This agrees well with the value of 20° obtained for the autophobic contact angle on platinum of 2-ethylhexanol. This liquid should behave as a "normal" liquid on its own monolayer because it can neither associate with nor desorb the film. This proves that a monolayer of 2-ethylhexanol is adsorbed on which the branched liquid alcohol cannot spread. Evidently, the autophobic behavior of the straight and branched chain acid and alcohols are caused by the same mechanism. This suggests the following generalization: any pure liquid compound which is polar, amphipathic, and unable to spread on one of these high energy surfaces behaves so because it can adsorb to form an oriented monolayer of low surface energy on which the liquid phase cannot spread. Further support to and discussion of this generalization will be found in reference 2.

It is believed that the concept of an autophobic liquid can be broadened to include many systems other than the restricted number and variety studied here. In the present study and in reference 1 it has been shown that low energy films can be laid down by liquids of a large variety of structural types. These liquids can be polar as in the present study or non-polar as some of those in reference 1. This investigation leads inevitably to the postulate that any liquid which (a) will adsorb on a high energy substrate to form a low energy film and (b) has a surface tension ($\gamma_{LV^{\circ}}$) above the critical surface tension (γ_c) of the adsorbed film will be non-spreading on itself, and therefore, autophobic.

Relative to the behavior of autophobic liquids on silica, it will be noted in Table II and Fig. 1 that the contact angles of the unbranched acids increase regularly with increasing chain length. As mentioned earlier the graphical point for hexanoic acid is off the curve due to impurity. The rectilinear relationship of $\cos \theta$ vs. $\gamma_{LV^{\circ}}$ for the family of n -alkanoic acids on silica can be explained by the same argument used earlier for their adsorption on α -alumina and platinum; *i.e.*, each of the acids adsorbs as a surface monolayer having roughly the same arrangement and packing of methyl groups, and the liquid acids cannot spread on that film.

It will be noted in Table II that the liquid acids exhibit smaller contact angles (and also smaller slopes in Fig. 1) on silica than on α -alumina or platinum. Furthermore, branching in the polar molecule lowers the contact angle of an acid or alcohol on silica but not to the extent that it is affected on α -alumina or platinum. These facts lead to the conclusion that the methyl groups of the monolayer of the n -alkanoic acids are not packed as closely on polished fused silica as on α -alumina or platinum, but equal packing of the methyl groups occur in the monolayer of n -octanol adsorbed on

(11) E. G. Shafrin and W. A. Zisman, "Hydrophobic Monolayers and Their Adsorption from Aqueous Solution," published in Symposium Monograph "Monomolecular Layers," p. 129, American Assoc. for the Advancement of Science, Washington, D. C., 1954.

these surfaces. The significant decreases observed for the autophobic contact angles with dehydration of the crystals mean that the acids and alcohols adsorb less well-oriented on the dehydrated surface. This can be explained readily if the principal mechanism in the oriented adsorption of these polar compounds on silica and α -alumina is through hydrogen bonding with the adsorbed water. When

this cannot occur the molecules will adsorb lying more nearly in the surface.

Acknowledgments.—It is a pleasure to thank Mrs. Elaine Shafrin for helpful discussions. We are indebted to Prof. R. Schiessler and The American Petroleum Institute for the several synthetic hydrocarbons (designated as PSC compounds) which were prepared by A. P. I. Project 42.

THE NATURE OF " γ -FeO"¹

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A black, ferromagnetic powder, the composition of which is approximately FeO, is produced by thermal decomposition of ferrous formate at temperatures near 250°. Lihl² has reported that this material possesses a spinel structure, and has designated it as " γ -FeO." A magnetic, X-ray and chemical study of this material is presented. It is not a simple material but contains at least two phases. The evidence suggests that it consists of Fe₃O₄, finely divided Fe or Fe₃C (or both) and perhaps a little α -FeO.

Introduction

Thermal decomposition *in vacuo* of ferrous formate at temperatures near 250° produces a finely-divided, ferromagnetic black powder. Lihl² has reported that the composition corresponds closely to FeO, with the addition of a few percentage by weight of carbon. Lihl's X-ray patterns indicated a spinel structure with a lattice parameter, $a = 8.375 \text{ \AA}$., about 0.1% smaller than that observed by him for Fe₃O₄. Lihl has designated this material " γ -FeO."

The existence of an iron oxide containing only ferrous ions and possessing a spinel structure should be of considerable interest from the standpoint of the ferrites. Fe₃O₄, which possesses the spinel structure and may be considered to be the prototype of the ferrites, exhibits an anomaly in magnetic properties at about -160°. The magnetocrystalline anisotropy below this temperature shows a lower symmetry and a larger magnitude than above it.³ In polycrystalline material, this results in a strong decrease in magnetization with decreasing temperature at intermediate field strengths⁴ (*cf.* Fig. 1). Verwey, *et al.*,^{5,6} have attributed this transition to the formation of an ordered arrangement among the ferrous and ferric ions present in Fe₃O₄. In the case of " γ -FeO," if it were truly a spinel iron oxide containing only ferrous ions, this ordering would not be possible and no transition would be observed. Because of the strong interest currently attached to the structure and theory of the ferrites, it seemed of interest to explore the properties of this material.

The magnetic properties reported here indicate that it is not a simple material, but rather contains at least two phases, one of which is Fe₃O₄. Chemical and X-ray evidence support this conclusion, and suggest that metallic iron also is present. On the basis of this study, it is suggested that " γ -FeO" is in reality Fe + Fe₃O₄ with perhaps a small amount of α -FeO. The iron is present as extremely small particles and may be in the form of cementite,⁷ Fe₃C, or essentially pure iron. Because of the possible importance of this material, the evidence is presented in this paper in some detail.

Preparation.—Type "L" Carbonyl iron⁸ was dissolved in Merck reagent formic acid, and the ferrous formate dihydrate precipitated under a CO₂ atmosphere. This was dehydrated and then thermally decomposed at 267–275°

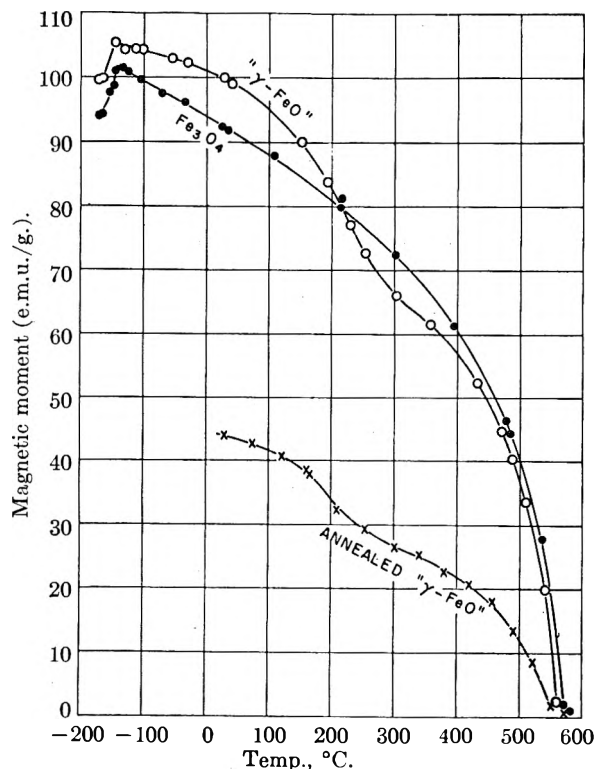


Fig. 1.—Weiss curves of " γ -FeO" and Fe₃O₄ at 4000 gauss.

(1) This work was supported in part by the Office of Naval Research.

(2) F. Lihl, *Monatsh.*, **81**, 632 (1950).

(3) C. H. Li, *Phys. Rev.*, **40**, 1002 (1932).

(4) P. Weiss and R. Forrer, *Ann. Phys.*, **12**, 279 (1929).

(5) E. J. W. Verwey, *Nature*, **144**, 327 (1939).

(6) E. J. W. Verwey and P. W. Haayman, *Physica*, **8**, 979 (1941).

(7) We are indebted to the reviewer for the suggestion that the second phase might be Fe₃C.

(8) General Aniline and Film Corp.

in vacuo. The product was analyzed chemically for ferrous and ferric ion. Table I gives the compositions of several specimens, expressed in terms of the equivalent amounts of FeO and Fe₂O₃ required to give the observed ferric and ferrous ion concentrations. The last line gives the composition calculated for Fe₃O₄, for comparison.

TABLE I
COMPOSITION OF " γ -FeO" SPECIMENS

Specimen	FeO, wt. %	Fe ₂ O ₃ , wt. %	Remainder (difference)
A	95.7	2.9	1.4
B	85.7	7.3	7.0
C	76.8	20.2	3.0
Fe ₃ O ₄	31.0	69.0	..

Magnetic Properties.—Figure 1 shows the magnetic moment per gram of specimen B of " γ -FeO" compared to that of Fe₃O₄ over a wide range of temperature. The uncertainty in these measurements, made with a Curie balance, is of the order of 5% in the moment. The temperatures are also not accurate at the extremes. The specimens were sealed in evacuated Vycor tubes to prevent oxidation during measurement.

The main features of these curves may be summarized as follows:

1. Two phases with different Curie points are present. The phase contributing the major proportion of the moment possesses a Curie point substantially the same as Fe₃O₄. The second phase possesses a Curie point near 200°.

2. Both the Fe₃O₄ and " γ -FeO" curves show the low temperature transition, at the same temperature.

3. Annealing the " γ -FeO" for two hours at 585° produced the curve marked Annealed " γ -FeO." A subsequent anneal for six hours at 485° almost restored the original curve.

These data indicate that at least two phases are present and are consistent with the view that " γ -FeO" consists of a mixture of Fe₃O₄ and either Fe or $\frac{1}{3}$ Fe₃C. The high curie point phase is readily identified with Fe₃O₄, because of the similarity in Curie point and the low temperature transition. The magnitude of the contribution made by this phase to the magnetic moment is roughly of the same order (0.8 to 0.9 that of Fe₃O₄) as expected from chemical analysis (0.7 to 0.8).

To satisfy the chemical composition, the low Curie point phase must be identified with "free" iron. The low Curie point around 200° coincides with that for Fe₃C (200–215°).⁹ A low Curie point, for pure iron, as compared to the bulk value¹⁰ of 770°, might also occur for extremely small particles.^{11,12} Careful examination of the X-ray diffraction patterns of " γ -FeO" revealed several faint lines that confirmed the presence of either Fe₃C or Fe. The faintness and breadth of these experimental lines, together with the similarity of the Fe₃C and Fe patterns, made it impossible to decide definitely between Fe₃C and Fe.

(9) R. Bernier, *Ann. Chim.*, **6**, 104 (1951).

(10) R. Bozorth, "Ferromagnetism," D. Van Nostrand Co., New York, N. Y., 1951, p. 54.

(11) H. Konig, *Naturwissenschaften*, **33**, 71 (1946).

(12) P. W. Selwood in the Chapter "Magnetism and Catalytically Active Solids" in "Advances in Catalysis," Vol. 3, Academic Press, Inc., New York, N. Y., 1951, p. 85.

Measurement of the breadth of the strongest of these faint lines indicated a crystallite diameter of about 135 Å. In order to determine whether this is sufficiently small to result in a reduced Curie point for Fe, measurements were made of the moment of an Fe powder containing 68% by weight of free Fe with an average diameter of 165 Å. The results are shown in Fig. 2. The Curie point initially appears to be well below 770°. At about 250°, sintering apparently occurs, resulting in an increase in Curie point. This is close to the temperature observed by other means¹³ for the onset of sintering in these powders. These data indicate that 165 Å. Fe has a Curie point considerably below that of bulk iron, with a value probably near 400°. It is therefore entirely reasonable that 135 Å. Fe should have a Curie point as low as 200°.

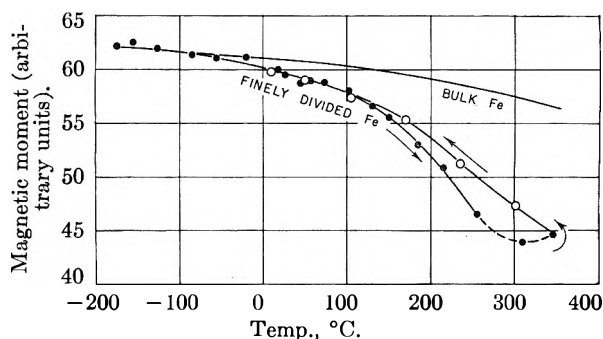
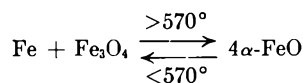


Fig. 2.—Weiss curves for bulk and finely divided Fe.

If the low Curie point phase is Fe, it should be possible to calculate roughly the weight percentage present from the corresponding contribution to the magnetic moment at low temperatures. These calculations consistently gave figures about one-half as large as predicted from the chemical analyses. If this phase were Fe₃C, a lower moment contribution would be expected, resulting in better agreement with the data.

Fe (or $\frac{1}{3}$ Fe₃C) plus Fe₃O₄ is unstable with respect to α -FeO above about 570°.¹⁴ In the following discussion, the symbol Fe will be used to indicate $\frac{1}{3}$ Fe₃C as well as pure iron. The equation for the reaction is



The results of the anneals illustrated in Fig. 1 can be explained on this basis. During the anneal at 585°, paramagnetic α -FeO was formed at the expense of the Fe and Fe₃O₄. Since the α -FeO made no contribution to the magnetic moment, the moment was reduced at all temperatures. At 485°, the effect of the anneal was to reverse the reaction and restore the initial condition. The development of α -FeO upon annealing " γ -FeO" above 570° was confirmed in the X-ray diffraction pattern. It was noticed that a slight irreversible rise occurred in the magnetic moment–temperature curve upon heating a specimen of " γ -FeO" to the Curie point for the first time. This indicates the

(13) A. D. Franklin and R. B. Campbell, *THIS JOURNAL*, **59**, 65 (1955).

(14) J. Benard, *Ann. Chim.*, **12**, 5 (1939).

presence of a small amount of α -FeO in the specimen as prepared.

X-Ray Measurements.—Measurements of the positions and intensities of the strongest lines in the X-ray diffraction patterns of both pressed briquettes and loose powders of specimen A were made using a GE XRD-3 spectrometer with an iron tube and a manganese filter. The relative intensities are listed in Table II, together with intensities for Fe₃O₄. The lattice constant for the " γ -FeO" was 8.386 Å., about 0.1% smaller than that for Fe₃O₄, 8.399 Å., confirming Lihl's² observations. This pattern for the " γ -FeO" is identical, within experimental error, to that for Fe₃O₄. More sensitive measurements with both the spectrometer and a powder camera revealed also the strongest (110) Fe line, with faint suggestions of the (200) and (211) lines.

TABLE II

X-RAY DIFFRACTION LINE INTENSITIES					
Line	" γ -FeO"	Fe ₃ O ₄	Line	" γ -FeO"	Fe ₃ O ₄
(111)	..	7	(333)	23	16
(220)	26	25	(511)		
(311)	100	100	(440)	30	25
(222)	5	6	(533)	..	3
(400)	22	17	(553)	..	9
(422)	12	4			

In the spinel structure, the oxygen ions form a face-centered cubic lattice, with the cations distributed in some of the interstices between the oxygen ions. In Fe₃O₄ the unit cell can be expressed as Fe₂₄O₃₂. The hypothetical " γ -FeO" unit cell might correspond to Fe₃₂O₃₂, with the extra cations distributed in some of the unoccupied interstices. Alternatively, vacancies might occur in the oxygen lattice, with a unit cell corresponding to Fe₂₄O₂₄. For the (440) line, the calculated intensities for the first possibility for many different ways of arranging the extra cations always disagreed with the observed intensity by at least a factor of 2. This line, in general, seems to be sensitive to the presence of the extra cations. The disagreement appears to rule out any Fe₃₂O₃₂ structure. Consideration of the ionic radii also makes this structure appear unlikely. The sum of the ionic radius¹⁶ for the oxygen ion (1.35 Å.) and the ferrous ion (0.80 Å.) is larger than any of the interstices present between the oxygen ions in Fe₃O₄. Since the radius for the ferrous ion is larger than that for the ferric ion (0.67 Å.), the lattice parameter for the Fe₃₂O₃₂ structure should be larger than for Fe₃O₄, not smaller as observed.

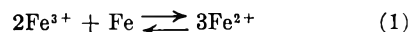
For the Fe₂₄O₂₄ structure the observed and calculated intensities were very similar except for the (222) line. Relative to the (311) line as 100, the calculated values were 12.5 for the Fe₂₄O₂₄ structure, and 7.0 for the Fe₃O₄. The observed values were 6.5 for Fe₃O₄ and 5.0 for " γ -FeO." This comparison suggests that this structure be excluded. Furthermore, the Fe₂₄O₂₄ structure calls for 7 to 8 vacancies per unit cell in the oxygen lattice, which seems to be an unlikely situation.

On the other hand, the X-ray data are consistent

(15) R. W. G. Wyckoff, "The Structure of Crystals," 2nd Ed., Chemical Catalog Co., New York, N. Y., 1931.

with a mixture of Fe (or $\frac{1}{3}$ Fe₃C) and Fe₃O₄. The lines corresponding to Fe or Fe₃C are extremely weak and broad, suggesting very small crystallites. Judging from the intensity of the strongest of these lines, it does not appear to be possible to account for all of the Fe corresponding to the chemical analysis. As mentioned above, the same situation appears for the magnetic data. It is possible that some of the metallic Fe or Fe₃C is present in particles so small as to make little observable contribution to either the magnetic moment or the observed diffraction line intensity.

Chemical Analysis.—In the normal analyses for these Fe oxides, the initial step is to dissolve the sample in acid under a non-oxidizing atmosphere. The amounts of ferrous and ferric ion are then determined in the solution. As a variant of this procedure, the free metal present is often determined by measuring the hydrogen evolved during the acid dissolution. This technique neglects the internal oxidation-reduction system possible when both ferric and metallic Fe (or Fe₃C) are present in the initial sample. During acid dissolution, the ferric ion already dissolved can oxidize and dissolve the free Fe



so that the final solution may contain only ferrous ion, and no hydrogen may be evolved at all. The standard free energy change of -55.7 kcal. per formula gram-equivalent¹⁶ for the reaction indicates a strong tendency for the reaction to proceed to the right. Under conditions in which as little as 0.5 weight percentage free iron could have been detected, no hydrogen was evolved during acid dissolution of these specimens. When a strong chelating agent (Versene Fe-3 Specific)¹⁷ was added to the acid solution to reduce the ferric ion activity, hydrogen was evolved from a sample of specimen A corresponding to 2 weight percentage free metal. This is well beyond experimental error, and indicates definitely that free metallic iron is present. Because even in the presence of the chelating agent the free energy change in the reaction must be expected to be large and negative, the 2 weight percentage figure can only be a lower limit to the free metal content. Fe (or $\frac{1}{3}$ Fe₃C) plus Fe₃O₄ should contain about 19 weight percentage free metal.

Conclusion

The Curie point, low temperature transition and X-ray diffraction pattern are all consistent with the presence of Fe₃O₄. The X-ray diffraction pattern and the chemical analysis both give positive evidence of the presence of either metallic iron or Fe₃C in very finely divided form. The magnetic data reveal the presence of a second phase which could easily be very fine Fe, but is more probably Fe₃C. The sum of this evidence strongly supports the view that Lihl's " γ -FeO" is actually a mixture of either Fe₃C or Fe and Fe₃O₄, with possibly a small

(16) Calculated from the standard electrode potentials given by B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., Houston, Texas, 1952, pp. 292, 304.

(17) The Versenes are proprietary products of the Bersworth Chemical Company, Framingham, Massachusetts.

amount of α -FeO present. The relative proportions of the three components probably vary somewhat depending on the conditions of preparation. It is also possible that both Fe₃C and finely divided Fe are present.

Acknowledgment.—Thanks are due Erik Klockholm for X-ray measurements, R. B. Campbell for preparation of the oxide, and P. A. Parkin for the chemical analyses. The support of the Office of Naval Research is gratefully acknowledged.

THE HEAT OF IMMERSION OF CARBON BLACK IN WATER, METHANOL AND *n*-HEXANE

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Heats of immersion have been measured on nine carbon blacks in water, methanol and *n*-hexane. The heats of immersion in the two polar, hydrogen bonding liquids are shown to be approximately linear functions of the oxygen content per unit surface area of the black, indicating that virtually all the oxygen in carbon black is present in the form of a surface complex. The heats of immersion in *n*-hexane are nearly constant for all carbon black. Removal of active sites by graphitization does not materially alter the over-all interaction energy between carbon black and non-polar adsorbates. This is interpreted as evidence for an accompanying loss of low energy sites in passing from the heterogeneous carbon black surface to the homogeneous surface of Graphon.

I. Introduction

Despite the rapid increase over the past decade in the literature dealing with heats of immersion¹⁻⁷ few generalizations have come to light regarding the dependence of the heat of wetting on the chemical constitution of both the solid and the wetting liquid. Harkins and Boyd¹ have shown that, in general, inorganic solids containing oxygen give high heats of immersion in polar, hydrogen bonding liquids and low heats in non-polar liquids. With hydrophobic solids this behavior is generally reversed.

Carbon black is an interesting material in that it is basically a hydrophobic solid, the surface characteristics of which can, however, be modified by oxidation. Commercial blacks contain appreciable amounts of chemically combined hydrogen, oxygen and sulfur.⁸⁻¹⁰ The disposition of the non-carbon constituents is not known with certainty except that the amount of hydrogen present usually exceeds by far the quantity which can be accommodated on the surface of the particles.¹⁰ It was expected that an investigation of the heat of immersion of various types of carbon black might yield interesting information regarding the dependence of the heat of wetting on composition and, in doing so, would furnish some evidence of the distribution of non-carbon constituents between the interior and the surface of the carbon black particles. The possible bearing of the results on such

problems as wettability and elastomer reinforcement is evident.

II. Experimental

Carbon Blacks.—A summary of pertinent data characterizing the carbon blacks investigated in the present study is given in Table I; these samples are representative of modern commercial rubber carbons. The designating symbols listed in column 2 of Table I are those universally adopted by the rubber industry: FT, fine thermal; SRF, semi-reinforcing furnace; FEF, fast extrusion furnace; HAF, high abrasion furnace; SAF, super abrasion furnace; EPC, easy processing channel; MPC, medium processing channel. As indicated in column 3 the carbons differ widely as to their method of preparation and raw material employed. For a description of the various carbon black processes the reader is referred to an excellent review by Smith.¹¹

The surface areas were determined from low temperature nitrogen adsorption data employing the simple Brunauer-Emmett-Teller isotherm.¹² A conventional volumetric adsorption apparatus was used. The blacks were extracted with benzene in a Soxhlet apparatus for 72 hours to remove adsorbed tars, dried at 75° *in vacuo* and stored in a desiccator over "Drierite." Prior to the heat of immersion measurement one to two and a half gram samples were weighed into thin-walled glass bulbs and outgassed for 18 hours at a pressure of less than one micron of mercury. No heat was employed in the final outgassing step as it was *not* intended to remove *chemisorbed* gases. Of necessity the final step in the sample preparation had to be different for the carbon-hydrogen-sulfur analyses; the samples were flushed with dry nitrogen (10 ml./min.) at 150° for one hour.

Apparatus.—The apparatus was a multiple calorimeter unit allowing a total of eight determinations to be made without reloading. The individual calorimeters consisted of 300 ml. wide-mouth Dewar flasks cemented into Formica rings. To these were bolted Formica lids which supported all the working parts of the calorimeter: heater, stirrer, bulb breaking device and a thermistor as the temperature sensing element. In this respect the calorimeter units differed in no important way from others reported in the literature.⁴ The Dewars were fastened to a plate from which they protruded into a water-bath. The calorimeter stirrers as well as the bath stirrers were driven from a common shaft by means of O-ring belts. The apparatus was located in a temperature controlled (25°) air-conditioned laboratory; the bath was not thermostated, but merely served to lag out fluctuations in room temperature. No difficulty whatever was encountered from this arrangement.

(1) G. E. Boyd and W. D. Harkins, *J. Am. Chem. Soc.*, **64**, 1190, 1195 (1942).

(2) P. R. Basford, G. Jura and W. D. Harkins, *ibid.*, **70**, 1444 (1948).

(3) F. L. Howard and J. L. Culbertson, *ibid.*, **72**, 1185 (1950).

(4) A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *THIS JOURNAL*, **57**, 649 (1953).

(5) F. E. Bartell and R. M. Suggitt, *ibid.*, **58**, 36 (1954).

(6) G. J. Young, J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, *ibid.*, **58**, 313 (1954).

(7) F. H. Healey, J. J. Chessick, A. C. Zettlemoyer and G. J. Young, *ibid.*, **58**, 887 (1954).

(8) D. S. Villars, *J. Am. Chem. Soc.*, **69**, 214 (1947); **70**, 3655 (1948).

(9) M. L. Studebaker, *India Rubber World*, **127**, 215, 225 (1952).

(10) R. B. Anderson and P. H. Emmett, *THIS JOURNAL*, **56**, 753 (1952).

(11) W. R. Smith, "Encyclopedia of Chemical Technology," Vol. 3, The Interscience Encyclopedia, Inc., New York, N. Y., 1949, pp. 34-65.

(12) S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

TABLE I
CARBON BLACK ANALYSES AND SURFACE AREAS

Carbon black	Type	Process	N ₂ surface area, m. ² /g.	C	Ultimate analyses, %		O ^a	Ash
					H	S		
P-33	FT	Gas thermal	13.7	99.22	0.48	0.00	0.24	0.06
Gastex	SRF	Gas furnace	27.6	97.52	.32	.09	.42	1.65
Philblack A	FEF I	Oil furnace	45.6	98.44	.32	.68	.38	0.18
Sterling SO	FEF II	Oil furnace	47.8	96.93	.31	1.22	.70	.84
Philblack O	HAF	Oil furnace	75.1	98.22	.30	.41	.83	.24
Philblack E	SAF	Oil furnace	142.6	97.31	.33	.43	1.69	.24
Wyx	EPC	Channel	114.2	95.84	.71	.02	3.40	.03
Acetylene black	...	Thermal	58.0	99.78	.07	.03	0.07	.05
Graphon ^b	93.7	98.47	.02	.02	0.12	1.37

^a By difference. ^b Channel black (MPC) graphitized at 3000°.

The electrical part of the apparatus consisted of a thermistor bridge, amplifier unit, Brown strip chart recorder, calibration unit and a.c. voltage regulator. Operation of the bridge as a differential thermometer was effected by using one of the calorimeters as a reference and incorporating its thermistor and the thermistor of the sample calorimeter into adjacent arms of the bridge circuit. The bridge output was fed to a pre-amplifier (V₁), through a voltage amplifier (V₂) and phase detector (V₃), to the recorder. The output of (V₂) was also fed through a voltage amplifier (V₄) to a null indicating meter. A recorder zero adjustment was provided in the phase detector to allow for recorder pen positioning. The calibration unit was constructed to provide a constant current to a 20-ohm constantan heater for a predetermined interval. The heater power supply consisted of a filament transformer, bridge rectifier and filter. Large capacities were required in the heater power supply to eliminate pickup between the heater and thermistor. A dummy heater was employed to keep the power supply loaded at all times. The timing action was accomplished by a holding relay and a self-cocking interval timer. In spite of the automatic timing feature a separate interval timer was built into the calibration circuit so that the actual heating time could be determined accurately to 1/100 second. The heating current was read on a high precision Weston milliammeter. Line regulation (AC) to the amplifier and calibration units, was provided by means of a General Electric regulator. At maximum sensitivity the calorimeter was capable of detecting changes of ten microdegrees. Actually, the temperature rise in the heat of immersion experiments was of the order of several millidegrees so that the results were not limited in accuracy by the calorimetry.

Procedure.—Two hundred milliliters of liquid was used in the immersion experiments. After loading the calorimeters and allowing the system to attain thermal equilibrium the stirrers were started, the bridge balanced and a rating curve established. A known amount of electrical energy was introduced into the sample calorimeter by means of the heater and the deflection recorded. The bridge was rebalanced, a new rating curve established, and the sample bulb broken. In all instances in which the sample bulb broke cleanly the heat of wetting was evolved in less than a minute. The net deflections were computed by extrapolating the "fore" and "after" rating curves to the mid-point of the operation.

Heat of Bulb Breaking.—Heat of bulb breaking experiments confirmed the conclusions of Bartell and Suggitt⁶ regarding the sources of this heat effect. However, since smaller bulbs (7/8 inch diameter) were used the heat of vaporization term did not cancel out the mechanical and strain energies. The mean heat of bulb breaking was determined as 0.26 cal. with an average deviation of 0.10 cal. A similar lack of reproducibility was observed by Bartell and Suggitt who reported an average deviation of 0.07 cal. The heat of fracture of the bulb represented by far the largest source of experimental error and was reflected in the reproducibility of the heat of immersion measurement which improved (relatively) with the magnitude of the total heat effect measured. In order to minimize this effect as many as five determinations were run on the lower surface area blacks and larger samples were employed. The average standard error of the values listed in Table II is ± 4 ergs/cm.².

TABLE II
HEATS OF IMMERSION OF CARBON BLACKS

Carbon black	Heat of immersion (ergs/cm. ²)		
	Water	Methanol	<i>n</i> -Hexane
FT	43	110	134 (?)
SRF	48	110	98
FEF I	47	84	94
FEF II	48	101	100
HAF	43	89	104
SAF	59	98	103
EPC	84	128	101
Acetylene	28	84	121
Graphon	31	78	103

III. Results and Discussion

Table II represents a summary of all determinations made. The heats of immersion of Graphon have also been measured by Zettlemyer and associates.^{6,7} Their values for water and *n*-hexane agree well within experimental error with those found in the present investigation; however, their heat of immersion in methanol is appreciably larger (102 ergs/cm.²).

If one assumes that the oxygen present in carbon black is distributed over the surface only, then the heat of immersion in hydrogen bonding liquids could be expected to be a function of the surface density of oxygen. Figure 1 indicates that this is indeed the case, even though the curve for water suffers from considerable scatter of the experimental points. It should be emphasized, however, that the point farthest removed from the curve represents the P-33 (FT) carbon, for which the total heat effect measured is by far the smallest and whose small oxygen content and surface area would render its position along the oxygen axis quite uncertain. Simple calculation shows that the oxygen density of the channel black sample corresponds to one atom of oxygen for 9 Å.², *i.e.*, roughly a monolayer. Thus, the increment in the heat of immersion from an oxygen free surface to a completely covered one is approximately 50 ergs/cm.². This is of the same order of magnitude as the difference in the energies of adhesion of water against fatty alcohols and hydrocarbons.

The heats of immersion in *n*-hexane for seven of the carbons are remarkably constant; no explanation is apparent for the slightly larger heats of immersion of thermal and acetylene blacks. This constancy of the heat of immersion in *n*-hexane is

perhaps not surprising as there is no possibility of hydrogen bonding and the forces involved in the interaction of non-polar hydrocarbons with carbon black must be almost entirely dispersion forces. A similar situation should prevail in the inverse case—the interaction of oxygen-free carbon with water and alcohols. Comparison of the energies of adhesion of Graphon and Acetylene black against water and methanol with that of carbon blacks in *n*-hexane leads to the values presented in Table III. The results show the interaction energies in polar-non-polar carbon black-liquid systems to be approximately the same regardless of which phase carries the polar groups.

TABLE III
ENERGIES OF ADHESION

Carbon	Liquid	Energy of adhesion, ^a ergs/cm. ²
All carbon blacks ^b	<i>n</i> -Hexane	142 to 152
Graphon	Water	149
	Methanol	128
Acetylene black	Water	146
	Methanol	134

^a Energy of adhesion = heat of immersion plus total surface energy of wetting liquid. ^b Except P-33 (FT) and Acetylene black.

A further point of interest is the behavior of Graphon. It is well known that this carbon possesses an almost completely homogeneous surface, while typical carbon blacks have strongly heterogeneous surfaces as indicated by high heats of adsorption at low surface coverages.^{13,14} The absence of sites of high energy in Graphon might be expected to result in somewhat lower heats of immersion. Since such were not realized the heats of immersion of Graphon and Spheron-6 (MPC) in liquid nitrogen and argon were calculated from the heat of adsorption data of Beebe and associates.^{13,14} The heat of immersion is readily shown to be

$$h_i = \frac{1}{S} \int_0^\infty (q - q_L) dn + h_L$$

where S is the specific surface area (in cm.²/g.), q the differential heat of adsorption, q_L the heat of liquefaction, n the number of moles adsorbed per gram of adsorbent and h_L the surface enthalpy of the liquid. Graphical integration of the heat of adsorption curves yields the results of Table IV. It will be noted that any loss in *over-all* interaction energy incurred in the removal of the high energy sites from channel black by graphitization is either too small to be measured by the methods available

(13) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, *J. Am. Chem. Soc.*, **69**, 95 (1947).

(14) R. A. Beebe, B. Millard and J. Cynarski, *ibid.*, **75**, 839 (1953).

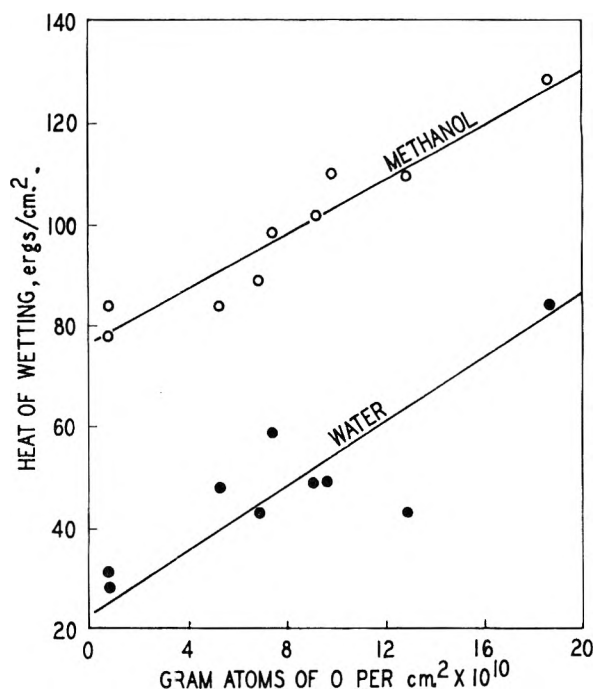


Fig. 1.—Heats of wetting of carbon black in methanol and water.

or the loss of high energy sites must be accompanied by a gain in sites of intermediate energy. This would be the case if the homogeneous surface of Graphon were of higher energy than some of the low energy sites which are also destroyed in graphitization. The removal of hydrogen in graphitization makes this appear more than plausible.^{15,16}

TABLE IV
HEATS OF IMMERSION FROM HEATS OF ADSORPTION

Carbon black	Liquid	h_i , ergs/cm. ²	Ref. for adsorption data
Spheron-6(MPC)	Nitrogen	105	13
Graphon	Nitrogen	95	13
Spheron-6(MPC)	Argon	106	14
Graphon	Argon	147	14

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(15) W. D. Shaeffer, W. R. Smith and M. H. Polley, *Ind. Eng. Chem.*, **45**, 172 (1953).

(16) M. H. Polley, W. D. Schaeffer and W. R. Smith, *THIS JOURNAL*, **57**, 469 (1953).

THE PROPERTIES OF NITRILE BINARY SYSTEMS AND THEIR RELATION TO POLYACRYLONITRILE SOLUBILITY

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It has been found that the relative solvent powers of liquids for tetracyanoheptane and for polyacrylonitrile are qualitatively the same. Measurements of heats of mixing and non-ideal volume changes on mixing glutaronitrile with other liquids have shown that the good nitrile solvents are characterized by heat evolution and volume expansion on mixing with glutaronitrile. A qualitative correlation between excess entropies of mixing and non-ideal volume changes on mixing has been found for the nitrile binary systems. Vapor pressure and viscosity data also have been obtained for some glutaronitrile binary systems. No correlation was found between viscosity and any of the other measured properties. It was concluded that good nitrile solvents must be composed of molecules with high dipole moments, a low hydrocarbon/polar group ratio and no self-hydrogen bonding power.

Introduction

The simplest polymer solution theory which has been moderately successful in explaining many experimental facts is based on an entropy of mixing term peculiar to long molecules and a heat of mixing term determined by the cohesive energy densities of the components of a solution. However, the cohesive energy density concept is inadequate in dealing with solutions composed of polar components, whether polymeric or non-polymeric. There seems to be a need for systematic investigations of the properties of solutions involving polar constituents.

The factors that determine the relative solvent powers of liquids for polyacrylonitrile have not been clearly defined.¹ The objective of the present work was to gain further insight into this specific problem. It was decided that a study of the properties of solutions of simple organic nitriles, which would serve as model compounds for the polymer, might be a useful approach.

First, the solubilities of the solid model compound, 1,3,5,7-tetracyanoheptane, in a variety of liquids are determined. These results are compared with the available qualitative solubility data for polyacrylonitrile, to see how well the model reflects the solubility of the polymer. Then several properties of solutions of glutaronitrile, a liquid at 25°, in other liquids are studied to get more detailed information about the nature of the interactions of essentially a short segment of the polyacrylonitrile molecule with other simple molecules. Emphasis is placed on getting limited data for a lot of binary systems involving nitriles rather than on getting precise and extensive data for only a few such systems.

Experimental

Solubility of Model Compounds.—Definite concentrations of tetracyanoheptane in a liquid were made in small glass tubes which were then sealed off. The solubility determinations were made by immersing the sealed tubes in a large oil-bath, raising the temperature of the bath at a rate of about 1/2°/minute with continuous agitation of the sealed tube and noting the temperature at which the last visible trace of solid material dissolved. In some cases the temperature of the oil-bath was raised and lowered across the solution temperature several times to check the accuracy of the measurement.

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(1) See E. E. Walker, *J. Appl. Chem.*, Aug. (1952) which appeared after the work reported here was completed.

Heats of Mixing.—The heat of mixing apparatus was constructed according to a design developed by Meares² with only minor modifications. A forty junction thermel was used rather than the specified twenty junction thermel to double the response to a given temperature change. The desired accuracy in measuring the potential drop across the thermel was then obtainable with a Leeds and Northrup Type K potentiometer and a sensitive galvanometer (0.0030A./mm.). The constant temperature environment for the twin calorimeter assembly was a 24" × 12" × 12" bath filled with water and equipped with a toluene-mercury regulator, an electronic relay circuit, a circulating pump and infrared lamp heaters. With this arrangement the temperature could be controlled to within $\pm 2^\circ \times 10^{-3}$ at 28°, the operating temperature and this control was found to be adequate. The device recommended by Sturtevant³ for measuring the electrical energy input to the heater coil was constructed and used in the present apparatus. A 10-ml. hypodermic syringe with a 6" needle which could be inserted directly into the outer mixing chamber of the calorimeter was used to introduce one of the liquid components into the apparatus.

Densities.—A U-tube pycnometer³ was used to measure the densities of pure liquids and solutions. The measurements were made in the constant temperature bath used for the heat of mixing work, which was kept at 28.0°. The accuracy of the density measurement was ± 0.0002 g./ml.

Vapor Pressures.—Two methods were used to get measurements of total vapor pressure of solutions at 20°. The vapor pressure of glutaronitrile at 20° is so small that the partial vapor pressure of the other component could be equated to the total vapor pressure.

The first method involved the use of a simple U-tube mercury manometer made of 10 mm. i.d. tubing. The difference in mercury level in the two arms of the manometer was read to ± 0.05 mm. with a cathetometer. The manometer was attached to a simple vacuum apparatus consisting of a mercury diffusion pump with a fore pump and various traps, stopcocks and ground glass attachment points. The major problem was in properly freeing the solution of dissolved air. Eight to ten cycles of freezing the solution, pumping on it and then melting were necessary to remove air from about 5 ml. of solution. A magnetically operated stirrer was used to agitate the solution prior to a measurement. After removal of dissolved air the tube containing the solution was placed in the water-bath which was maintained at $20.0^\circ \pm 2 \times 10^{-3}$. This method was too time consuming to get many results but some data for ethanol, dioxane and nitromethane with glutaronitrile were obtained.

Some vapor pressure measurements were made by a second method which involved a determination of the intensity of absorption of infrared radiation by a 10-cm. cell filled with vapor at the equilibrium vapor pressure of a solution.⁴ No trace of any glutaronitrile infrared bands appeared. The variation of the intensity of an absorption band of the other

(2) P. Meares, *Trans. Faraday Soc.*, **45**, 1066 (1949).

(3) A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1949, p. 731.

(4) The measurements were made by C. R. Bohn of this Laboratory, who also developed the technique.

component was measured as a function of solution concentration. The intensity of the band was taken to be directly related to the concentration of the other component in the vapor phase according to Beer's law. Wide bore tubing (10 mm. i.d.) between the solution container and the absorption cell was used so that an equilibrium vapor pressure could be obtained in a reasonably short time even with a small pressure (about 1 mm.) of air left in the system. The method proved to be quite sensitive and reproducible and was used to get vapor pressure data for ethanol, dioxane and dimethylformamide with glutaronitrile.

Viscosities.—The viscosity measurements were made at 28.0° with an Ubbelohde viscometer. Water was used as the calibrating liquid. Kinetic energy corrections were applied when necessary. Density data were already available for conversion of measured flow times to absolute viscosities in centipoises. The normal precautions were taken to get reliable results.

Source and Purity of Materials.—Most of the liquids used in the present work were either Eastman Kodak white label or B and A Analar reagent grade products. The liquids classed as "good" polyacrylonitrile solvents were obtained from sources within this Laboratory.

The 1,3,5,7-tetracyanoheptane was prepared by W. G. Vosburgh of this Laboratory.

Results and Discussion

Solubility of Tetracyanoheptane.—Tetracyanoheptane represents a short segment of the polyacrylonitrile polymer molecule. It is a crystalline solid melting at 102°. The temperature at which 20 wt. % of this substance dissolved completely has been determined for about thirty liquids as solvents. These results are given in Table I and in Fig. 1 which is a graph of solution temperature *versus* mole % tetracyanoheptane in solution. The key as to which numbered point refers to a given solvent on Fig. 1 is given in the first column of Table I.

TABLE I

SOLUBILITY DATA FOR TETRACYANOHEPTANE

Key to Fig. 1	Solvent	Soln. temp. of 20 wt. % tetracyanoheptane in °C.	ΔF^e ($x_2 = 1/2$), cal./mole
1	Tetramethylene sulfone	15.5	-265
2	Dimethylformamide	13.0	-185
3	Dimethyl acetamide	23.0	-130
4	γ -Butyrolactone	26.0	-100
5	Propylene carbonate	34.0	-70
6	N-Acetylmorpholine	44.0	-40
7	Glutaronitrile	40.5	
8	Nitroethane	41.0	+40
9	Acetonylacetone	50.0	+45
10	Cyclopentanone	47.5	+75
11	Propionitrile	39.0	+75
12	Acetone	41.0	+80
13	Ethylene cyanohydrin	48.0	+110
14	Dioxane	57.5	+150
15	Pyridine	58.0	+175
16	Cyclohexanone	63.0	+190
17	Methyl ethyl ketone	63.0	+230
18	Ethylene bromide	79.0	+245
19	Chloroform	76.5	+280
20	Formamide	66.0	+320
21	Acetic acid	77.0	+370
22	Toluene	94.0	+455
23	Ethanol	90.0	+510

The relative solvent power of the various liquids for tetracyanoheptane can be compared with an "ideal" melting point depression or solubility curve which is included in Fig. 1. This curve was

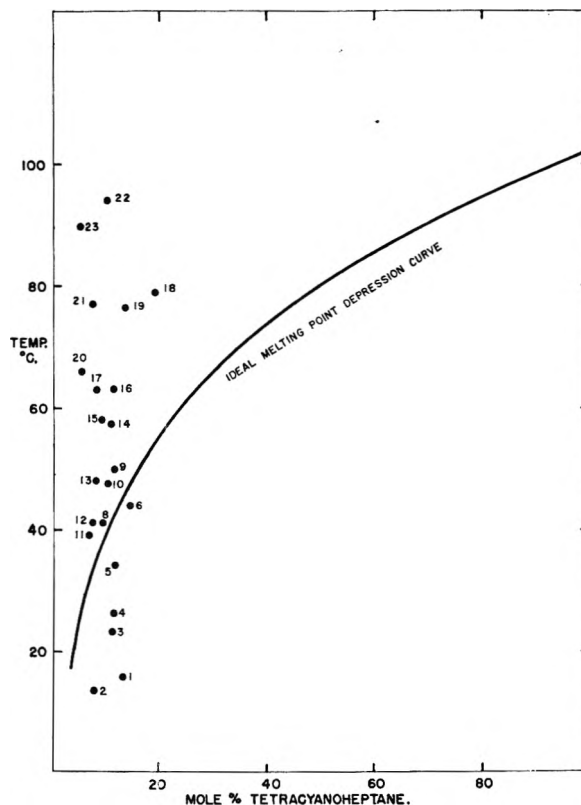


Fig. 1.—Solubility of 20 wt. % tetracyanoheptane in 23 liquids. The key to the numbered points is given in Table I. The curve labeled "ideal melting point depression curve" was calculated from solubility data for tetracyanoheptane in glutaronitrile.

obtained by assuming that glutaronitrile is an ideal solvent for tetracyanoheptane (no excess free energy of mixing)⁵ and that therefore the approximate melting point depression equation

$$4.575T \log_{10} 1/x_2 = \Delta H_f(1 - T/T_m) \quad (1)$$

where T is solution temperature, x_2 is mole fraction of solute, ΔH_f is molar heat of fusion and T_m is the melting point of the solute, is applicable for this solvent and solute.

The relative solvent power of liquids for tetracyanoheptane is closely related to the excess free energy of mixing (ΔF^e) of those liquids with the nitrile. Approximate ΔF^e values are given in Table I and were obtained from the solubility data with the aid of the following assumptions; that equation 1 with $\Delta \bar{F}_2^e$ (partial excess free energy of tetracyanoheptane in the mixture) added to the right-hand side is applicable, that $\Delta \bar{F}_2^e$ is independent of temperature, that $\Delta \bar{F}_2^e = \text{constant}^6 x_1^2$ where x_1 is the mole fraction of solvent, and that at $x_1 = 1/2$, $\Delta \bar{F}_2^e = \Delta F^e$. The only reason for making this conversion of solubilities into ΔF^e values is that the latter are in a more suitable form for comparison with some of the results in subsequent sections of the paper and do provide some orientation for those accustomed to thinking in terms of ΔF^e .

(5) Solution theory predicts a small departure from ideal solvent power because of a difference in the sizes of the molecules of glutaronitrile and tetracyanoheptane but this small effect will not be considered here.

(6) This assumption may be particularly crude for highly polar binary systems.

The major point of interest lies in a comparison of relative solvent power of liquids for tetracyanoheptane and for polyacrylonitrile. It is very difficult to make quantitative solubility measurements with this polymer because of the fact that its solutions have a strong tendency to supercool, which makes it hard to decide whether equilibrium has been established. However, an extensive semi-quantitative set of data on relative solvent power of liquids for polyacrylonitrile exists.¹ Those liquids which have been found to be better than "ideal" solvents for tetracyanoheptane (liquids italicized in Table I) are also those which can be classed as good solvents for the polymer; dissolve at least 5–10 wt. % polymer below 110–120°. The rest of the liquids which are worse than "ideal" solvents for tetracyanoheptane have no appreciable solvent power for the polymer up to at least 170–190°. Therefore tetracyanoheptane does reflect without exception the relative solvent power of liquids for the polymer. A similar comparison for a polyamide, for which some quantitative solubility data in a group of liquids were available,⁷ and for a model substance for it⁸ showed that the model compound reflected the solubility behavior of the polymer, again without exception in this more quantitative test.

The absolute solubility of a semi-crystalline polymer such as polyacrylonitrile must be determined largely by its melting point and heat of fusion and by an entropy of mixing term dependent on the large differences in molecular size between polymer and solvent.⁹ However, the differences in solvent power for polyacrylonitrile among different liquids seem to be primarily dependent on the properties of the nitrile group itself, on the nature of the interactions between nitrile groups and solvent molecules. In subsequent sections of this paper a more detailed examination of such interactions is presented.

Heats of Mixing of Glutaronitrile Binary Systems.—Heats of mixing (ΔH) glutaronitrile with about forty other liquids have been measured at 28.0°. In most cases, results at about 40 and 60 mole % glutaronitrile in solution were obtained and plausible heat of mixing curves for each binary system were drawn. In this way a useful estimate of the magnitude and position of the maximum of each heat of mixing curve was obtained. All of the experimental results are given in Table II along with the estimated quantities, maximum heat of mixing (ΔH_{\max}) and position of the maximum as mole fraction of glutaronitrile (x_{\max}). A negative ΔH corresponds to heat evolution on mixing. In Table II, the liquids are arranged in order of decreasing $-\Delta H_{\max}$ and increasing $+\Delta H_{\max}$.

The sign and magnitude of ΔH_{\max} reflects the balance of power between solute (glutaronitrile)–solvent and solvent–solvent interaction. The solute–solvent interaction is a constant factor for all the solutions, with the familiar assumption that the interaction between a specific pair of molecules is independent of the environment, and need not

be considered in a discussion of the differences among the solvents.

All of the liquids that contain N–H or O–H groups in the molecule show $+\Delta H_{\max} > 150$ cal./mole. Self association of solvent molecules through hydrogen bonds must strongly outweigh the solvent–solute interaction for these substances. The nitrile group has apparently little tendency to function as an acceptor for a hydrogen bond in spite of its high dipole moment.

Among the liquids that evolve heat on mixing with glutaronitrile are all those that are good solvents for tetracyanoheptane and polyacrylonitrile (the liquids italicized in Table II). However, there are also several poor solvents in this group. A relatively strong interaction between solute (nitrile) and solvent is a necessary but not sufficient condition for good solvent power for nitriles. In other words, for the poor solvents in this group, an unfavorable excess entropy of mixing must exist which will be discussed later. With the exception of chloroform, all the liquids in this group contain one or more exposed oxygen atoms in the molecule.

The remainder of the liquids can be placed in a third arbitrary group with $\Delta H_{\max} = 0$ to $+150$ cal./mole. The small positive ΔH_{\max} for adiponitrile and propionitrile reflect the expected almost ideal behavior of these liquids with glutaronitrile. The weakly polar liquids, toluene and ethylene bromide have ΔH_{\max} close to $+150$ cal./mole. Most of the other liquids in this group are closely related to liquids that evolve heat on mixing with glutaronitrile but are prevented from appearing in the latter group for one of the following reasons.

In the first place, as the hydrocarbon/polar group ratio in a solvent molecule increases, the heat of mixing shifts toward larger positive values. The data in Table II for acetone, methyl ethyl ketone, and diethyl ketone indicate that each additional methylene group adds about $+45$ cal./mole to the heat of mixing. Each methylene group adds a fixed amount to the strength of the solvent–solvent interaction as indicated by the regular increase in boiling points of the ketones but evidently adds relatively less to the solvent–solute interaction. Data for other homologous series in Table II illustrate the same trend.

The other factor that prevents a negative heat of mixing with glutaronitrile for some of the liquids with $\Delta H_{\max} = 0$ to $+150$ cal./mole, seems to be the poor accessibility of the polar group of the solvent molecule for interaction with the solute. The two closely related molecules, diethyl ketone and cyclopentanone, have ΔH_{\max} values of $+70$ and -13 cal./mole, respectively, and this difference can be attributed to the more exposed position of the carbonyl group in the latter molecule.

Volume Changes on Mixing for Glutaronitrile Binary Systems.—The densities of the pure liquid and of a 50 mole % solution with glutaronitrile were determined for about thirty binary systems at 28°. The densities were converted to molal volumes by substitution into the equation $V = (M_1x_1 + M_2x_2)/d$ where V is molal volume, M_1 and M_2 and x_1 and x_2 are the molecular weights and mole fractions of the components and " d " is the density.

(7) G. J. Van Amerongen, *J. Polymer. Sci.*, **6**, 471 (1951).

(8) Unpublished solubility data on hexamethylene dipropionamide, as a model for G6 polyamide, obtained by M. K. Phibbs.

(9) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

TABLE II
HEAT OF MIXING DATA FOR GLUTARONITRILE WITH OTHER

Liquid	LIQUIDS AT 28°			z_{max} glutaronitrile	Ethylene cyano- hydrin	45.1	+188	+195	.50
	Mole % glutaronitrile	ΔH , cal./mole	ΔH_{max}						
Chloroform	60.3	-212	-240	.43	Ethylenediamine	51.7	+209		
	40.7	-240			Propionic acid	60.0	+242	+270	.48
<i>N</i> -Acetylmorpholine	41.1	-97	-104	.60	Formamide	35.2	+242	+320	.61
	60.1	-104			Ethanolamine	38.3	+324	+346	.54
<i>Dimethylacetamide</i>	41.1	-83	-84	.45	Methanol	38.1	+373	+405	.51
	60.2	-74				63.9	374		
Dioxane	38.5	-62	-80	.67	Ethylene glycol	37.8	+411	+430	.55
	59.5	-79				60.1	+428		
Nitromethane	37.3	-41	-42	.47	<i>N</i> -Methylacetamide	39.0	+372	+455	.63
	55.0	-40				57.9	+446		
Nitroethane	37.5	-33	-36	.51		62.5	+453		
	58.6	-34			<i>N</i> -Ethylacetamide	39.8	+419	+465	.58
<i>Dimethylformamide</i>	26.2	-25	-35	.51		58.2	+464		
	56.0	-35			Ethanol ¹⁰	42.6	+500	+510	.50
Acetone	65.3	-33				59.1	+498		
	84.3	-17			Propanol	16.5	+310	~+630 (extrap.)	
Acetonylacetone	40.9	-25	-26	.50		30.3	+400	} partial miscibility	
	62.4	-22				42.3	+480		
<i>Tetramethylene sulfone</i>	40.0	-23	-25	.50		62.1	+552		
	60.7	-22			Carbon tetrachloride				
γ -Butyrolactone	49.1	-25	-25	.51	Triethylamine			} Partially miscible with glutaronitrile	
	37.8	-21	-24		Diethyl ether				
<i>Propylene carbonate</i>	58.1	-24			Octane				
	37.4	-18	-23						
Methyl acetate	56.2	-23		.52	The deviation of the experimental molal volume in ml./mole from the ideal molal volume at 50 mole % glutaronitrile has been taken as a useful measure of the maximum non-ideal volume change on mixing (ΔV_{max}), on the assumption that the deviation curve is symmetrical about 50 mole % glutaronitrile. The results for ΔV_{max} are given in Table III. A positive ΔV_{max} indicates a non-ideal volume expansion on mixing with glutaronitrile.				
	59.3	-18	-20						
Cyclopentanone	40.0	-19		.47	The significance of these results is brought out clearly in Fig. 2 which is a plot of ΔH_{max} versus ΔV_{max} . Each point on the plot represents a different glutaronitrile binary system. The outstanding feature of the plot is that all of the "good" polyacrylonitrile solvents for which data were obtained appear in the lower right quadrant characterized by heat evolution and volume expansion on mixing with glutaronitrile. The rest of the liquids are spread over the other three quadrants.				
	40.4	-12	-13						
Adiponitrile	59.2	-10			Some correlation between non-ideal volume changes on mixing and excess entropies of mixing (ΔS^e) for glutaronitrile binary systems is evident. The inset to Fig. 2, which is a schematic plot of ΔH_{max} versus $T\Delta S^e_{\text{max}}$, can be compared with the $\Delta H_{\text{max}} - \Delta V_{\text{max}}$ plot of Fig. 2. The diagonal line of the schematic plot, $\Delta F^e = 0$ (locus of ideal and pseudo-ideal ¹¹ solvents for glutaronitrile), separates the plot into regions of better ($\Delta F^e_{\text{negative}}$) and worse ($\Delta F^e_{\text{positive}}$) than ideal solvent power. If a linear relation existed between $T\Delta S^e$ and ΔV , a line such as the dashed diagonal line drawn on Fig. 2				
	38.9	+4							
Propionitrile	36.5	+19	+19	.38	(10) The term pseudo-ideal was first used to refer to binary systems for which Raoult's law was obeyed yet which did not exhibit zero heats of mixing, by Kendall (see S. Glasstone, "Text-Book of Phys. Chem.," D. Van Nostrand Co., New York, N. Y., p. 668). The term ideal will be used in referring to both ideal and pseudo-ideal systems in this paper unless otherwise specified.				
	58.7	+14							
Ethyl acetate	39.9	+20	+20	.40					
	61.4	+14							
1-Nitropropane	39.8	+19	+23	.48					
	40.9	+21	+25						
Methyl ethyl ketone	59.8	+21							
	42.1	+30							
2-Nitropropane	41.5	+52	+58	.53					
	61.1	+55							
Cyclohexanone	41.2	+65	+65	.43					
	58.1	+56							
Pyridine	39.6	+63	+69	.52					
	60.2	+66							
Diethyl ketone	41.1	+72							
	40.7	+77	+78						
<i>n</i> -Butyraldehyde	56.7	+67		.43					
	44.6	+109	+124						
Ethylene bromide	58.6	+124		.60					
	60.6	+122							
Toluene	21.2	+140	+167	.42					
	37.2	+165							
Acetic acid	58.0	+155							
	71.1	+133							
	72.5	+128							
	82.1	+77							

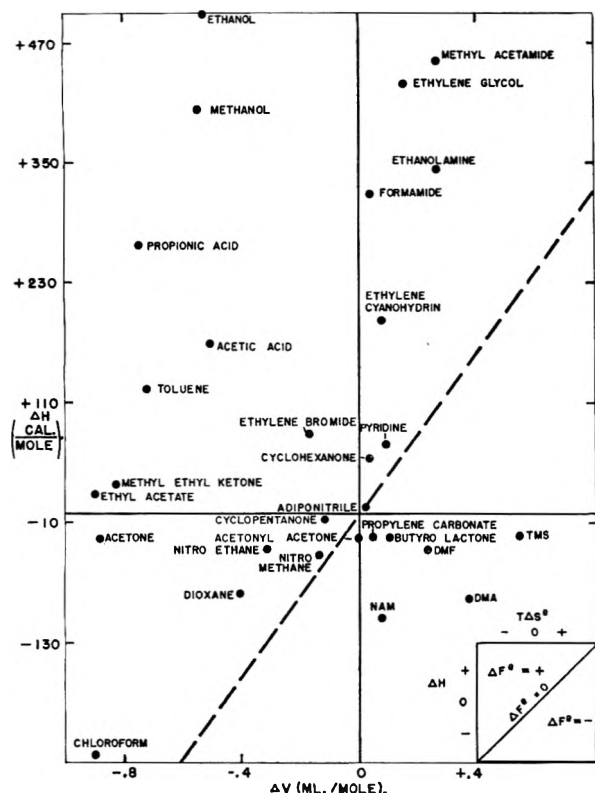


Fig. 2.— $\Delta H_{\max} - \Delta V_{\max}$ map for glutaronitrile binary liquid systems. The ordinate and abscissa of this plot represent the maximum heat of mixing and the maximum non-ideal volume change on mixing for each liquid with glutaronitrile: DMF, dimethylformamide; DMA, dimethylacetamide; TMS, tetramethylene sulfone; NAM, N-acetylmorpholine. The significance of the inset plot in the lower right corner and of the dashed diagonal line is described in the text.

would divide the $\Delta H_{\max} - \Delta V_{\max}$ plot into better and worse than ideal solvent regions. With the exception of acetonylacetone, the dashed line does actually separate the plot into such regions according to the solubility data for tetracyanoheptane and polyacrylonitrile. A rough estimate of $T\Delta S^e$ values for glutaronitrile binary systems can be obtained by substituting the ΔF^e values for tetracyanoheptane into the second law of thermodynamics ($\Delta F^e = \Delta H - T\Delta S^e$). Admittedly this is a crude procedure but a comparison of such $T\Delta S^e$ values with the ΔV data indicates that no general linear relation between $T\Delta S^e$ and ΔV exists. However, a qualitative correlation between the two quantities is evident for most of the binary systems. It is interesting to note that in a recent theoretical treatment of binary liquid systems composed of spherical molecules with radially symmetric force fields, a linear relation between ΔV and $T\Delta S^e$ was derived.¹¹

The ΔV data can be used to effect a crude conversion of heats of mixing at constant pressure (ΔH_p) to heats of mixing at constant volume (ΔH_v). Such a conversion is only useful if ΔH_v bears a closer relation to ΔF^e than does ΔH_p or for comparison with a theory that predicts only a value

TABLE III
NON-IDEAL VOLUME CHANGES ON MIXING GLUTARONITRILE WITH OTHER LIQUIDS AT 28°

Liquid	ΔV_{\max} (ml./mole of soln.) + and - signify expansion and contraction, resp.	$(\Delta H_v)_{\max}$, (calcd.)
Tetramethylene sulfone	+0.54	-116
Dimethylacetamide	+ .37	-135
N-Methylacetamide	+ .27	+410
Ethanolamine	+ .26	+300
Dimethylformamide	+ .23	- 70
Ethylene glycol	+ .15	+401
γ -Butyrolactone	+ .09	- 40
Pyridine	+ .09	+ 52
N-Acetylmorpholine	+ .07	-115
Ethylene cyanohydrin	+ .07	+182
Cyclohexanone	+ .03	+ 54
Adiponitrile	+ .02	+ 2
Propylene carbonate	+ .02	- 26
Formamide	+ .02	+315
Acetonylacetone	.00	- 25
Cyclopentanone	- .12	+ 3
Nitromethane	- .14	- 19
Ethylene bromide	- .17	+101
Nitroethane	- .32	+ 9
Dioxane	- .41	- 26
Acetic acid	- .51	+253
Ethanol	- .53	+587
Methanol	- .55	+461
Toluene	- .72	+210
Propionic acid	- .75	+370
Methyl ethyl ketone	- .83	+131
Acetone	- .89	+ 75
Ethyl acetate	- .90	+123
Chloroform	- .92	-127

for ΔH_v such as the regular solution theory.¹² The conversion can be made with the following assumptions: that¹³ $\Delta H_v = \Delta H_p - T(\alpha/\beta)\Delta V$ where α and β are the isobaric coefficients of thermal expansion and isothermal compressibility of the solution, respectively, that the empirical relation,¹² $T(\alpha/\beta) = (-2950 + 23.7T_b + 0.020T_b^2 - RT)/V$ where T_b is the boiling point in Å. and V the molal volume, is applicable and finally that arithmetic mean values of $T(\alpha/\beta)$ calculated from results for the two components are valid for a given concentration. The second assumption is particularly crude but no better procedure is available. Results for ΔH_v calculated in this way are given in Table II. The general conclusion is that the ΔH_v values are more in line with relative solvent power or ΔF^e than are ΔH_p values, which is an obvious consequence of the signs of ΔV . However, the majority of the poor solvents with $-\Delta H_p$ still have $-\Delta H_v$.

Vapor Pressures and Excess Free Energies of Mixing of Glutaronitrile Binary Systems.—No sufficiently rapid and accurate method of measuring vapor pressures of solutions has been found which permitted getting data for more than a few glutaronitrile binary systems within a reasonably short time. Total vapor pressure data were determined for glutaronitrile binary systems with ethanol and dioxane by both the static and infra-

(12) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes," 3rd Edition, Reinhold Publ. Corp., New York, N. Y.

(13) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1947).

(11) I. Prigogine and V. Mathot, *J. Chem. Phys.*, **20**, 49 (1952).

red methods, with nitromethane by the static method and with dimethylformamide by the infrared technique at 20°. All of the results are included in Table IV.

TABLE IV

TOTAL VAPOR PRESSURES OF GLUTARONITRILE BINARY SYSTEMS AT 20.0°

Liquid	Mole % glutaronitrile	Vapor pressure Static method	Vapor pressure Infrared ^a method	$\Delta F_{\text{max}}^{\text{e}}$ (calcd.), cal./mole
Dioxane	0.0	27.4		+110
	18.8		24.1	
	32.0	20.0		
	39.4		19.6	
	48.2	16.2		
	57.3		14.4	
	64.5	12.4		
	65.2	11.9		
	67.8	11.3		
	78.2		7.2	
Ethanol	0.0	44.6		+450
	10.9		43.5	
	12.5	42.3		
	23.0	42.1		
	24.3		41.3	
	38.0	41.8		
	42.3		40.2	
	63.5	37.3		
65.7	36.3			
Nitromethane	0.0	26.3		+ 35
	25.1	20.4		
	41.4	16.3		
	55.6	12.4		
Dimethylformamide	0.0	2.31		- 40
	17.0		1.91	
	38.5		1.39	
	54.4		1.03	
	75.9		.56	

^a Vapor pressure data determined from $\left(\frac{\text{optical density of vapor over soln.}}{\text{optical density of vapor over solvent}} \right) \times \text{vapor pressure of solvent}$.

Excess free energies of mixing were obtained from pressure data as follows. The vapor pressure of glutaronitrile at 20° is negligible (about 0.001 mm.) and therefore the total vapor pressure of a solution could be set equal to the partial vapor pressure of the other component. The partial vapor pressure of glutaronitrile was then obtained using a graphical integration method based on the Gibbs-Duhem relation.¹² Values for $\Delta F_{\text{max}}^{\text{e}}$ were calculated from the partial vapor pressures and are given in Table IV. These values of $\Delta F_{\text{max}}^{\text{e}}$ for glutaronitrile binary systems can be compared with the crude estimated results for $\Delta F_{\text{max}}^{\text{e}}$ given in Table I for the corresponding tetracyanoheptane binary systems. The approximate agreement for the three binary systems involving each of the nitriles is all that could be expected and does indicate that the more extensive but less reliable $\Delta F_{\text{max}}^{\text{e}}$ values of Table I provide a useful reflection of the correct $\Delta F_{\text{max}}^{\text{e}}$ results for the corresponding glutaronitrile binary system.

Viscosity of Glutaronitrile Binary Systems.—The viscosities of several binary solutions involving glutaronitrile were measured to find out whether there was any correlation between this dynamic

property and any of the other properties studied above. For this purpose, some measure of the departure from ideal behavior for viscosity curves of binary systems is necessary. There is no real theoretical guidance on this question. An examination of viscosity curves of binary systems which are known to be almost ideal indicates that plots of $\log \eta$, where η represents viscosity *versus* mole fraction, are usually almost straight lines. This was confirmed in the present work from the results for the glutaronitrile-propionitrile system which was found to be an almost ideal system in previous sections. The deviation of the $\log \eta$ -mole fraction plot from a straight line was quite small for this system as indicated in Table V where all the viscosity data are presented. This is an especially sensitive test case because the viscosities of propionitrile and glutaronitrile are so different. Deviations of the experimental $\log \eta$ plots from a straight line relation ($\Delta \log \eta$) were therefore assumed to provide a significant measure of departure from ideal behavior and values for such deviations at 50 mole % glutaronitrile for each system are given in Table V.

A detailed comparison of the $\Delta \log \eta$ data with the results for heat of mixing, non-ideal volume changes on mixing and excess free energies of mixing does not reveal even a qualitative correlation between viscosity and any of the other properties. It has often been assumed that the viscosity of a liquid is closely related to molal free volume (volume not occupied by molecules/mole)¹⁴ and it seems reasonable that non-ideal volume changes on mixing should reflect changes in the free volume on mixing. A non-ideal increase in volume on mixing should, on this basis, effect a non-ideal decrease in viscosity on mixing. There are several examples in Table V (*i.e.*, ethanol, chloroform) which when compared with the ΔV_{max} data exhibit the opposite behavior to that expected from the above discussion. The same kind of contradiction is found when an attempt is made to find correlation between viscosity and either heat of mixing or excess free energy of mixing data.

The one feature reflected in these viscosity results is that those liquids which are known to be extensively self-associated in the pure liquid phase show large "non-ideal" viscosity decreases on mixing with glutaronitrile. Ethanolamine, N-methylacetamide, ethanol, *m*-cresol and ethylene cyanohydrin are in this category because of their strong hydrogen bonding power. Acetic acid is associated only to the dimer form. The viscosity data have not added a great deal to an understanding of glutaronitrile binary systems.

General Discussion of the Correlation between Solvent Power and Molecular Properties.—It is notable that those liquids which are "good" solvents for polyacrylonitrile and are better than "ideal" solvents for tetracyanoheptane are composed of molecules with unusually high dipole moments. In the following Table VI the dipole moments (solution in benzene measurements) for all those liquids which evolved heat on mixing with glutaronitrile are listed.¹⁵ There is a clear distinc-

(14) I. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

(15) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948.

TABLE V

VISCOSITY OF GLUTARONITRILE BINARY SYSTEMS AT 28°

Liquid	Mole % glutaronitrile	Viscosity (η) (cps.)	$\Delta \log \eta_{\text{non-ideal}} \times 10^{32}$
Ethanolamine	0.0	16.85	+186
	35.6	7.70	
	64.6	5.73	
	100.0	5.67	
N-Methylacetamide	0.0	4.25	+124
	35.7	3.85	
	64.7	3.63	
Ethanol	0.0	1.04	+ 78
	32.9	1.57	
	63.1	2.54	
	67.0	6.06	
<i>m</i> -Cresol	0.0	11.36	+ 65
	36.2	7.80	
	67.0	6.06	
	67.0	6.06	
Ethylene cyanohydrin	0.0	3.22	+ 60
	35.2	3.50	
	64.7	4.05	
	64.7	4.05	
Toluene	0.0	0.53	+ 52
	33.4	1.07	
	64.1	2.19	
	64.1	2.19	
Dioxane	0.0	1.16	+ 26
	35.0	1.88	
	64.9	3.13	
	64.9	3.13	
Dimethylformamide	0.0	.78	+ 23
	35.1	1.49	
	65.2	2.72	
	65.2	2.72	
γ -Butyrolactone	0.0	1.63	+ 7
	33.1	2.42	
	65.5	3.66	
	65.5	3.66	
Propionitrile	0.0	.40	- 10
	35.3	1.05	
	64.6	2.44	
	64.6	2.44	
Chloroform	0.0	0.52	- 82
	35.0	1.42	
	72.5	3.39	
	72.5	3.39	
Acetic acid	0.0	1.11	-136
	35.1	2.68	
	64.3	4.05	
	64.3	4.05	

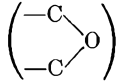
^a $\Delta \log \eta = [\log \eta (\text{st. line}) - \log \eta (\text{experimental})]$ at mole % glutaronitrile = 50, + signifies non-ideal decrease in viscosity on mixing.

tion between those liquids with dipole moments above 3.5 *D* which are good solvents for nitriles and those liquids with dipole moments below 3.5 *D* which are poor nitrile solvents. The distinction is confirmed by other examples from the extensive semi-quantitative data¹ available on solvent power of liquids for polyacrylonitrile. The closely related substances succinic anhydride and acetic anhydride with dipole moments of 4.2 and 2.5 *D* are good and poor solvents for polyacrylonitrile, respectively. Likewise, cyclic ethylene carbonate and dimethyl carbonate have dipole moments of 4.1 and 1.0 *D* and are good and poor solvents for polyacrylonitrile, respectively.

The high dipole moments of the cyclic molecules in these examples are understandable because the rest of the molecule is held to a fixed position with respect to the carbonyl groups and the partial moments of the C—O bonds support those of the C=O bonds. However, in acetic anhydride and dimethyl carbonate the methyl groups are free to rotate and therefore the partial bond moments of

TABLE VI

DIPOLE MOMENTS OF LIQUIDS THAT EVOLVED HEAT ON MIXING WITH GLUTARONITRILE

Good nitrile solvents	Dipole moment (debyes)	Poor nitrile solvents	Dipole moments (debyes)
Tetramethylene ^a sulfone	4.4	Chloroform Dioxane	1.3 0.4
Dimethylacetamide	3.8		1.9
Dimethylformamide	3.8	Nitromethane	3.1
N-Acetylmorpholine ^a	3.8	Nitroethane Acetone	3.2 2.8
γ -Butyrolactone	4.1	Methyl acetate	1.8
Propylene carbonate ^a	4.1	Cyclopentanone	3.0

^a Dipole moments for these substances were not available but the values given are those for closely related compounds for which data were available.¹⁵

the C—O groups are just as often in a direction to oppose the moment of the C=O group and no increase in dipole moment over that of the C=O group results.

Evidently a high dipole moment is one requirement for a good nitrile solvent. When all of the liquids, rather than just those that evolve heat on mixing with glutaronitrile, are considered other limitations in addition to a high dipole moment are required to characterize good nitrile solvents.

Heat of mixing results for glutaronitrile binary systems suggest, and solubility data for polyacrylonitrile¹ confirm, the fact that a good nitrile solvent must be a substance composed of molecules with a relatively low number of carbon atoms/polar group ratio. Perhaps the ratio of the surface areas of the hydrocarbon and polar group parts of a molecule would be more pertinent but would also be more difficult to specify correctly.¹⁶ An increase in relative hydrocarbon content in a solvent molecule promotes stronger solvent-solvent interaction at the expense of solvent-solute interaction which is reflected in poorer solvent power for polyacrylonitrile and the model compounds for it. The above argument implies that changes in excess entropy of mixing with a nitrile on going from one homolog to another do not completely counterbalance the above-mentioned changes in heats of mixing.

Cyclization of a molecule effects some improvement in solvent power. For example, cyclopentanone is a considerably better solvent for tetracyanoheptane than methyl ethyl ketone, in spite of the less favorable hydrocarbon/polar group ratio for the cyclic molecule. It can be seen from the heat of mixing results that cyclopentanone exhibits stronger interaction with glutaronitrile than either methyl ethyl ketone or diethyl ketone. It was suggested earlier that the more exposed position of the carbonyl group in the cyclic molecule might be responsible for the stronger interaction with a nitrile although it is conceivable that some change in the electronic structure of the carbonyl group on cyclization is also partially responsible for the effect. A comparison of the calculated ΔF^e values from Table I with the ΔH_{max} data for the cyclopentanone-nitrile and methyl ethyl ketone-nitrile bi-

nary systems suggests that a favorable change in $T\Delta S^\circ$ was also effected on cyclization; favorable in the sense that $T\Delta S^\circ$ has a less negative value for cyclopentanone than for methyl ethyl ketone. A reason for this entropy of mixing difference is not apparent and the effect seems to merit further study.

Another major restriction on good nitrile solvents is that no appreciable hydrogen bonding between solvent molecules is permissible. A comparison of the isomers, dimethylformamide and N-methylacetamide, both of which have a dipole moment of 3.8 D and the same low hydrocarbon/polar group ratio, illustrates the importance of this effect. Dimethylformamide has no appreciable self-hydrogen bonding power (no strong hydrogen bonds between two molecules of dimethylformamide), evolves heat on mixing with glutaronitrile and is a good nitrile solvent. N-Methylacetamide has strong self-hydrogen bonding power, absorbs a large amount of heat on mixing with glutaronitrile and is a poor solvent for nitriles. The term self-hydrogen bonding power implies that one solvent molecule has both acceptor and donor points for a hydrogen bond, that are accessible for interactions.

No study of the solvent power of strong acids for nitriles has been made in the present work. However, it is known that concentrated sulfuric acid is a good polyacrylonitrile solvent¹ and is probably a good nitrile solvent in general. The restrictions on good nitrile solvents noted above, high dipole moment, low hydrocarbon/polar group ratio and little self-hydrogen bonding power, obviously would have to be relaxed for very strong acids.

No explanation of the high dipole moment requirement for good nitrile solvents has been found. No argument based only on differences in energies of interaction (*i.e.*, ΔH_v) can be applicable because several poor solvents with dipole moments below 3.5 D evolve as much heat on mixing with glutaronitrile as do the good solvents. Probably some element of matching of dipole moments of solvent

and solute is involved because glutaronitrile has a dipole moment of 3.9 D . Van Arkel¹⁷ developed an expression for heats of mixing of binary systems including the effect of dipole-dipole interaction which does predict that ΔH_v is zero when the dipole moments of solvent and solute are equal and the dispersion forces of the two components are also equal. It is possible to proceed a little further by including the effect of dipole-induced dipole interaction explicitly into the Van Arkel expression. One can then see the possibility of $-\Delta H_v$ when the dispersion forces of solvent and solute are almost equal and when there is a slight mismatch in dipole moments of solvent and solute combined with the restriction that $\alpha_1 > \alpha_2$ when $\mu_2 > \mu_1$ or $\alpha_2 > \alpha_1$ when $\mu_1 > \mu_2$ where α_1 and α_2 and μ_1 and μ_2 represent the polarizabilities and dipole moments of the polar groups of the solvent and solute, respectively.

Any mention of dipole-induced dipole interaction and polarizability of a polar group brings up the whole question of acid-base interaction in the Lewis sense. For example, it is conceivable that, if the amide group of dimethylformamide is slightly basic with respect to a nitrile group of glutaronitrile, some part of the high solvent power of dimethylformamide for nitriles might be attributed to weak acid-base interaction. However, it does not seem worthwhile to try to elaborate such concepts based only on energies of interaction¹⁸ because, as noted above, an important part of the problem involves finding an explanation for the non-ideal volume expansions on mixing and for the positive excess entropies of mixing for the good solvent-nitrile binary systems.

Acknowledgment.—The author would like to acknowledge the many helpful discussions with Dr. C. E. Black throughout the course of this work.

(17) A. E. Van Arkel, *Trans. Faraday Soc.*, **42B**, 81 (1946). See also ref. 12, p. 167.

(18) An acid-base interaction implies a free energy of interaction but the entropy contribution is sometimes ignored in explanations of such interactions.

A THERMODYNAMIC STUDY OF LIQUID METALLIC SOLUTIONS. VI. CALORIMETRIC INVESTIGATIONS OF THE SYSTEMS BISMUTH-LEAD, CADMIUM-LEAD, CADMIUM-TIN AND TIN-ZINC

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A high temperature calorimeter recently developed by the author has been used for determination of the heats of mixing in the three liquid systems bismuth-lead, cadmium-lead, cadmium-tin at 350 and 450° and in tin-zinc at 430 and 525°. The results have been compared with data obtained in earlier calorimetric work and with integral and differential heat data calculated from e.m.f. equilibrium studies. In some cases the calorimetric heat data for moderately dilute solutions have been combined with equilibrium information derived from the binary phase diagram, and used for calculation of entropy deviations. These deviations agree well with data obtained from e.m.f. studies alone. In the temperature range covered the heat of mixing was found to be essentially independent of temperature for bismuth-lead and for cadmium-lead, while negative deviations from the Kopp-Neumann rule were found in cadmium-tin and tin-zinc. It is suggested that these deviations may be explained by the volume expansion believed to accompany the process of mixing.

Introduction

The available quantitative information on the heats of mixing and heats of formation of alloys has been derived from calorimetric and from equilibrium investigations. By the calorimetric method we measure integral heat data directly, while equilibrium investigations similarly yield differential quantities. A comparison of the two sets of data is possible only after differentiation of the calorimetrically determined data with respect to composition, or after integration of the differential quantities.

Up to the present time the calorimetric data have generally been much too inaccurate to permit a reasonably reliable evaluation of differential quantities. The calculation of integral data from equilibrium information, on the other hand, also has been associated with considerable uncertainties, particularly in the extrapolations of data for more concentrated solutions into the unexplored dilute range. It is therefore not surprising that the agreement between the two sets of integral heat data often has been far from satisfactory, although in most cases the results have agreed to within 20-30%.

In an earlier communication¹ the author has reported the development of a new high temperature calorimeter, which permits accurate determinations of heats of mixing and heats of solution in alloy systems. The objective of the present series of investigations is to use this apparatus for a systematic exploration of the thermochemical properties of solid and liquid alloys, and in particular of the alloys formed by group B metals. In the present communication special attention has been given to a comparison with data obtained in earlier equilibrium studies and to the dependence of the heat of mixing on temperature.

For this purpose the following liquid systems were selected: bismuth-lead, cadmium-lead, cadmium-tin, and tin-zinc. These systems have all been well explored by the e.m.f. method, and it was believed that the comparison therefore would be of special interest. Among the mentioned systems bismuth-lead was known to have a relatively small negative ΔH of mixing, while all the others have a positive ΔH with maxima ranging from about 2000 to 3000 j./g. atom.

Experimental

As the details of operation of the high temperature reaction calorimeter have been reported elsewhere, it is here sufficient to state that the apparatus is designed to operate at temperatures up to about 500°, and that it is particularly suitable for measurement of heat effects of the order of 500 joules. Under favorable conditions an accuracy of about $\pm 1\%$ can normally be achieved. Unfortunately the present work on tin-zinc was performed during the summer months when the rather considerable temperature fluctuations in the laboratory had an unfavorable influence on the experimental precision. This accounts for the somewhat larger spread of the experimental results for this system.

In this investigation stock metals of 99.9+ % purity were used. The experiments on tin-zinc were performed at $430 \pm 2^\circ$ and at $525 \pm 3^\circ$, while the other systems were studied at $350 \pm 2^\circ$ and $450 \pm 2^\circ$. The over-all temperature was measured by a chromel-alumel thermocouple, calibrated at the melting point of zinc. The fluctuations in experimental temperature of ± 2 (3) degrees over extended periods of time had no detectable effect on the determined heats of mixing. No particular difficulties resulted from the high volatility and reactivity of cadmium and zinc.

The actual mixing experiments were carried out as reported for the introductory investigation of the system lead-tin.¹ As in this case, a second sample of pure metal frequently was added to the alloy formed in the first experiment. The molar heat of mixing for the final alloy was then calculated by adding the two measured heat terms. As the results derived from these double experiments are liable to be more uncertain than the results of single experiments, they are identified in the figures by a short vertical bar through the experimental point.

Results

The experimentally determined molar heats of mixing, ΔH^M , are tabulated in Tables I-IV and are plotted *versus* composition in Figs. 1-4. The tables and figures also give values for the calculated quantity, $\Delta H^M/x_1x_2$, where x_1 and x_2 are the mole (atomic) fractions of the two components. The figures further contain integral heat data from Kawakami's calorimetric study² as well as data given in the most recent e.m.f. study.

Bismuth-Lead.—For this system the results of 27 calorimetric experiments are reported, 15 at 350° and 12 at 450°. In this temperature range the heat of mixing is independent of temperature within experimental error. The results differ radically from the calorimetric data given by Kawakami,² but agree reasonably well with the e.m.f. study by Strickler and Seltz.³ Additional data for this and other systems are given by Weibke and Kubas-

(1) O. J. Kleppa, *THIS JOURNAL*, **57**, 175 (1954).

(2) M. Kawakami, *Sci. Rep. Tôhoku. Imp. Univ.*, **119**, 915 (1927).

(3) H. S. Strickler and H. Seltz, *J. Am. Chem. Soc.*, **58**, 2084 (1936).

chewski.⁴ These are on the whole in less satisfactory agreement with the present results.

Cadmium-Lead.—A total of 29 experiments are reported for this system, 21 at 350° and 8 at 450°.

TABLE I

MOLAR INTEGRAL HEATS OF MIXING IN Bi(l)-Pb(l)			
Total g. atoms	Composition x_{Bi}	ΔHM , joule/g. atom	$\Delta HM/x_{Bi}x_{Pb}$, joule
(a) At 350 ± 2°			
1.3705	0.0442	-154	-3640
1.4276	.0824	-279	-3690
0.8060	.09195	-312	-3740
.8925	.1800	-589	-3990
.6594	.1847	-597	-3960
.4823	.2638	-804	-4140
.7741	.3055	-905	-4270
.6077	.4157	-1063	-4380
.3112	.4575	-1087	-4380
.5484	.5191	-1100	-4410
.4175	.6819	-922	-4250
.7286	.6917	-897	-4210
.5897	.8546	-494	-3980
1.4028	.8844	-390	-3810
1.3199	.9400	-214	-3790

(b) At 450 ± 2°

1.4812	0.0540	-188	-3680
1.1401	.0928	-320	-3800
1.5597	.1016	-351	-3850
1.2567	.1770	-579	-3970
0.6075	.1930	-612	-3930
0.7283	.3269	-930	-4230
0.6334	.5796	-1073	-4400
0.5086	.7331	-818	-4180
1.1204	.7571	-763	-4150
1.4508	.8654	-465	-3990
0.9762	.8689	-454	-3990
1.3508	.9243	-253	-3620

TABLE II

MOLAR INTEGRAL HEATS OF MIXING IN Cd(l)-Pb(l)			
Total g. atoms	Composition x_{Cd}	ΔHM , joule/g. atom	$\Delta HM/x_{Cd}x_{Pb}$, joule
(a) At 350 ± 2°			
1.1617	0.0493	435	9300
1.1749	.0576	514	9480
1.1781	.0740	647	9440
1.2305	.1024	882	9600
0.9296	.1362	1123	9540
1.2694	.1406	1177	9740
0.7098	.1479	1208	9590
0.7142	.1929	1566	10060
1.0806	.2571	1888	9880
0.8188	.2613	1924	9970
.8257	.3240	2305	10530
.4984	.3391	2286	10200
.6670	.5061	2648	10590
.6962	.7329	2326	11880
.8416	.8185	1885	12690
.6040	.8448	1712	13060
.9314	.8658	1538	13240
.9862	.8844	1398	13680
.7579	.9089	1137	13730
.8667	.9303	942	14530
.9222	.9458	754	14710

(b) At 450 ± 2°

1.0836	0.0924	793	9460
0.6823	.1239	1030	9490
1.1878	.1720	1377	9670
0.7717	.2254	1723	9870
0.6161	.6579	2565	11400
0.5114	.7926	2059	12520
1.1980	.8956	1291	13810
1.1330	.9470	739	14720

TABLE III

MOLAR INTEGRAL HEATS OF MIXING IN Cd(l)-Sn(l)			
Total g. atoms	Composition x_{Cd}	ΔHM , joule/g. atom	$\Delta HM/x_{Cd}x_{Sn}$, joule
(a) At 350 ± 2°			
1.1105	0.0540	369	7220
1.3572	.0573	387	7160
1.0163	.0584	394	7170
0.7969	.1115	711	7180
1.1866	.1147	727	7160
0.8176	.1195	772	7340
1.1069	.1354	871	7440
1.0638	.1398	874	7270
0.8442	.2119	1200	7190
0.9184	.2162	1265	7470
1.2224	.2514	1374	7300
0.7361	.2914	1534	7430
1.0229	.3496	1687	7420
0.9485	.4500	1929	7790
0.4151	.5996	2028	8450
0.8106	.7541	1722	9290
0.9073	.7996	1476	9210
0.6536	.8134	1464	9650
1.1154	.8793	1087	10240
0.6941	.8807	1086	10340
0.8183	.8866	988	9830
0.9142	.9167	823	10780
1.0390	.9440	590	11160

(b) At 450 ± 2°

0.9016	0.0300	193	6630
0.8739	.0401	256	6650
0.9090	.0503	322	6740
1.4895	.0547	353	6830
0.9114	.0796	497	6780
.9557	.0868	539	6800
.8503	.0918	558	6690
.9356	.1745	987	6850
.5787	.2065	1137	6940
.6983	.3424	1609	7150
.5706	.5619	1879	7630
.4442	.7218	1674	8340
.6528	.7264	1679	8450
1.1136	.8413	1221	9150
0.5607	.8457	1202	9210
1.0226	.9161	745	9690

We again find that the heat of mixing appears to be independent or very nearly independent of temperature. The agreement with the recent e.m.f. study by Elliott and Chipman⁵ is excellent, while Kawakami's data seem to be too low.

Cadmium-Tin.—The results of 39 experiments are reported, 23 at 350° and 16 at 450°. We here note for the first time a dependence of ΔH on temperature, corresponding to negative deviations from

(4) F. Weibke and O. Kubaschewski, "Thermochemie der Legierungen," Berlin, 1943.

(5) J. F. Elliott and J. Chipman, *Trans. Faraday Soc.*, **47**, 138 (1951).

TABLE IV

MOLAR INTEGRAL HEATS OF MIXING IN Sn(1)-Zn(1)			
Total g. atoms	Composition x_{Zn}	ΔH^M , joule/g. atom	$\Delta H^M/x_{Sn}x_{Zn}$, joule
(a) At $430 \pm 2^\circ$			
1.2264	0.0551	506	9720
1.2177	.0991	920	10300
1.0176	.1203	1093	10330
0.8884	.1365	1195	10140
.5351	.1730	1531	10700
4846	.1749	1515	10500
.4114	.2134	1775	10570
.4352	.2385	1986	10940
.5451	.2393	2073	11390
.4045	.2393	1968	10810
.3187	.2673	2232	11400
.4519	.3674	2838	12210
.5118	.3677	2781	11960
.3549	.4636	3130	12590
.3501	.5058	3322	13290
.3533	.5482	3390	13690
.3803	.5632	3412	13870
.3455	.6387	3346	14500
.3375	.6848	3145	14570
.4717	.7546	2909	15710
.3776	.7675	2898	16240
.5636	.8498	2328	18240
0.7104	.8780	2036	19010
1.0916	.9235	1337	18930
1.1276	.9430	1147	21340
1.1714	.9472	1055	21100
(b) At $525 \pm 3^\circ$			
0.6752	0.1237	977	9010
.4739	.2235	1716	9890
.5622	.3456	2411	10660
.4206	.3703	2494	10700
.3116	.4895	2837	11350
.3104	.6795	2897	13300
.4361	.7703	2737	15470
.5315	.8029	2494	15760
.9616	.9214	1411	19480
1.5243	.9481	953	19370

the Kopp-Neumann rule for the heat capacity of the mixture.

The agreement with Elliott and Chipman's e.m.f. data is less perfect than for the system cadmium-lead, while we find once more that our results are higher than those given by Kawakami for the same composition.

Tin-Zinc.—For this system a total of 36 experiments are reported, among which 26 were performed at 430 and 10 at 525° . In spite of the less satisfactory precision the dependence of ΔH on temperature is again well illustrated.

The agreement of the present data with those reported by Kawakami is here somewhat better than for the other three systems. We also note that our results for 430° (but not those for 525°) agree well with Taylor's e.m.f. data for about 500° .⁶

Discussion

The author has previously suggested the use of the quantity $\Delta H^M/x_1x_2$ as an aid in the plotting of integral heat data for binary systems.¹ This quantity is a particularly convenient measuring

stick for the energetic asymmetry in the system, and we note that the value of $\Delta H^M/x_1x_2$ for $x = 0$ is equal to the relative partial molal heat content of the minor component in its infinitely dilute solution in the major component. We recall also that the very simplest types of solution theories, such as Hildebrand's "regular" solution theory for components of equal volumes and the zeroth approximation of the "quasi-chemical" theory, predict a completely symmetrical, parabolic heat of mixing curve. In these cases the quantity of $\Delta H^M/x_1x_2$ will be constant, independent of composition (and temperature).

It is apparent that in the four systems covered in the present investigation $\Delta H^M/x_1x_2$ is far from independent of composition. In fact the systems cadmium-tin, cadmium-lead and tin-zinc exhibit a large degree of energetic asymmetry, increasing in the order mentioned. It may be pointed out that this is also the order of increasing relative difference in atomic volumes of the two components. It is noted that the solution of the component with the larger atomic volume in the component with the smaller volume (Cd, Zn) is always associated with a larger heat absorption than the opposite process. This is in agreement with a rule found to be valid in many binary liquid mixtures.

The system bismuth-lead differs radically from the other three systems and has a nearly symmetrical negative heat (ΔH) of mixing curve. However, the quantity $\Delta H^M/x_1x_2$ is far from independent of composition and has for equi-atomic mixtures fallen to a value about 25% below the terminal values. It is noted that the plots of $\Delta H^M/x_1x_2$ for the other systems exhibit similar negative deviations from the straight line connecting the two terminal values. We shall show that these deviations may possibly be accounted for by the short range order (or clustering) present in the mixtures.

Short Range Order.—According to the quasi-chemical theory the Helmholtz energy of mixing for one mole of a simple binary mixture is given by the expression⁷

$$\Delta E^M \cong x_1x_2\lambda \left(1 - 2x_1x_2 \frac{2\lambda}{zRT} \right) \quad (1)$$

In this expression z is the coördination number (which is assumed to be the same in the mixture and in the pure components and which we set ~ 10 for simplicity), while the single interaction parameter λ is independent of composition and given by

$$N(2w_{12} - w_{11} - w_{22})$$

Here w_{12} , w_{11} and w_{22} are the potential energies of the 12, 11 and 22 bonds, and N is Avogadro's number. We recall that the first term on the right-hand side in the expression above represents the zeroth approximation where the effect of short range order (or clustering) is neglected, while the second term takes this effect into account.

As we are dealing with a process in the condensed phase we may disregard the small difference between H and E , and get

$$\Delta H^M / x_1x_2 \cong \lambda \left(1 - 2x_1x_2 \frac{2\lambda}{zRT} \right) \quad (2)$$

(6) N. W. Taylor, *J. Am. Chem. Soc.*, **45**, 2865 (1923).

(7) O. J. Kleppa, *ibid.*, **72**, 3346 (1950).

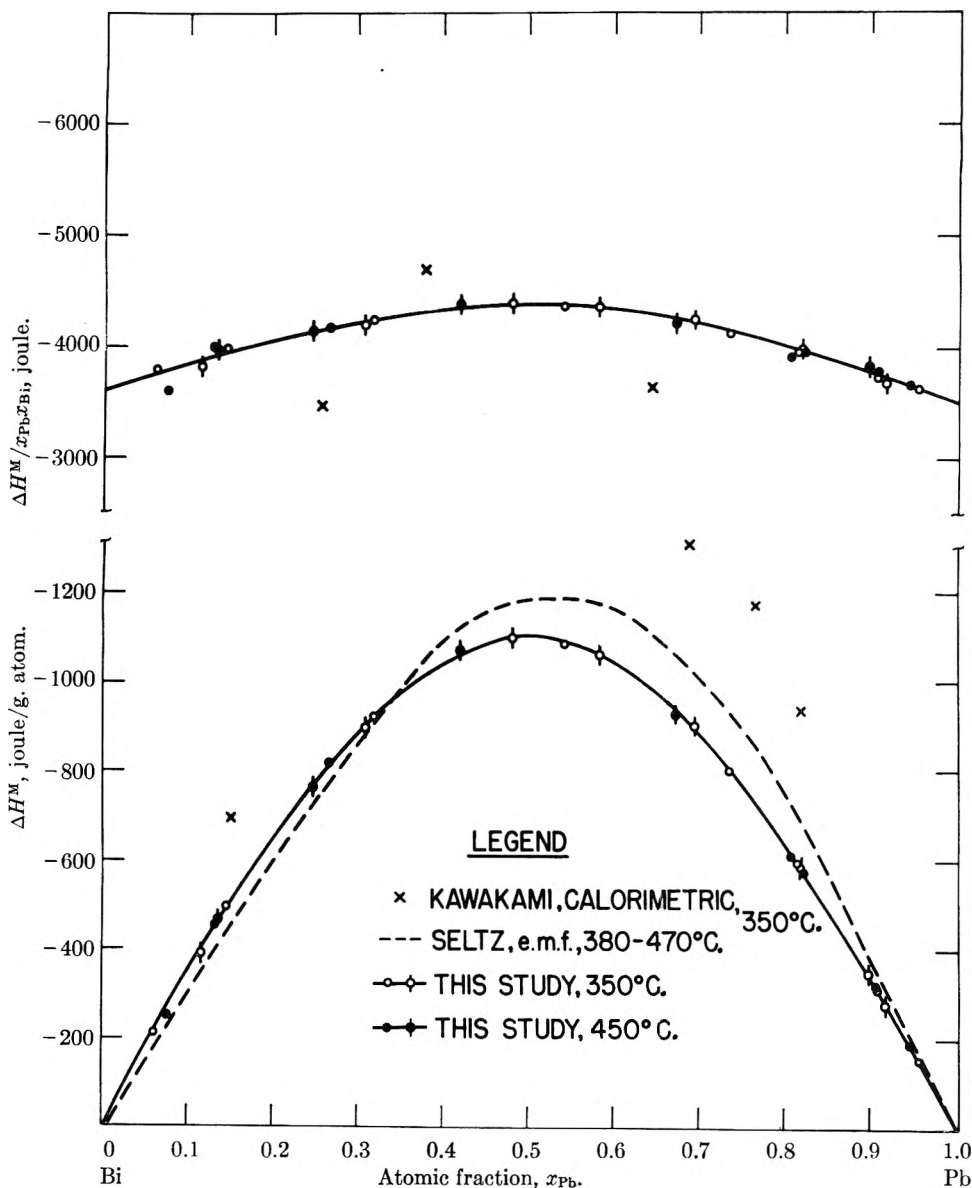


Fig. 1.—Heats of mixing in Bi(1)-Pb(1).

We now leave the domain of strict applicability of the quasi-chemical theory, and assume arbitrarily that the relations above are still valid if we let λ vary linearly with concentration. For any concentration we may then obtain a value for λ by interpolating linearly between the two terminal values of $\Delta H^M/x_1x_2$. By inserting this value in (2) we may calculate a value for $\Delta H^M/x_1x_2$ which may be compared to the experimental value. For equiatomic mixtures in the four systems under consideration such a comparison is presented in Table V.

When the experimental uncertainties and the arbitrary nature of the various assumptions are taken into account, it seems that the agreement between the calculated and observed values of $\Delta H^M/x_1x_2$ is as good as can be expected.

Differential Quantities.—It is recalled that in e.m.f. experiments the relative partial molal heat content of the more electro-positive component is obtained through the temperature dependence of the chemical potential. The corresponding quan-

TABLE V
EFFECT OF SHORT RANGE ORDER ON THE HEAT OF MIXING
(DATA IN KILOJOULES)

System (temp., °C.)	$\lambda_{0.5}$	Calcd. ($\Delta H^M/x_1x_2$) _{0.5}	Obsd.
Bi-Pb (400)	-3.6	-3.8	-4.4
Cd-Pb (400)	12.4	9.6	10.7
Cd-Sn (350)	9.5	7.8	8.0
Cd-Sn (450)	8.6	7.4	7.5
Sn-Zn (430)	16.3	11.7	13.2
Sn-Zn (525)	15.0	11.6	11.5

ties for the other component may be obtained from an integration of the Gibbs-Duhem-Margules relation. However, these values will normally be associated with greater uncertainty. From the integral heat data reported above, on the other hand, we may derive the differential quantities of either component by means of suitable graphical or analytical methods. We shall here give special attention to the partial molal quantities in moderately dilute solutions only.

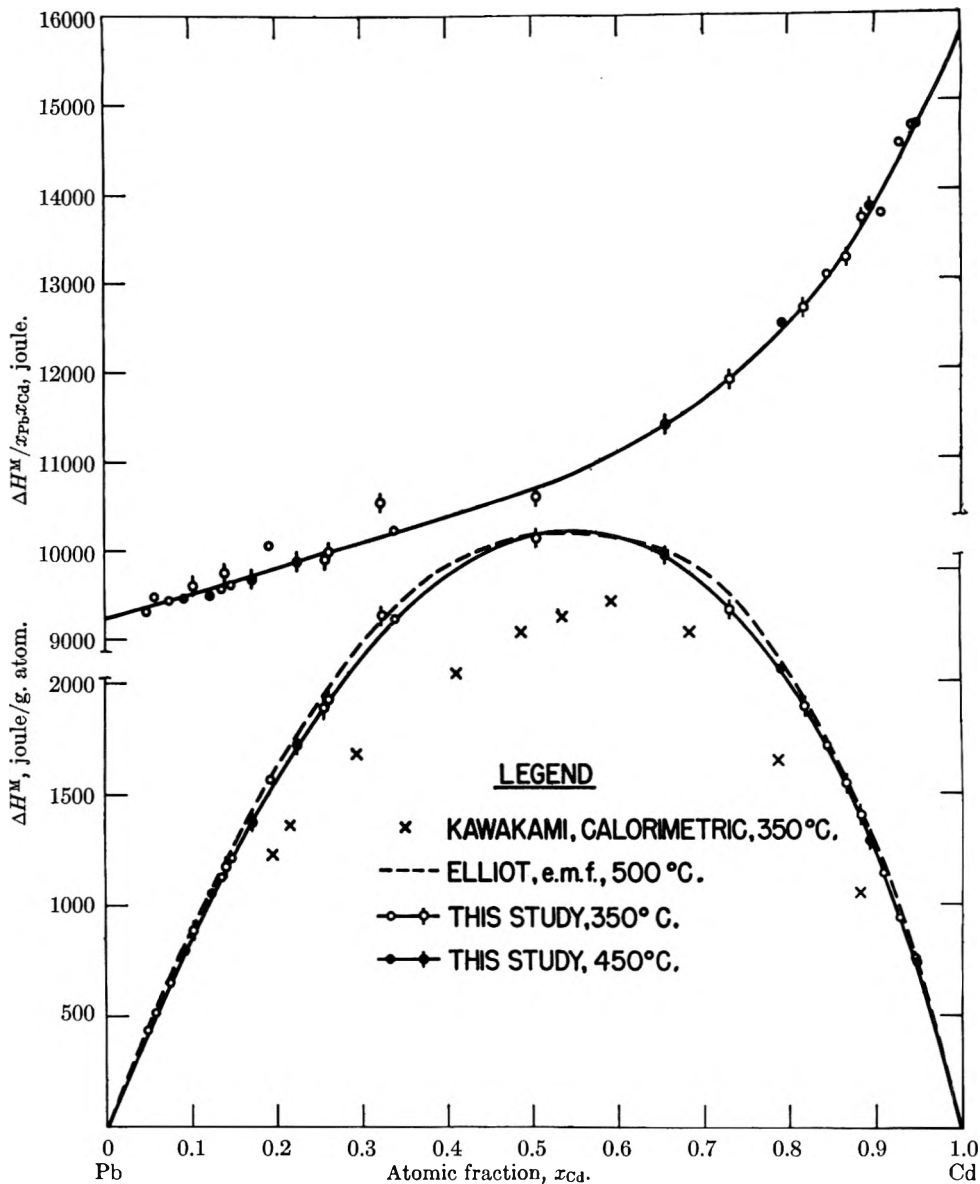


Fig. 2.—Heats of mixing in Pb(1)-Cd(1).

For dilute solutions we may expand the integral molar heat of mixing in powers of the mole fraction of the minor component, x

$$\Delta H^M = (\Delta H^M)_{x=0} + x \left(\frac{\partial \Delta H^M}{\partial x} \right)_{x=0} + \frac{1}{2} x^2 \left(\frac{\partial^2 \Delta H^M}{\partial x^2} \right)_{x=0} + \dots \quad (3)$$

The first term on the right-hand side is by definition zero, while $(\partial \Delta H^M / \partial x)_{x=0} = a$ is equal to the relative partial molal heat content of the minor component in its infinitely dilute solution. The coefficient of x^2 , which we shall denote by b , for simplicity, similarly provides a measure for the curvature of ΔH^M at $x = 0$.

By definition we have $\Delta H^M = x \bar{L}_1 + (1 - x) \bar{L}_2$.

If the two first non-zero terms only are used in the expansion, the expressions for the two partial molal heat contents, \bar{L}_i , relative to the pure components, will be particularly simple

$$\bar{L}_1 \text{ (minor component)} = a + 2bx - bx^2 \quad (4)$$

$$\bar{L}_2 \text{ (major component)} = -bx^2 \quad (5)$$

We note that a plot of $\Delta H^M/x$ versus x for moderate values of x should yield a straight line, with slope b and intercept a at $x = 0$. In general it is of course impossible to predict how far into the non-dilute concentration range the simple linear relationship will hold. This introduces certain ambiguities, particularly in the determined value of b . In the case of the systems considered it was found that the plots indicated a linear relationship up to $x \sim 0.2$ or more. In Table VI are given values for a and b from the present investigation along with data from earlier e.m.f. studies.

An approximate value of b may sometimes be obtained from the binary equilibrium phase diagram in the vicinity of the melting point of the pure component. We recall that if solid solubility is negligible, and if the difference in heat capacity between the pure solid and the pure undercooled liquid may be neglected, the chemical potential at the liquidus (of the component present in both phases, referred to the pure undercooled liquid) will be given by

$$\mu - \mu^\circ = (T - T_m) \Delta H_f / T_m \quad (6)$$

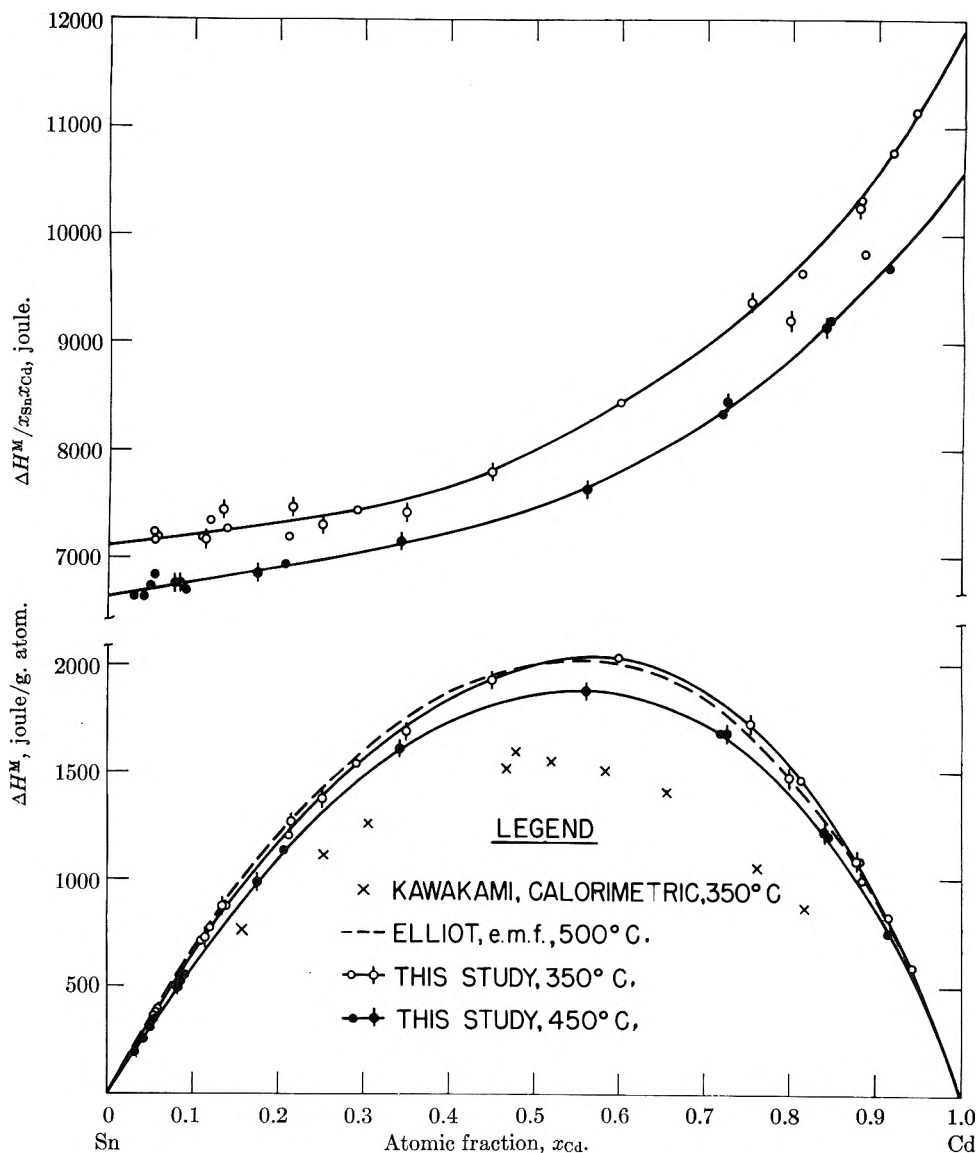


Fig. 3.—Heats of mixing Sn(1)-Cd(1).

Here ΔH_f is the heat of fusion, T_m the melting temperature of the pure metal, while T is the liquidus temperature. For the excess chemical potential at the liquidus we get

$$\mu - \mu_{ideal} = \mu - \mu^\circ - RT \ln(1 - x) \quad (7)$$

where $(1 - x)$ is the mole fraction of the solvent. If it is now assumed that in these liquid solutions the partial molal entropy of this component is ideal, we have simply $\mu - \mu_{ideal} = \bar{L}_2$. We may get a value for b by plotting \bar{L}_2 versus x^2 . Of course we do not in advance know whether the assumption of an ideal entropy of mixing is valid, and we shall therefore use the designation b' for the quantity calculated from the phase diagram. For the systems covered in the present investigation data on the liquidus have been taken from Hansen⁸ and on the heats of fusion from Kubaschewski and Evans.⁹ In the cases where a reasonably reliable evaluation of b' was possible the value has been included in Table VI.

(8) M. Hansen, "Aufbau der Zweistofflegierungen," Berlin, 1936.
 (9) O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," London, 1951.

TABLE VI
 HEATS OF MIXING IN MODERATELY DILUTE SOLUTIONS ACCORDING TO EQUATIONS 3-5 (DATA IN KILOJOULES)

Alloy		This study, 350°		E.m.f., ~500°		Phase
Major	Minor	a	b	a	b	diag.,
component						m.p.
						b'
Pb	Bi	-3.6	1.8	-3.9	0.3
Bi	Pb	-3.7	2.5	-2.9	0.3	~5
Pb	Cd	9.2	-7.0	9.2	-8.0
Cd	Pb	15.6	-30	15.5	-30	~-16
Sn	Cd	7.2	-7.0	7.5	-7.5
Cd	Sn	11.8	-23	11.5	-25	~-7
Sn	Zn	9.7 ^a	-6.0 ^a	10.0	-6.3
Zn	Sn	23 ^a	-50 ^a	19	-60	~-24

^a Data for 430°.

We notice that the earlier e.m.f. data and the results of the present investigation agree quite well, although due to the dependence of the heat of mixing on temperature, the agreement for cadmium-tin and tin-zinc to some extent is fortuitous. The agreement is particularly satisfactory for the system cadmium-lead where no such temperature de-

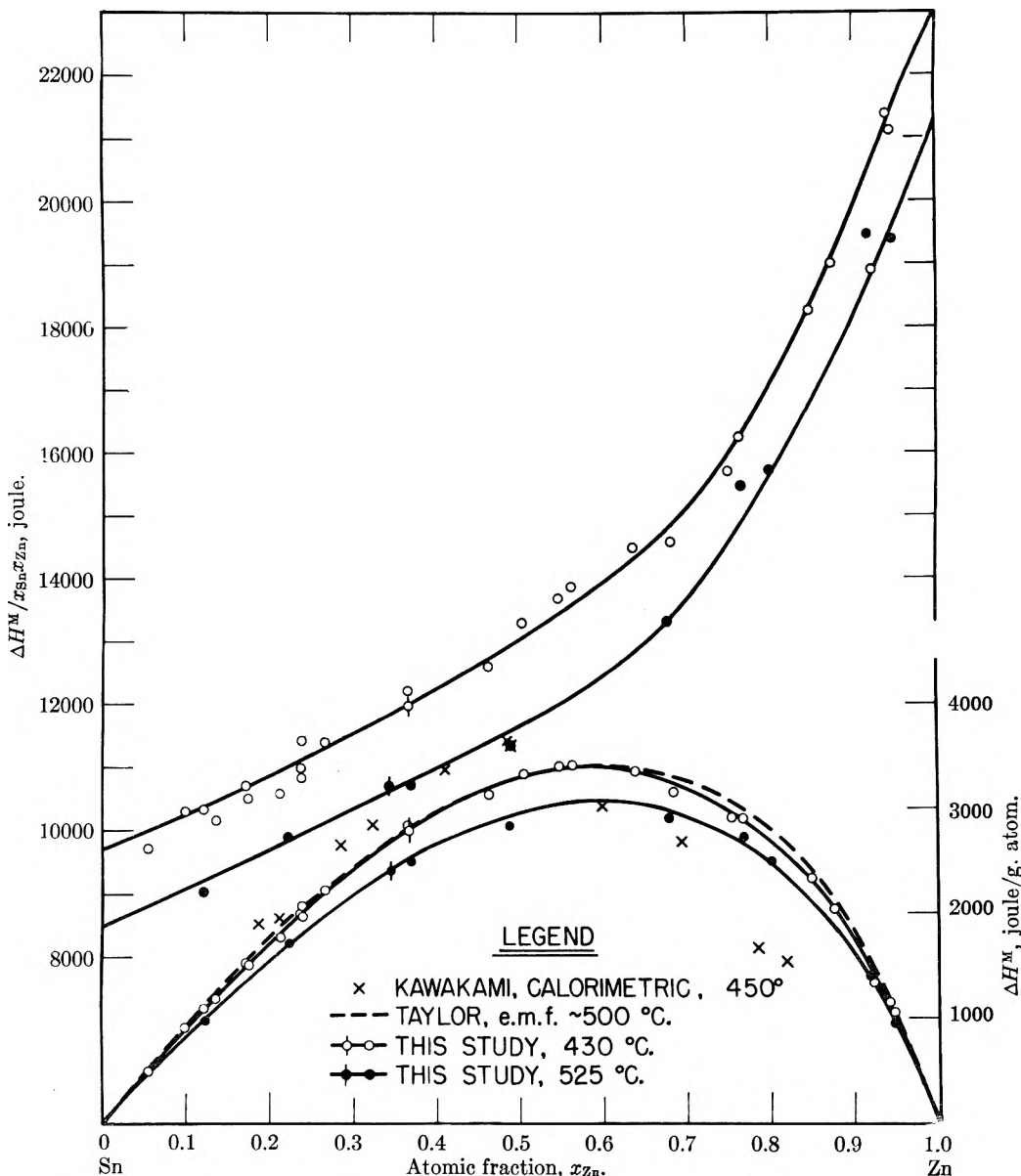


Fig. 4.—Heats of mixing in Sn(1)–Zn(1).

pendence is indicated. In fact the nearly perfect harmony of the reported data for this system with the results of the careful e.m.f. investigation of Elliott and Chipman lends added weight to all the calorimetric data reported in the present investigation.

A similar harmony is not observed in the comparison with values for b' derived from the liquidus. It is noted that the latter method tends to give values which are algebraically considerably higher than those obtained by the other two methods. Thus a partial molal entropy larger than ideal is indicated in all cases. If we make the simplifying approximation that the b 's are independent of temperature, we may combine the calorimetric and liquidus data in order to evaluate the excess partial molal entropies for the major component, $\Delta S_2 + R \ln(1-x)$. Elementary thermodynamics gives

$$\Delta S_2 + R \ln(1-x) = Ax^2 = -[(b-b')/T_m]x_2 \text{ joule/deg. g. atom (8)}$$

In Table VII we have recorded values of A calculated in this manner along with the corresponding quantity obtained from e.m.f. studies alone. The agreement between the two sets of values for A is as good as could possibly be expected.

TABLE VII

EXCESS PARTIAL MOLAL ENTROPIES OF MAJOR COMPONENT IN MODERATELY DILUTE SOLUTIONS ACCORDING TO EQUATION 8 (DATA IN JOULE/DEG. G. ATOM)

Alloy		A (eq. 8)	
Major component	Minor component	This study + liquidus, m.p.	E.m.f. alone, ~500°
Pb	Bi	..	4
Bi	Pb	~ 5	4
Pb	Cd	..	2-4
Cd	Pb	~24	17
Sn	Cd	..	4
Cd	Sn	~27	25
Sn	Zn	..	6-8
Zn	Sn	~38	25

Temperature Dependence of the Heat and Entropy of Mixing.—The present investigation shows that in the systems bismuth-lead and cadmium-lead there is little or no dependence of the heat (and entropy) of mixing on temperature. In cadmium-tin and tin-zinc, on the other hand, the heats and entropies of mixing tend to decrease with increasing temperature. We find that for equi-atomic mixtures of cadmium-tin the average deviation from the Kopp-Neumann rule for the heat capacity of the mixture between 350 and 450° is about -1.5 joule/g. atom deg., while the corresponding figure for tin-zinc in the temperature interval 430 to 525° is -3 joule/g. atom deg. If we assume that these deviations are independent of temperature, we calculate the resulting decrease in the entropies of mixing to be about 0.2 and 0.4 joule/deg. g. atom, respectively. For these two systems the increase in temperature is also accompanied by some decrease in energetic asymmetry, most clearly illustrated by the data for cadmium-tin. For this system we note that the relative partial molal heat content for cadmium in its dilute solutions in tin falls from 7200 joule/g. atom at 350° to about 6700 joule/g. atom at 450°, while the corresponding value for tin in cadmium falls from 11800 to 10500 joule/g. atom. If we make the same assumptions as before, we find that the equivalent reductions in the partial molal entropies are about 0.7 and 1.9 joule/deg. g. atom, respectively.

The new information on the temperature dependence of the heat and entropy of mixing cannot be compared with results from equilibrium work. However, we may correlate the information with the available data on entropy deviations in the four systems. According to the aforementioned e.m.f. investigations we have the following excess entropies of mixing for equi-atomic mixtures at about 500°: bismuth-lead 0.4; cadmium-lead 0.8; cad-

mium-tin 1.5; tin-zinc 2.3 joule/deg. g. atom. The estimated uncertainty in these values is about 0.4 joule/deg. g. atom. We note the obvious correlations between the *negative* deviations from the Kopp-Neumann rule and the largest excess entropies.

By making use of the arguments first advanced by Scatchard¹⁰ the author has previously attempted to correlate the excess entropies of mixing frequently found in liquid alloy systems with the volume expansion resulting from the mixing.¹¹ On the basis of the information then available on the density of liquid metals and alloys it was not possible to find definite support for this correlation. However, an imperfect correlation was found between measured excess entropies and the relative volume difference between the two components.¹² It now seems that results for cadmium-tin and tin-zinc obtained in the present work can best be explained by the volume expansion believed to accompany the process of mixing.

It must be expected that this volume expansion, as well as the heat and entropy terms associated with it should become smaller as we go to higher and higher temperatures. This would account for the observed negative deviations from the Kopp-Neumann rule.

Acknowledgments.—The author is indebted to Dr. N. H. Nachtrieb for stimulating discussions and for reading the present manuscript. He also wishes to acknowledge discussions with Dr. J. W. Cahn and other members of the staff of the Institute for the Study of Metals. The present work has been supported in part by the Office of Naval Reserve through contract No. N-6ori-02004 with the University of Chicago.

(10) G. Scatchard, *Trans. Faraday Soc.*, **33**, 160 (1937).

(11) O. J. Kleppa, *J. Am. Chem. Soc.*, **73**, 385 (1951).

(12) O. J. Kleppa, *Tidskr. Kjem. Bergvesen, Met.*, **9**, 140 (1951).

A COMPARATIVE STUDY OF NON-IONIC DETERGENT ADSORPTION BY¹ RADIOTRACER, SPECTROPHOTOMETRIC AND SURFACE TENSION METHODS

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A comparative study of the adsorption of non-ionic alkyl aryl polyoxyethylated detergents on sand by different methods has been made in an attempt to determine the fundamental mechanisms of non-ionic detergent adsorption. The techniques used in this study were: (1) the radiotracer method with which the C¹⁴-tagged ethylene oxide chains (hydrophilic) were traced, (2) the spectrophotometric method, with which the phenol groups (hydrophobic) were determined, and (3) the surface tension method, with which the surface-active species were determined. The adsorption and suspension isotherms of RLS-3066-90 and Igepal CO-710 have been determined. The adsorption of RLS appears to follow the Langmuir isotherm. The adsorption determined by the surface tension method is greater than that determined by spectrophotometry which, in turn, is greater than that determined by the radiotracer method. These differences are interpreted to indicate selective adsorption of smaller molecular species. Polyoxyethylated non-ionic detergents are mixtures of different molecular species with various ethylene oxide chain lengths. The anomalous maxima and minima of the Igepal adsorption isotherms may be explained, respectively, by selective adsorption of smaller molecular species at lower concentrations with more uniform adsorption at higher concentrations, and the adsorption of a multimolecular layer. The anomalous adsorption and suspension isotherms of Igepal, although different in shape, also may be correlated by these postulates.

Introduction

The adsorption of detergents on sand is of primary concern in their use as additives in the secondary recovery of petroleum by water flooding. Such adsorption, if extensive and irreversible, would result in a great enough detergent loss to affect adversely the economical use of such additives. Previous investigations in this Laboratory showed that non-ionic detergents were generally effective in displacing petroleum from sand surfaces.² Experimental studies of the rate of non-ionic detergent-zone movement in sand columns were made and the results compared with the values calculated by the chromatographic theory from adsorption of the detergent at the sand-water interface.³ Few studies of the adsorption of non-ionic detergents have been reported. A comparative study of the adsorption of non-ionic alkyl aryl polyoxyethylated detergents on sand by different methods has been made in an effort to determine the fundamental mechanisms of non-ionic detergent adsorption. The techniques used in this study were: (1) the radiotracer method with which the C¹⁴-tagged ethylene oxide chains (hydrophilic) were traced, (2) the spectrophotometric method with which the phenol groups (hydrophobic) were determined, and (3) the surface tension method with which the surface-active species were determined.

The distribution of polyoxyethylene chain lengths in a detergent of this type is represented by Poisson's distribution formula.⁴ Therefore, analysis for either the hydrophobic or hydrophilic elements alone does not necessarily result in knowledge of the behavior of the other group. Further, analysis for the surface-active species does not necessarily afford a clear indication of the behavior of the bulk of the detergent molecules. A combination of these

three methods affords an unusual opportunity to follow the several detergent elements during the adsorption process.

Experimental

Materials.—The Tip Top sand, 140–200 mesh, used in these experiments had been employed in previous experiments with other non-ionic, non-radioactive detergents. The sand originally had been cleaned with hot chromic acid. Before reuse, the sand was carefully cleaned of detergents with chloroform, acetone and water. The surface area of the sand was 300 cm.² per gram as determined by microscopic measurements and sieve analysis.

Non-radioactive Igepal CO-710 and RLS-3066-90 and the radioactive analogs of Igepal CO-710 and RLS-3066-90 were used as received from the General Aniline and Film Corporation. The radioactive detergents were tagged with C¹⁴ in the polyoxyethylene chain. Both detergents consisted of 100% active ingredient and are actually mixtures of different molecular species varying in their ethylene oxide chain lengths according to Poisson's formula.⁴ The radioactive carbon atoms were assumed to be randomly distributed among the different molecular species comprising the detergent.

Procedures.—The general procedure for the three methods consisted of calibration with detergent solutions of various known concentrations. Known volumes of the solutions were shaken with known amounts of sand on a Burrell "wrist-action" shaker for several hours and centrifuged to remove suspended sand. The supernatant liquids were then analyzed, and the amount of adsorption was calculated from the observed change in concentration. Identical containers and solution volumes were used for calibrations and adsorption experiments in order to minimize effects due to adsorption on the container walls and at the solution-air interface. Under these conditions such effects on calculated values of adsorption were negligible. Any error introduced into calculation of adsorption from aqueous solutions by assuming zero concentration of water at the solid-water interface is negligible for dilute solutions and the magnitude of adsorption herein reported.⁵ Experiments in this Laboratory showed that equilibrium was reached within an hour in shaking a similar detergent solution with sand under similar experimental conditions.¹ The shaking time was the same for each detergent with the three methods. The temperature was that of an air-conditioned room (25 ± 1°).

Radiotracer Method.—An end-window Geiger counter with a mica-window thickness of 1.7 mg./cm.² and diameter of 2.8 cm. was used for detecting C¹⁴ radiations. To eliminate the self-absorption and yet obtain enough counts, a 0.2-ml. aliquot portion of the solution was transferred to a steel planchet (50 mg./cm.²) to make a large drop 1.8 cm.

(1) Presented before the Division of Physical and Inorganic Chemistry at the 126th National Meeting of the American Chemical Society, which was held in New York, N. Y., September 12–17, 1954.

(2) H. N. Dunning, R. T. Johansen and Lun Hsiao, *Petroleum Engineer*, **26**, No. 1, B-82 (Jan. 1954).

(3) H. N. Dunning and Lun Hsiao, *Producers Monthly*, **18**, No. 1, 24 (Nov. 1953).

(4) R. L. Mayhew and R. C. Hyatt, *J. Am. Oil Chem. Soc.*, **29**, No. 9, 357 (1952).

(5) M. L. Corrin, E. L. Lind, A. Roginsky and W. D. Harkins, *J. Colloid Sci.*, **4**, 485 (1949).

in diameter which was evaporated to dryness under an infrared lamp. The thickness of the source thus prepared was less than 0.1 mg./cm.² for concentrations up to 1,000 p.p.m., the most concentrated solution used. A circular area on the planchet, 1.8 cm. in diameter, was cleaned and a 0.2-ml. aliquot portion of the more concentrated solutions carefully transferred and evaporated, so that the surface-active solution would not spread beyond the cleaned area. For the more dilute solutions, a small amount of non-radioactive detergent solution was added to the drop, if necessary, to cause it to spread over the desired area. The source thickness was still less than 0.1 mg./cm.² with this method. Some deviations in the source diameter and distribution of the evaporated residue were observed. However, including statistical and geometrical fluctuations, the counting reproducibility was about 3%.

Self-absorption and self-scattering are usually neglected for thin sources. Henriques⁶ and Libby's⁷ formula for self-absorption is

$$\frac{I}{I_0} = \frac{1 - e^{-\alpha d}}{\alpha d}$$

where I is radioactivity transmitted, I_0 is radioactivity before self-absorption, α is the mass absorption coefficient, and d is the source thickness in mg./cm.². With $d = 0.1$ mg./cm.² and using Solomon's⁸ value of $\alpha = 0.29$ for C^{14} , I/I_0 is 0.99 (1% error).

There is some uncertainty in self-scattering, which results in a β -ray angular distribution depending on the source thickness. A counter subtending a solid angle less than 2π at the source would record a greater fraction of the emerging radiations from thick sources than from thin sources.⁹ The self-scattering effect generally reaches a maximum at a source thickness equal to 0.05–0.1 R , where R is the range of the β -radiation.¹⁰ The subtended solid angle in these experiments was nearly 2π , with the source very close to the counter window. Since 0.1 mg./cm.² corresponds to only about 0.003 R for C^{14} radiations, this would approach the thickness insensitive region of isotropic distribution near zero thickness.⁹ Furthermore, with sources of small thickness, saturation backscattering (generally reached at 0.2 R) from the planchet would mask the self-scattering effect. Therefore, it seems justifiable to neglect this effect with source thicknesses less than 0.1 mg./cm.

Spectrophotometric Method.—Absorbance was measured with a Beckman DU spectrophotometer at 276 $m\mu$, a wave length of maximum absorbance for detergents containing a phenol group. The calibration curves were linear in accordance with Lambert-Beer's law. Distilled water, shaken with sand under the same conditions as with the detergent solutions, was used as the reference for the analysis of equilibrated solutions after adsorption. This method is complicated by the stable suspension of fine sand particles by the detergent solutions. These suspensions make the validity of measurements below 50 p.p.m. very doubtful and may lead to erroneous results if the suspension of sand particles depends on detergent concentration.

A method using two wave lengths was adopted to minimize errors caused by sand suspensions. Assume $x_1/x_2 = A_{01}/A_{02}$, where x_i is the absorbance due to sand suspension in detergent solution, and A_{0i} is that in distilled water at λ_i . A_{01} was determined experimentally. One wave length was always 276 $m\mu$, and the other was 262 $m\mu$ for Igepal and 265 $m\mu$ for RLS, so chosen as to give proper absorbance. Then

$$C_{eq} = a_1(A_1 - x_1) = a_2(A_2 - x_2)$$

where C_{eq} is the equilibrium detergent concentration corrected for sand suspension, a_i is the conversion factor (or reciprocal absorptivity) from the linear calibration curve at λ_i , and A_i is the absorbance of the detergent solution containing fine sand suspensions measured at λ_i , using sand suspension in distilled water as reference. The three unknowns, C_{eq} , x_1 and x_2 , were solved from the above three independent equations. This method happens to be a com-

bination of the conventional method and the "y-reference" method¹¹ of relative absorptometry¹² for two component systems.

Surface Tension Method.—Surface tension values at 25°C. were determined by the du Nouy method using a platinum ring of 4.0-cm. radius and a combination thermostat-elevating platform¹³ to control the temperature. The calibration curves of surface tension versus "log C " were linear in the concentration range just below the critical micelle concentration. Equilibrium solutions were diluted accurately by weight to this range before analysis. Theoretical ring corrections for the method¹⁴ were not applied in the calibration and analysis because only relative surface tension values were required for the determination of adsorption isotherms. An empirical correction factor² of 0.93 was used for the calculation of adsorption at solution-air interface.

Results

The adsorption isotherms of RLS and Igepal on Tip Top sand are shown in Figs. 1 and 2, respectively. For both detergents at equilibrium concentrations below 300 p.p.m., the extent of adsorption determined by the surface tension method is greater than that determined by spectrophotometry, which, in turn, is greater than that determined by the radiotracer method. The relative extent of adsorption of RLS determined by the three methods remains the same at higher concentrations, but the spectrophotometric isotherm of Igepal decreases more rapidly than does the radiotracer isotherm and apparently crosses it at 375 p.p.m. At concentrations immediately below the minimum in adsorption the difference between these two isotherms is of the same order as the experimental error. The surface tension isotherm of this detergent approaches the other two isotherms near the concentration 375 p.p.m.

The surface tension-concentration curves of these detergents are shown in Fig. 3. Uncorrected values of surface tension (dynes per cm.) are plotted against log C , where C is the concentration in p.p.m. The critical micelle concentrations (where the surface tension curve begins to become horizontal¹⁵) of RLS and Igepal are 11 and 60 p.p.m., respectively. At concentrations lower than these¹⁶ the curves are linear, indicating the approach to a close-packed monomolecular layer.¹⁵ An area of 63 sq. Å. per average molecule of Igepal adsorbed at the solution-air interface was calculated with the Gibbs adsorption equation assuming concentration to be equal to activity at such low concentrations. The areas per average molecule of Igepal adsorbed at the sand-solution interface calculated from the maximum and minimum adsorption observed with each method were: (a) spectrophotometry, 39 to 101 sq. Å.; surface tension, 26 to 42 sq. Å.; and radiotracer, 53 to 77 sq. Å. These values were calculated by assuming monomolecular films and using a *molecular weight* for Igepal calcu-

(11) E. Allen and E. M. Hammaker, *Anal. Chem.*, **24**, 1295 (1952).

(12) (a) C. F. Hiskey, *ibid.*, **21**, 1440 (1949); (b) C. F. Hiskey and D. Firestone, *ibid.*, **24**, 342 (1952).

(13) H. N. Dunning and R. T. Johansen, *Rev. Sci. Instru.*, **24**, 1154 (1953).

(14) (a) W. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930); (b) B. B. Freud and H. Z. Freud, *ibid.*, **52**, 1772 (1930).

(15) (a) C. R. Bury, *Phil. Mag.*, **4**, 980 (1927); (b) C. R. Bury and J. Browning, *Trans. Faraday Soc.*, **49**, 209 (1953).

(16) The surface tension curves at such low concentrations were reproducible with careful measurements, and were in general agreement with results obtained in the Central Research Laboratory, General Aniline and Film Corp.

(6) F. C. Henriques, Jr., G. B. Kistiakowsky, C. Margnetti and W. G. Schneider, *Ind. Eng. Chem., Anal. Ed.*, **18**, 349 (1946).

(7) W. F. Libby, *ibid.*, **19**, 2 (1947).

(8) A. K. Solomon, R. G. Gould and C. B. Anfinsen, *Phys. Rev.*, **72**, 1097 (1947).

(9) R. G. Baker and L. Katz, *Nucleonics*, **11**, No. 2, 14 (1953).

(10) L. E. Glendenin and A. K. Solomon, *Sci.*, **112**, 623 (1950).

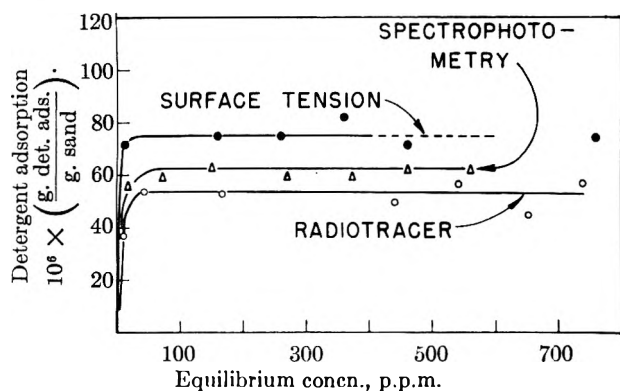


Fig. 1.—Adsorption isotherms of RLS-3066-90 on Tip Top sand.

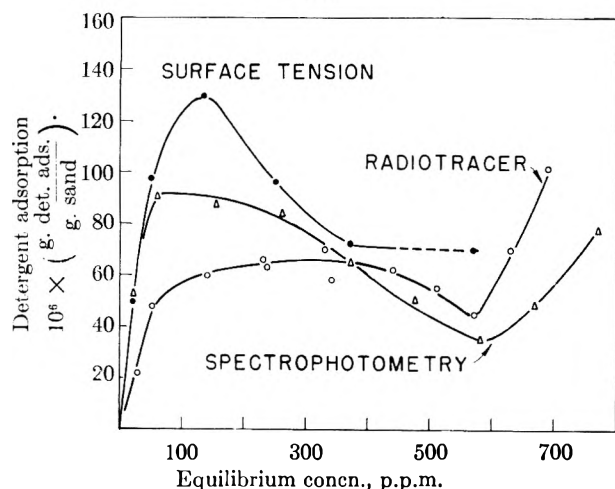


Fig. 2.—Adsorption isotherms of Igepal CO-710 on Tip Top sand.

lated from an average ratio of 10.5 moles of ethylene oxide per mole of alkyl phenol. This molecular weight should be regarded only as a number average. Because RLS is a new experimental product, information as to its exact composition and average molecular weight was not available. However, it has a higher molecular weight and approximately the same cloud point as Igepal and therefore a mole ratio of ethylene oxide to phenol greater than 10.5.

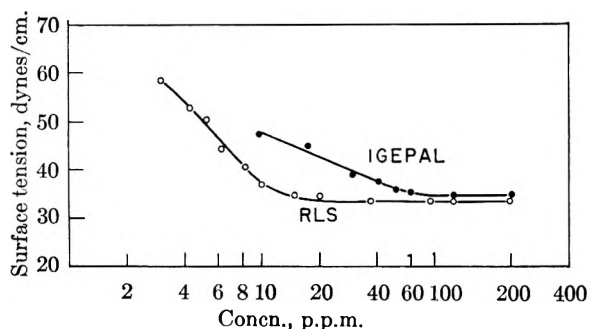


Fig. 3.—Surface tension-concentration curves for Igepal CO-710 and RLS-3066-90.

The suspending powers of these two detergents (in terms of absorbance of sand suspensions) obtained by two wave length spectrophotometry are shown in Fig. 4. As expected, detergent solutions have greater sand suspending power than does distilled water. Although this absorbance is small

compared to the absorbance of the detergent at concentrations above 50 p.p.m., these suspensions cause rather large errors at lower concentrations. The suspending power of RLS rises sharply at very low concentrations and quickly levels off at higher concentrations. The suspending power of Igepal, after an initial rise, gradually decreases at higher concentrations.

Discussion

Adsorption Isotherms.—Because these non-ionic detergents are mixtures of different molecular species of various ethylene oxide chain length, the calibration curve used in either method is actually a combination of the calibration curves (if actually determined) of the different molecular species. The concentration obtained by analysis of the equilibrated solution using the calibration curve may not be the true value because the calibration curve may be no longer valid if the molecular weight spectrum in the solution is not the same as it was before adsorption. Only if the detergent adsorbed on the sand has the same relative distribution of molecular species as the original detergent will the adsorption isotherms obtained by different methods agree with each other within experimental errors.

From their adsorption isotherms, the distribution of molecular species of RLS adsorbed on sand resembles the original distribution more closely than with Igepal. The extent of adsorption of RLS indicated by surface tension is higher than that by spectrophotometry and the latter higher than that by radiotracer. This would indicate that relatively more of the molecular species having less than average chain lengths were adsorbed, since the smaller the molecular species, the lower the specific radioactivity and the higher the surface activity¹⁷ and the specific absorptivity. Furthermore, the surface activity is more sensitive to the distribution of molecular species than is the specific absorptivity. Earlier experiments with series of similar detergents indicate that adsorption generally increases with decreasing chain length.

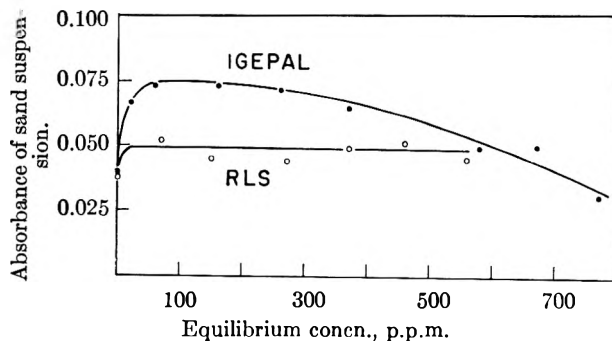


Fig. 4.—Suspension isotherms of RLS-3066-90 and Igepal CO-710.

At concentrations below 375 p.p.m., the adsorption isotherms of Igepal are arranged as with RLS. The extent of adsorption indicated by surface tension is greater than that by spectrophotometry which, in turn, is greater than that by the radiotracer method. However, unlike the isotherms of

(17) H. N. Dunning, H. J. Gustafson and R. T. Johansen, *Ind. Eng. Chem.*, **46**, 591 (1954).

RLS, the isotherms of Igepal exhibit a maximum¹⁸ and minimum. Maxima and minima in adsorption isotherms of ionic detergents have been observed.^{19,20} The maximum observed with ionic detergents could be accounted for by assuming that the equilibrium between the long-chain ions, gegenions, and micelles is governed by mass action.²¹ The long-chain ion activity would go through a maximum with respect to over-all concentration of the electrolyte. At higher concentrations the rising adsorption after the minimum was attributed²⁰ to the increased size of micelles (due to high concentration of salt added) which were believed to be adsorbed after the critical micelle concentration was reached. These explanations cannot be applied to the adsorption of pure non-ionic detergents.²²

The relative positions of the three isotherms below the maxima are predicted from the effect of selective adsorption on the various methods as discussed for RLS. Beyond the maxima, it is believed that relatively more of the larger molecular species are adsorbed; therefore the adsorption isotherms by surface tension and by spectrophotometry begin to decline, while the adsorption isotherm by radiotracer method is still increasing slowly. But the larger the molecule, the less the number of molecules adsorbed per unit area. When this effect dominates, the adsorption indicated by the radiotracer method begins to decrease. If at lower concentrations the lower molecular weight species are selectively adsorbed, and at higher concentrations the adsorption becomes less specific, there may be a point where the relative distribution of molecules adsorbed on sand is the same as in the original detergent. That is, the selective adsorption of lower molecular weight species observed at lower concentrations will progressively decrease until at this concentration adsorption is non-specific. At this point the three methods should indicate the same adsorption. This is the point where the adsorption isotherms by spectrophotometry and by radiotracer method converge (375 p.p.m.). The adsorption isotherm determined by surface tension misses this point, but only by a small amount. The area per average molecule adsorbed on sand at this point was calculated to be 55 sq. Å., comparable with the area of 63 sq. Å. calculated from adsorption at the solution-air interface. The increasing adsorption after the minimum may be attributed to the adsorption of a second layer of molecules. BET-type adsorption isotherms for non-ionic detergents on Tip

(18) The anomalous maximum in adsorption exhibited by the Igepals has been observed in earlier studies in this Laboratory and in other laboratories. Other detergents, presumably of similar composition and manufacturing procedures but prepared by other manufacturers, do not exhibit this decrease in adsorption at higher concentrations commonly exhibited by the Igepals. Therefore, this must be viewed as atypical behavior for polyoxyethylated alkyl phenols in general.

(19) L. H. Flett, L. F. Hoyt and J. E. Walter, *Am. Dyestuff Reporter*, (March 3, 1952).

(20) A. L. Meader, Jr., and B. A. Fries, *Ind. Eng. Chem.*, **44**, 1636 (1952).

(21) (a) G. S. Hartley and R. C. Murray, *Trans. Faraday Soc.*, **31**, 183 (1935); (b) M. J. Vold, *J. Colloid Sci.*, **5**, 506 (1950).

(22) Dr. P. B. Lorenz of this Laboratory kindly measured the conductivities of solutions of these detergents. They are essentially free of ionic materials. The specific conductivities of 1000 p.p.m. solutions of RLS and Igepal were 7.0×10^{-6} and 2.1×10^{-6} mho cm., respectively. The specific conductivity of the water used in preparing these solutions was 0.88×10^{-6} mho cm.

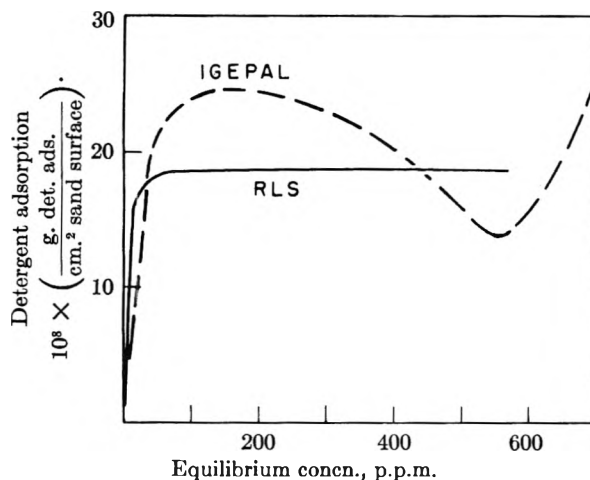


Fig. 5.—Composite adsorption isotherms of Igepal CO-710 and RLS-3066-90.

Top sand have been observed in this Laboratory.³ The minimum of the adsorption isotherm by surface tension does not agree with that by the radiotracer method, and the results become quite erratic at concentrations above 400 p.p.m.

The postulated change in selective adsorption could explain an inversion of the spectrophotometric and radiotracer isotherms if it is assumed that at higher equilibrium concentrations, the higher molecular weight species are selectively adsorbed. Since the difference between these two isotherms above 400 p.p.m. is of the order of experimental errors, such speculations seem unjustified at present.

Suspension Isotherms.—The suspending power of non-ionic detergents arises from the adsorption of the detergents on solid particles, presumably owing to a charge induced on the solid particles by dipole orientation.²³ It was speculated²⁴ that a complete monomolecular layer was necessary to produce the most stable dispersions. Therefore, with Igepal, higher molecular weight species with relatively larger area per molecule adsorbed at higher concentrations should have a smaller suspending power than lower molecular weight species adsorbed at lower concentrations, since solid particles so coated would have a lower induced charge at saturation of the surface.

If these postulates apply, the suspending power of RLS would be expected to remain relatively constant while the suspending power of Igepal decreased due to the decrease in selective adsorption at higher concentrations observed previously for Igepal. When a second layer of Igepal molecules is adsorbed, the charge induced by this second layer would oppose the charge induced by the first layer. Thus, the suspending power may still decrease, while the adsorption rises again after the minimum as a second layer of molecules is being adsorbed.

Composite Adsorption Isotherms.—The results obtained with the radiotracer and spectrophotometric methods were averaged to give composite adsorption isotherms for Igepal and RLS. These isotherms are shown in Fig. 5. Results obtained with the surface tension method are not included in

(23) R. D. Vold and C. C. Konecny, *THIS JOURNAL*, **53**, 1276 (1949).

(24) K. N. Kathju, *Paint-Oil. Chem. Rev.*, **99**, No. 8, 30 (1937)

these composites because the surface activity of a detergent may be caused largely by a small portion of highly surface-active material. Thus, results obtained by the surface tension method are especially susceptible to erroneous interpretation. As discussed previously, the errors in the spectrophotometric and radiotracer methods caused by the Poisson distribution of polyoxyethylene chain lengths generally are of opposing types and hence are mutually compensating. Therefore, adsorption isotherms determined by a combination of these two

methods furnish a reliable indication of detergent adsorption. These isotherms are expressed in terms of amount of detergent adsorbed per square centimeter of sand surface and thus should be applicable to general treatment so long as a clean silica surface is involved.

The authors wish to thank the General Aniline and Film Corporation for furnishing the samples of detergents and Drs. C. F. Jelinek, J. M. Lambert, R. L. Mayhew, and J. P. McCullough for helpful discussions.

METAL-POLYELECTROLYTE COMPLEXES. II. COMPLEXES OF COPPER WITH CROSS-LINKED POLYACRYLIC AND POLYMETHACRYLIC ACIDS¹

BY HARRY P. GREGOR, LIONEL B. LUTTINGER AND ERNST M. LOEBL

Contribution from the Department of Chemistry of the Polytechnic Institute of Brooklyn, New York

Received October 12, 1954

Complexity constants for the systems cross-linked polymethacrylic acid-copper(II) and cross-linked polyacrylic acid-copper(II) are presented. The complexation behavior resembles that of the polyacrylic acid-copper systems previously reported. The principal difference observed with the cross-linked polymers is that the maximum coordination number was 2. The complexation constants with the resins were somewhat weaker than with the soluble polymers, but many orders of magnitude greater than for the monomeric analogs. Acrylic resins form stronger complexes than methacrylic resins; complexation becomes weaker with increasing degree of cross-linking.

Complexity constants of copper with a linear polyelectrolyte (polyacrylic acid) have been reported in the first paper in this series.² The present paper is concerned with complex formation between copper(II) and a cross-linked polyelectrolyte. Three different resins were used. The systems were studied in the absence of neutral salt, in 0.2 and 2 *M* sodium nitrate. The theory and the methods employed follow those already presented.²

In brief, titration data taken in the absence of copper are compared with those taken in the presence of copper at the same concentration of neutral salt, and the complexity constants are found graphically by a modification of the method of Bjerrum.³ Two of the resins were prepared in this Laboratory⁴ by copolymerization of methacrylic acid with 1 and 9% divinylbenzene (DVB), respectively, as cross-linking agent; they are referred to henceforth as DVB-1 and DVB-9. The third was resin Amberlite XE 89, a cross-linked polyacrylic acid polymer, prepared and supplied to us by the Rohm and Haas Company. Swelling studies on this resin⁵ indicate that its degree of effective cross-linking corresponds to an analogous polymethacrylic acid polymer prepared with 1-2% DVB as cross-linking agent.

(1) A portion of this work is abstracted from the Dissertation of Lionel B. Luttinger submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, June 1954. Paper presented at the XIIIth International Congress of Pure and Applied Chemistry, Stockholm, July 29, 1953.

(2) H. P. Gregor, L. B. Luttinger and E. M. Loebel, *THIS JOURNAL*, **59**, 34 (1955).

(3) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen, 1941.

(4) F. Bernstein, Dissertation, Polytechnic Institute of Brooklyn, 1952.

(5) H. P. Gregor and F. Bernstein, in preparation.

Experimental

Conditioning of the Resins.—Particles whose size was about twenty mesh were selected for these experiments. Before use, they were conditioned by cycling alternately with large excesses of 1 *M* hydrochloric acid and 1 *M* sodium hydroxide. After a final regeneration with acid, the resins were washed with distilled water until the solution had a conductance of about 5 micromhos and gave no test for chloride ion. The resin samples were allowed to air-dry until free-flowing; their moisture content was determined by drying to constant weight in a vacuum oven at 60°.

Method of Titration.—Small samples of resin (~0.3 g.) were shaken with standard carbon dioxide-free potassium hydroxide until equilibrium was attained, as indicated by a constant pH, reached within 24 hours. A further quantity of base was then added, and the shaking repeated. In this manner, titration curves for the resins could be constructed, the end-points of which gave the capacity of the resin toward potassium hydroxide. The capacities thus found for dry resin in 2 *M* sodium nitrate were: DVB-1, 11.4 meq./g.; DVB-9, 8.28; XE 89, 11.5. In the presence of copper, equilibrium was attained more slowly; the titrations were not carried beyond a final pH of about 5 so as to avoid copper hydroxide precipitation.

The titration data of the resins in the absence of copper followed the modified Henderson-Hasselbalch equation,⁵ $pH = pK_a - n \log(1 - \alpha)/\alpha$, where α is the degree of neutralization with base. The values of pK_a and n thus obtained are summarized in Table I, where the corresponding values obtained with linear polyacrylic acid (PAA)² are also listed for comparison.

Determination of Complexity Constants.—The method used for calculating the complexity constants of the copper-resin systems is the same as that reported previously for copper-PAA.² In addition, the Bjerrum method was checked independently by following the free copper concentration in the solution phase analytically. This was possible because the ambient solution is free of complex ions. The copper concentration was followed by removing aliquots of the supernatant solution and analyzing colorimetrically for the copper-ammonia complex.

The calculations were based on the assumption that the free copper ions were equally distributed inside and outside the resin. This assumption can hold only when the Donnan equilibrium is swamped through the presence of a large excess of counter ions.

Results and Discussion

Results in Absence of Copper.—Comparisons can be drawn between the following three pairs of systems: PAA *vs.* XE 89, comparing a linear with a cross-linked polymer having the same monomeric unit; XE 89 *vs.* DVB-1, comparing resins of about the same effective degree of cross-linking with different monomer units; DVB-1 *vs.* DVB-9, comparing resins identical except for the degree of cross-linking.

For the first comparison, it is seen that the resin (XE 89) is apparently a weaker acid than the linear material; this is true throughout the range of salt concentrations. This apparent difference is probably the result of the Donnan distribution. The local concentration of fixed carboxylate ions is very much higher (about 1–2 molal for completely neutralized systems) in the resin than in the linear material, and therefore the ratio of internal to external cationic activities is higher for the resin. For the same "inside" hydrogen ion activity, the measured outside *pH* will be higher with the resin than with the linear material, and thus the apparent dissociation constant for the resin (based on this measured *pH*) will be lower. This apparent difference will decrease with increasing salt concentrations.

TABLE I

pK_a AND n VALUES FOR CROSS-LINKED POLYMETHACRYLIC AND ACRYLIC ACIDS AND FOR LINEAR POLYACRYLIC ACID

Resin	Concn. of NaNO ₃ , M	n	pK_a
PAA (0.01 N)	0	2.0	6.17
	0.2	1.7	4.91
	2	1.4	4.30
XE 89	0	2.1	7.32
	0.2	1.8	5.66
	2	1.7	4.82
DVB-1	0	2.0	7.59
	0.2	2.0	6.10
	2	1.8	5.40
DVB-9	0	2.0	8.25
	0.2	2.0	6.62
	2	2.0	5.94

Similarly, the n values decrease with increasing salt concentration in both cases, but the decrease is less pronounced with the resin. This effect appears to be based upon the fact that the effective salt concentration in the resin is always smaller than that in the ambient solution, again due to Donnan effects.⁶

The second comparison, between XE 89 and DVB-1, shows that the methacrylic acid polymer is a weaker acid than the corresponding acrylic one under all conditions. This probably reflects the inductive effect of the methyl group which is shown also in the corresponding monomeric analog (*e.g.*, propionic and isobutyric acids). Also, it is noted that increasing the salt concentration has less effect upon pK_a and n with the methacrylic polymer than with the acrylic polymer. This might be attributed to the greater flexibility of the acrylic polymer.

The third comparison, between DVB-1 and DVB-9, shows an apparent decrease in acid strength with increasing cross-linking. The n parameter for DVB-9 is less affected by salt. These effects are in concordance with expectation, based on the fact that the higher cross-linked resin sorbs less salt and is more rigid.

Complexation Results.—Figure 1 shows plots of \bar{n} *vs.* $p[HA]/[H^+]$ for DVB-1 and DVB-9 (methacrylic), and XE 89 (acrylic) resins in 0.2 M sodium nitrate; these are representative of similar plots obtained in other salt concentrations which are not shown in the figure. Again, as in the case of the copper complexes with linear PAA described earlier,² points corresponding to different copper concentrations fall on the same line, attesting to the general validity of the approach used. One significant difference can be observed between the plots for the linear and cross-linked compounds. In the latter case the plots show a definite tendency to flatten out toward a value of $\bar{n} = 2$ as $p[HA]/[H^+]$ becomes more negative. This is strong evidence for a maximum coordination number of two in this case as opposed to a higher one (possibly four) in the linear case.

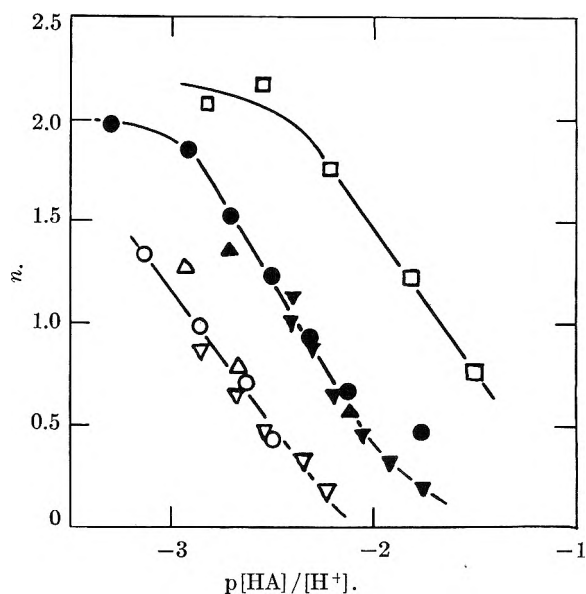


Fig. 1.—Modified Bjerrum plots for cross-linked acrylic (XE 89) and methacrylic acids (DVB-1, DVB-9) and Copper(II) in 0.2 M NaNO₃: XE 89, 0.00428 M Cu(II) (□); DVB-1, 0.00328 M Cu(II) (▲); 0.00656 M Cu(II) (●); 0.0164 M Cu(II) (▼); DVB-9, 0.00328 M Cu(II) (△); 0.00656 M Cu(II) (○); 0.0164 M Cu(II) (▽).

The explanation for this presumably lies in the considerable rigidity of the polyelectrolyte chain in the cross-linked resin which prevents ring closure involving more than two neighboring groups.

Values of complexation constants for the copper-resin systems are given in Table II. For comparison, the data with linear PAA are also included. The presentation of the data is organized in the same fashion as in the corresponding table in the report on linear PAA,² except the last column here (K_2') which gives the over-all conventional complexation constant for the two-step reaction, calculated from colorimetric data.

(6) H. P. Gregor, F. Guttoff and J. I. Bregman, *J. Colloid Sci.*, **6**, 245 (1951).

TABLE II
COMPLEXATION CONSTANTS OF COPPER WITH CROSS-LINKED AND LINEAR CARBOXYLIC ACIDS

Polymer acid	Concn. of NaNO ₃ , M	log B _{av}	B ₂	b ₁ /b ₂	K ₂	K ₂ '
PAA (0.01 N)	0	-1.19	4.2 × 10 ⁻³	2.1	9.1 × 10 ⁹	
	0.2	-1.17	4.6 × 10 ⁻³	0.76	3.0 × 10 ⁷	
	2	-0.99	1.05 × 10 ⁻²	0.33	9.6 × 10 ⁶	
XE 89	0.2	-1.67	4.57 × 10 ⁻⁴	1.2	9.55 × 10 ⁷	
	2	-1.70	3.98 × 10 ⁻⁴	1.4	1.73 × 10 ⁶	
DVB-1	0	-2.35	2.00 × 10 ⁻⁵	0.31	3.02 × 10 ¹⁰	1.4 × 10 ⁷
	0.2	-2.40	1.59 × 10 ⁻⁵	0.77	2.51 × 10 ⁷	3.2 × 10 ⁶
	2	-2.70	3.98 × 10 ⁻⁶	13	2.51 × 10 ⁵	9.3 × 10 ⁴
DVB-9	0	-2.70	3.98 × 10 ⁻⁶	0.31	1.26 × 10 ¹¹	5.1 × 10 ⁷
	0.2	-2.89	1.66 × 10 ⁻⁶	2.7	2.88 × 10 ⁷	8.3 × 10 ⁵
	2	-3.06	6.03 × 10 ⁻⁷	31	5.75 × 10 ⁵	1.0 × 10 ⁵

Observation of the values for the complexation constants B₂ in column four shows the following trends: in all resin systems the complexation is considerably weaker than in the linear case; this is again undoubtedly due to the greater rigidity of the cross-linked chains. This view is borne out by comparison between the values found for the DVB-9 and DVB-1 resins; the more highly cross-linked and therefore "stiffer" DVB-9 system shows the smaller constants. Also, both methacrylic systems show lower constants than the acrylic resin XE 89, which can be considered more flexible.

The variation of B₂ with salt concentration is again slight; it is, however, in opposite directions in the case of the linear and cross-linked materials. Examination of column five makes the reason for this apparent. While the spreading factor b₁/b₂ increases with increasing salt concentration for cross-linked systems, it decreases for linear PAA. This shows that while b₁, the constant for the first step, is quite unaffected by salt concentration changes, the second constant b₂ decreases considerably for cross-linked systems but increases for linear sys-

tems. It can be surmised that the latter is due to the chain contraction which brings successive complexing groups into closer proximity with one another and which outweighs a simple activity effect which alone is operative in the cross-linked case.

The discrepancy between the values of K₂, obtained from B₂ by the use of equation 6 of reference 2, and of K₂', obtained directly from copper analyses, is considerable in low salt concentrations. Part of this discrepancy undoubtedly is due to the lack of significance of the constant K₂ as explained in reference 2, and part of it reflects the lack of validity of the assumption that the Donnan equilibrium is swamped inside the resin particle, as was pointed out above. The agreement at high salt concentrations is satisfactory, as expected.

This investigation was supported in part by a research grant, RG 2934(C2), from the Division of Research Grants of the National Institutes of Health, Public Health Service. We also wish to express our gratitude to the Rohm and Haas Company which provided us with samples of the polyacrylic acid resin used in this investigation.

THE REACTION OF ACTIVE NITROGEN WITH NEOPENTANE¹

BY M. ONYSZCHUK² AND C. A. WINKLER

¹Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, Canada

Received October 14, 1954

Besides large quantities of hydrogen cyanide, small amounts of ethylene, acetylene, propylene and propane were recovered from the reaction of active nitrogen with neopentane. Second-order rate constants were calculated for the reaction at eight temperatures between -40 and 350°. An Arrhenius plot showed a pronounced curvature with definite indication of two activation energies; the average values of these were 2.0 ± 0.5 and 7.1 ± 0.6 kcal./mole in the range -40 to 115° and 150 to 350°, respectively, with corresponding steric factors of about 10⁻⁶ and 10⁻³. This observation was interpreted to indicate a composite reaction due to alternative modes of active nitrogen attack on the neopentane molecule, to the presence of two reactive species in the active nitrogen stream, or possibly to the influence of simultaneous hydrogen atom reactions.

Activation energies have been estimated for the reactions of active nitrogen with ethane,³ propane,⁴ and isobutane,⁵ *i.e.*, for reactions involving hydrocarbons containing bonds between a primary carbon

atom and a primary, secondary and tertiary carbon atom, respectively. To examine further the behavior of various carbon-carbon bonds in these reactions, it was of interest to investigate the active nitrogen-neopentane reaction in which bonds between a quaternary and primary carbon atoms would be concerned.

Experimental

The apparatus and analytical methods used in this investigation have been described in previous papers from this

(1) With financial assistance from the National Research Council of Canada.

(2) Holder of National Research Council Studentships 1952-1954.

(3) H. Blades and C. A. Winkler, *Can. J. Chem.*, **29**, 1022 (1951).

(4) M. O. Onyszchuk, L. Breitman and C. A. Winkler, *ibid.*, **32**, 351 (1954).

(5) R. A. Back and C. A. Winkler, *ibid.*, **32**, 718 (1954).

Laboratory. The molecular nitrogen flow rate was maintained constant at 5.83×10^{-6} mole per sec., which gave a pressure of 1.34 mm. of mercury in the flow system, while neopentane flow rates were varied from about 5×10^{-7} to 1.5×10^{-6} mole per sec. The flow rate of active nitrogen, produced by a condensed discharge, remained constant during the course of a series of experiments at any given temperature, and changed only after the reaction vessel was cleaned with chromic acid and re-poisoned with meta-phosphoric acid.

Two grades of neopentane, obtained from Phillips Petroleum Company, were used; one was "pure grade" with a minimum purity of 99 mole %, the other was "research grade" with a certified purity of 99.87 mole % (the most probable impurity was isobutane). Both grades of neopentane were used after the usual procedure of degassing and a simple trap-to-trap distillation.

In one series of experiments with 99% neopentane complete analysis of reaction products was made.⁶ Three or more experiments were conducted at each of seven temperatures in the range 55 to 250°. Temperatures were attained and manually controlled to within $\pm 5^\circ$ by an electrically heated furnace, and were measured with a copper-constantan thermocouple situated at the outlet of the hydrocarbon jet in the center of the reaction vessel. Three experiments were also made at a reaction flame temperature of -40° , during which the walls of the reaction vessel were kept at Dry Ice temperature.

After the reaction vessel was cleaned and re-poisoned so that a different active nitrogen concentration prevailed,⁷ some check experiments were made with neopentane of 99.87% purity, but without complete product analysis. The results obtained for analyses of hydrogen cyanide and total $C_2 + C_3$ hydrocarbons confirmed the essential characteristics of the reaction established in the preceding series of experiments, and since the data for the 99% neopentane are more complete, only the results of these experiments are reported in detail.

Results

Hydrogen cyanide was the principal product of the active nitrogen-neopentane reaction and the only one that contained nitrogen. It was recovered in yields of 92–99% of the neopentane consumed by reaction at 250°, while the percentage neopentane converted to products varied from 5.8% at the highest to 33.5% at the lowest neopentane flow rate used. From Fig. 1, which illustrates the yields of products from experiments with 99% neopentane, it is evident that complete consumption of active nitrogen, indicated by constant hydrogen cyanide production, was attained only at 250° for neopentane flow rates greater than about 6×10^{-6} mole per sec. The maximum yield of hydrogen cyanide, 4.6×10^{-6} mole per sec., presumably corresponds to the concentration of active nitrogen available for reaction with neopentane at any temperature. For reaction temperatures less than 250°, the observed gradual increase in hydrogen cyanide formation with increasing neopentane flow rate represents a progressive depletion in concentration of active nitrogen.

Secondary products, recovered in measurable amounts at all neopentane flow rates, were ethylene, acetylene, propylene and propane. Ethane was also detected but only in trace quantities. The variations in yields of secondary products with neopentane flow rate, shown in Fig. 1, indicate a general behavior similar to that observed in the propane reaction.⁴

Since the sum of secondary products from the neopentane reaction, as in the propane system, ac-

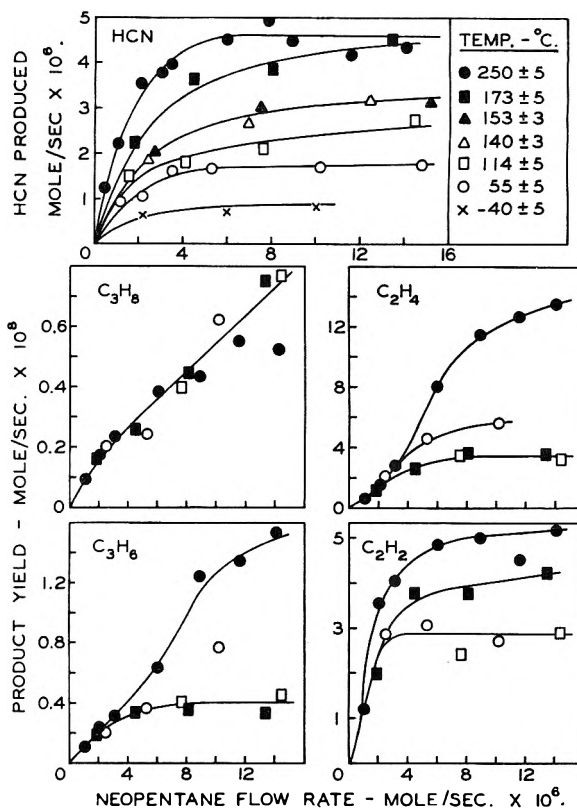


Fig. 1.

counted for less than 10% of hydrocarbon consumption, the neopentane that reacted was almost completely degraded to hydrogen cyanide. This suggests that the mechanism of the neopentane reaction probably consists of an initial step which is rate-controlling followed by a series of rapid consecutive reactions which produce hydrogen cyanide. If the primary attack of active nitrogen on neopentane is considered to be rate-determining, the over-all reaction can be shown to obey the second order rate law.³ Streamline and turbulent flow conditions in the spherical reaction vessel were assumed as alternatives for the calculation of second-order rate constants, with the results summarized in Table I, together with those derived from experiments with 99.87% neopentane.

TABLE I
SECOND-ORDER RATE CONSTANTS AT VARIOUS TEMPERATURES FOR THE ACTIVE NITROGEN-NEOPENTANE REACTION

Temp., °C.	Streamline flow	Turbulent flow
	$k \times 10^{-4}$, l. mole ⁻¹ sec. ⁻¹	$k \times 10^{-4}$, l. mole ⁻¹ sec. ⁻¹
99% Neopentane		
-40 ± 5	0.37	1.0
55 ± 5	1.5	4.7
114 ± 5	2.5	8.1
140 ± 3	3.3	12
153 ± 3	3.8	15
173 ± 5	7.2	40
250 ± 5	20	110
99.87% Neopentane		
-35 ± 5	0.67	1.8
47 ± 3	1.6	4.7
150 ± 5	6.4	23
245 ± 5	14	83
360 ± 5	43	410

(6) We are grateful to Dr. H. I. Schiff of this department for mass spectrometer analyses.

(7) G. S. Trick and C. A. Winkler, *Can. J. Chem.*, **30**, 915 (1952).

Although values for turbulent flow were consistently higher than those for streamline flow, an Arrhenius plot, shown in Fig. 2, clearly indicates

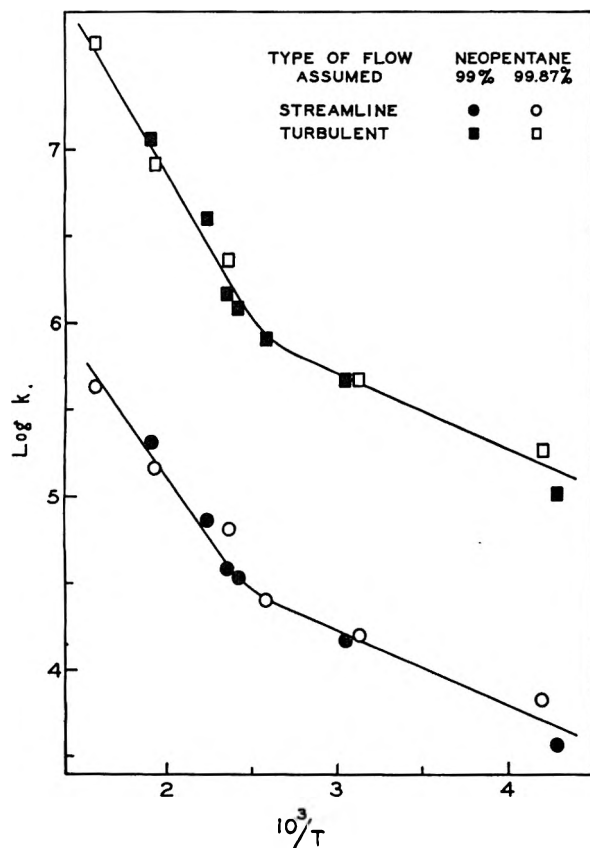


Fig. 2.

a parallel behavior for both sets of data. Since reproducible results were obtained with both grades of neopentane in spite of a difference in experimental conditions, it is concluded that the curvature in the activation energy plot is a genuine effect. From the slopes of the two nearly linear portions of the plots, the activation energies shown in Table II were estimated. Actual flow conditions were probably somewhere between the two extremes assumed and the individual values of the activation energies may be taken to represent the limits within which the true values probably lie. Frequency factors, A , in the Arrhenius equation, calculated for the reaction at 55 and 250°, are recorded in Table III, together with steric factors, P , calculated from collision theory by using 3.0 and 6.0 Å for the collision diameters of atomic nitrogen⁸ and neopentane,⁹ respectively.

TABLE II
ACTIVATION ENERGIES FOR THE ACTIVE NITROGEN-NEOPENTANE REACTION

Temp. range, °C.	E , kcal./mole		Av.
	Streamline flow	Turbulent flow	
-40 to 115	2.0	2.0	2.0 ± 0.5
150 to 350	6.5	7.7	7.1 ± 0.6

(8) J. H. Greenblatt and C. A. Winkler, *Can. J. Research*, **B27**, 732 (1949).

(9) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

Discussion

The following table indicates the relative position of neopentane, with its bonds between quaternary and primary carbon atoms, in a series of hydrocarbons for which activation energies and steric factors have now been estimated for the reactions with active nitrogen

Hydrocarbon	E , kcal./mole	P
Methane	11	5×10^{-3}
(Neopentane)	7.1	10^{-4} to 10^{-2}
Ethane	7.0	10^{-3} to 10^{-1}
Propane	5.6	10^{-4} to 10^{-2}
<i>n</i> -Butane	3.6	4×10^{-4}
Isobutane	3.1	4×10^{-4}
(Neopentane)	2.0	10^{-6} to 10^{-8}

It is possible that suitable extension of experimental conditions might show some of the reactions other than that with neopentane to be characterized by two activation energies. Only in the study of the ethane reaction³ were rate constants determined at several temperatures, and a linear plot was obtained over the range 100 to 300°. However, experiments were not extended to lower temperatures, where the curvature in the activation energy plot for neopentane becomes apparent.

The obvious conclusion to be drawn from the detection of two activation energies for the neopentane reaction is that the over-all reaction is composite. This might be attributed to different modes of active nitrogen attack on the neopentane molecule, to the presence of two reactive species in the active nitrogen stream, or possibly to the influence of hydrogen atom reactions which produce radicals that react rapidly with active nitrogen. It is improbable that surface effects at low temperatures would give rise to the non-linear Arrhenius plot. If surface were responsible, erratic yields of hydrogen cyanide might be expected for experiments at low temperatures, since some condensation and slight polymerization of hydrogen cyanide on the walls of the reaction vessel were observed after several experiments at -40°. No such behavior was apparent at higher reaction temperatures, yet reproducible results were obtained at any given temperature.

Active nitrogen reaction with neopentane in two different ways immediately suggests that one activation energy corresponds to attack at a methyl group, the other to attack at the central carbon atom. The smaller steric factor, about 5×10^{-5} , would be reasonably assigned to the latter. However, this is, in turn, associated with the smaller activation energy of 2 kcal. per mole. It is difficult to conceive of a mode of attack at the central carbon atom that would have an activation energy lower than reaction at the primary carbon atoms, and at the same time satisfactorily account for the relatively small change in composition of secondary products with temperature. In fact, it is difficult to understand how the focus of reaction at the quaternary carbon atom could give rise to the products isolated at any temperature. However, the unusual behavior of neopentane in other reactions makes it difficult to rule out different modes of active nitrogen attack. For example, compared with

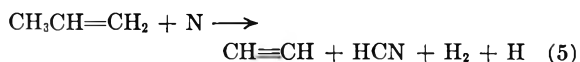
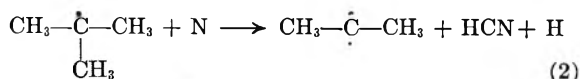
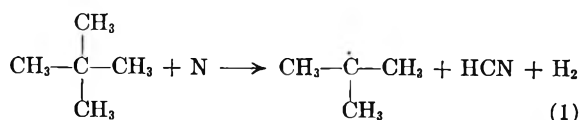
TABLE III
KINETIC CONSTANTS FOR THE ACTIVE NITROGEN-NEOPENTANE REACTION

Flow condition assumed	Temp., °C.	k	A l. mole ⁻¹ sec. ⁻¹	Z	P	E , kcal./mole
Streamline	55	1.5×10^4	3.2×10^6	3.0×10^{11}	1.1×10^{-6}	2.0
	250	2.0×10^6	1.0×10^8	3.7×10^{11}	2.7×10^{-4}	6.5
Turbulent	55	4.7×10^6	1.0×10^7	3.0×10^{11}	3.3×10^{-6}	2.0
	250	1.1×10^7	1.8×10^{10}	3.7×10^{11}	4.9×10^{-3}	7.7

the lower paraffins neopentane is surprisingly inert to mercury photosensitization. The low quantum yield found by Darwent and Steacie¹⁰ was attributed to the predominant role of symmetry of the neopentane molecule in this reaction. In this way neopentane resembles methane rather than ethane which has carbon-hydrogen bonds of strength similar to those in neopentane. On the other hand, neopentane behaves like ethane in reaction with atomic hydrogen produced by a discharge, since both reactions proceed at approximately the same rate, with activation energies of about 9 kcal. per mole, assuming a steric factor of 0.1.¹¹ Unlike the results for other paraffins, the most remarkable feature of the atomic hydrogen-neopentane reaction at 24° is the comparatively high yield of ethane and its increase with increasing hydrogen atom concentration.

An alternative interpretation of the two activation energies in the active nitrogen-neopentane reaction may involve the presence of two reactive species in active nitrogen, which perhaps react with neopentane at different rates. Since no apparent differences were observed in the composition of secondary products recovered in the two activation energy regions, both species would probably have to react by similar, though perhaps not identical, mechanisms. It is generally agreed that nitrogen atoms are produced in the discharge tube, and it is

likely that they constitute a chemically reactive species. It would seem, therefore, that the type of reaction mechanism involved might be analogous to those previously outlined with the assumption of atomic nitrogen as the only active species.^{4,5} Briefly, this would involve for neopentane the following main reactions



Reactions 4 and 5 might be followed by further reactions of nitrogen atoms with ethylene¹² and acetylene.¹³ If reaction 1 is the rate-controlling step, while subsequent reactions are very rapid, this mechanism predicts extensive conversion of neopentane to hydrogen cyanide and relatively small recovery of secondary unsaturated products, in agreement with the kinetic behavior shown in Fig. 1.

(10) B. deB. Darwent and E. W. R. Steacie, *Can. J. Research*, **B27**, 181 (1949).

(11) W. R. Trost and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 361 (1948).

(12) J. Versteeg and C. A. Winkler, *Can. J. Chem.*, **31**, 1 (1953).

(13) J. Versteeg and C. A. Winkler, *ibid.*, **31**, 129 (1953).

THE REACTION OF ACTIVE NITROGEN WITH AMMONIA¹

By G. R. FREEMAN² AND C. A. WINKLER

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec¹

Received October 14, 1954

Active nitrogen has been found to destroy ammonia to an optimal extent which is independent of temperature over a wide range, and which represents approximately one-sixth of the total activity in the nitrogen, determined from its ability to form hydrogen cyanide with ethylene. It is concluded that there are at least two chemically reactive species in active nitrogen.

The reactions of active nitrogen with a number of hydrocarbons (and alkyl halides) have been studied in this Laboratory, and tentatively interpreted by assuming atomic nitrogen to be the only reactive species in the active nitrogen. However, a recent investigation of the analogous reaction with

neopentane³ has indicated that more than one reactive species may exist in active nitrogen. The present study of the ammonia-active nitrogen reaction appears to provide unambiguous information on this point. Previous studies by Willey and Rideal⁴ indicated that ammonia was readily decomposed

(1) With financial assistance from the National Research Council of Canada.

(2) Holder of a Fellowship under the National Research Council of Canada.

(3) M. Onyszczuk and C. A. Winkler, *J. Phys. Chem.*, **59**, 368 (1955).

(4) (a) E. J. B. Willey and E. K. Rideal, *J. Chem. Soc.*, 669 (1927); (b) J. K. Dixon and W. Steiner, *Z. physik. Chem.*, **B17**, 327 (1932).

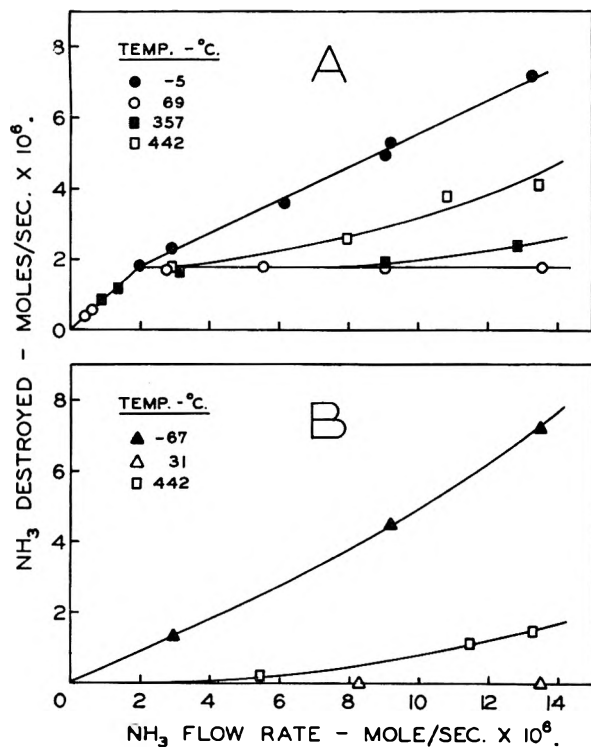


Fig. 1.

to nitrogen and hydrogen by active nitrogen, while Dixon and Steiner⁵ observed a low reactivity.

Experimental

The apparatus was essentially the same as that described in earlier papers.⁵

Anhydrous ammonia (Canadian Industries Ltd.) and C.P. ethylene (Ohio Chemical Co.) were used.

The molecular nitrogen flow rate was 9.2×10^{-5} mole/sec., corresponding to a pressure of 1.43 mm. in the reaction vessel. In some experiments, where hydrogen atoms replaced active nitrogen, the molecular hydrogen flow rate was 6.9×10^{-5} mole/sec., which gave an operating pressure of 0.85 mm.

In several experiments, the reaction vessel was surrounded by powdered Dry Ice. While the wall temperature may be assumed to have been approximately -78° , the temperature of the gases in the reaction vessel, as indicated by a glass encased thermocouple, was of the order -5° and -68° during the active nitrogen and hydrogen atom reactions, respectively.

Condensable products were collected in a trap containing 10 ml. of standard sulfuric acid, immersed in liquid nitrogen. The amount of ammonia passed into the reaction vessel was estimated from the change in pressure in a storage vessel of known volume, while the amount remaining unreacted was determined by titration to methyl red end-point of the excess acid after it had been allowed to melt in the trap. The amount of ammonia consumed was then given by the difference between these quantities. The presence of hydrogen cyanide did not affect the titration.

Hydrogen cyanide was analyzed by the Liebig-Dénigès method.⁶

To test for hydrazine, the condensable products were collected in a trap containing 3 ml. of concd. hydrochloric acid, immersed in liquid nitrogen. To the warmed trap, 15 ml. of distilled water and one ml. of carbon tetrachloride were added, followed by 0.01 N potassium iodate added dropwise to the continuously shaken mixture. Blank experiments indicated that the iodine liberated by 0.05 mg. of hydrazine imparted sufficient color to the carbon tetrachloride to permit its detection.

Results and Discussion

The yellow after-glow of active nitrogen has been observed to be quenched at all except very low flow rates of hydrocarbons or alkyl chlorides. With ammonia, however, the after-glow was not quenched completely even at the highest flow rates used.

No hydrazine was detected as a product from the active nitrogen-ammonia reaction over the temperature range -5 to 440° . The reaction products may therefore be assumed to be hydrogen and nitrogen only.

The relation between ammonia flow rate and the amount destroyed by active nitrogen is shown in Fig. 1A for different temperature conditions. The increased amounts of ammonia consumed at the low and high temperatures, relative to the optimal value at 69° , were suspected to be due to secondary hydrogen atom attack. This was verified by studying the hydrogen atom-ammonia reaction over the same temperature range, with the results shown in Fig. 1B. No hydrazine was detected in the products of the hydrogen atom reaction at any temperature. Although a more intensive study of the reaction is contemplated for its obvious intrinsic interest, present results are adequate to conclude that a change of mechanism in the hydrogen atom reaction probably occurs with change of temperature, and that the reaction between active nitrogen and ammonia is unaffected by temperature over the range investigated. It follows, therefore, that the constant amount (1.77×10^{-6} mole/sec.) of ammonia destroyed at 69° , for ammonia flow rates above 2×10^{-6} mole/sec., corresponds to complete consumption of the active nitrogen with which ammonia is capable of reacting.

When ethylene alone, and mixtures of ethylene and ammonia were subjected to attack by the active nitrogen, the results shown in Fig. 2 were obtained. As in previous studies, the constant rate of HCN formation with ethylene flow rates above about 9×10^{-6} mole/sec. may be taken to represent complete consumption of the active nitrogen which can react with ethylene. It is apparent, then, that active nitrogen produced under similar conditions was capable of producing HCN from ethylene at a rate 5.7 times greater than it was capable of destroying ammonia. Having regard particularly for the negligible influence of temperature on the ammonia reaction, the difference in behavior of ammonia and ethylene is difficult, if not impossible, to explain by any reasonable scheme based on a single reactive species in active nitrogen such as, for example, partial deactivation by ammonia without decomposition.

On the other hand, it is readily explained if two reactive species are assumed to be present, one of which is capable of reacting with ammonia while the other, or both, may react with ethylene.⁷

The possible identities of the two reactive species are largely a matter of conjecture. However, since there appears to be no evidence for the pres-

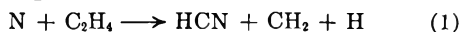
(7) Although the present results do not preclude the possibility that more than two reactive species are present in active nitrogen (for example, different excited states of atoms and/or molecules), it seems reasonable as a working hypothesis to limit consideration to two until such time as further investigation might require recognition of more than this number.

(5) (a) H. Blades and C. A. Winkler, *Can. J. Chem.*, **29**, 1022 (1951); (b) J. H. Greenblatt and C. A. Winkler, *ibid.*, **B27**, 721 (1949).

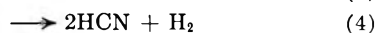
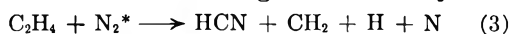
(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1946.

ence of significant quantities of ions,^{8,9} it seems reasonable to suggest that the two species are atoms and excited molecules or N_3 . It also seems reasonable to assume that nitrogen atoms, rather than excited molecules or N_3 , might attack the ammonia molecule at the site of its free pair of electrons to cause the high rate of destruction observed experimentally. The present results also indicate that a facile equilibrium does not exist between the two species, whatever their identities.

The energy required to dissociate an N_3 or an excited N_2 molecule should make the reaction of these particles with ethylene slower, and of higher activation energy, than the reaction of nitrogen atoms. However, if excited molecules are assumed to be the second reactive species, the relatively high rate of the active nitrogen-ethylene reaction might be explained by assuming a chain reaction initiated by atomic nitrogen, for example



Some formation of HCN might also occur by



If N_3 were the other reactive species, the reactions would be essentially the same as those of N (with the additional production of N_2), and no chain reaction would seem to be possible unless hydrogen atoms or hydrocarbon fragments were the chain carriers.

It might be suggested that if reaction (3) occurred the destruction of ammonia should be greater

(8) J. M. Benson, *J. Appl. Phys.*, **23**, 757 (1952).

(9) R. E. Worley, *Phys. Rev.*, **73**, 531 (1948).

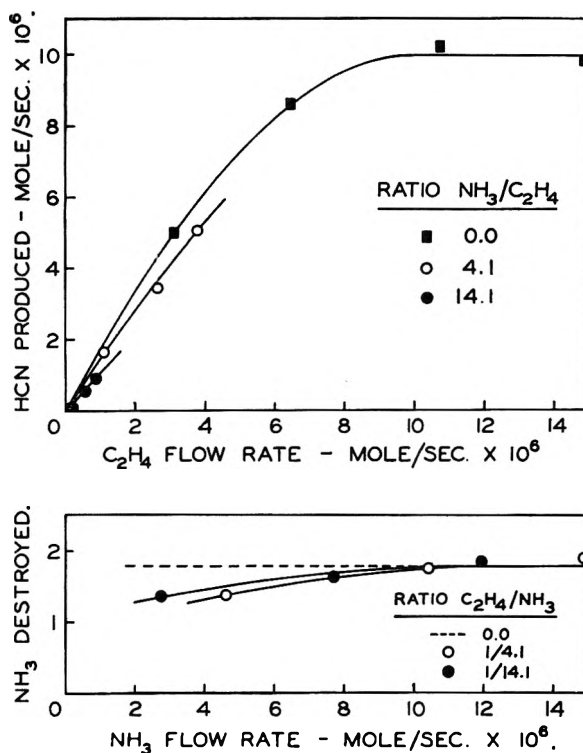


Fig. 2.

in the presence of appropriate amounts of ethylene than in pure ammonia. However, a nitrogen atom formed in such a reaction would be available for attacking ammonia in an ammonia-ethylene mixture only if it were not rapidly consumed by the CH_2 radical formed simultaneously with it.

CONDUCTANCES OF SOME QUATERNARY AMMONIUM BROMIDES AND IODIDES IN DIMETHYLFORMAMIDE AT 25°¹

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Received October 15, 1954

The conductances of several quaternary ammonium bromides and iodides in dimethylformamide have been measured at 25°. In each case, the observed slope of the plot of the equivalent conductance versus the square root of the concentration was more negative than that predicted by the Onsager equation. Limiting equivalent conductances and dissociation constants have been determined by the Shedlovsky extrapolation method. The quaternary ammonium halides being dissociated to a lesser extent than some potassium and sodium halides is strong evidence that the latter cations are rather highly solvated in dimethylformamide. Bromides were found to be $1.6 \pm 0.1 \text{ ohm}^{-1} \text{ cm.}^2$ more conducting than the corresponding iodides. Data are presented showing that the ratio of the conductance in acetone to that in dimethylformamide is 2.32 ± 0.09 for each of seventeen salts.

Introduction

The objective of this investigation has been to extend the study of electrolytes in dimethylformamide by comparing the conductimetric behavior of several quaternary ammonium bromides and iodides with that of potassium and sodium bromides and iodides. In a previous paper² from this Laboratory, it has been reported that the potassium and sodium salts, with the exception of sodium bromide

which has a dissociation constant of 0.13, are completely dissociated in dimethylformamide. These results were rather surprising owing to the fact that this solvent has a dielectric constant of only 36.71.³ Although the exact cause of the pronounced dissociation of the alkali halides was unknown, it was suspected to be the result of solvation effects. Inasmuch as quaternary ammonium ions are considered to be practically non-solvated in most solvents, whereas the degrees of solvation and effective sizes

(1) Based in part upon research performed under a contract with the U. S. Army Signal Corps.

(2) D. P. Ames and P. G. Sears, *THIS JOURNAL*, **59**, 16 (1955).

(3) G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

of the potassium and sodium ions vary from solvent to solvent, it was believed that some evidence of cationic solvation effects might be obtained through a comparative study of the conductimetric behavior of these cations having common anions in dimethylformamide.

Experimental

Dimethylformamide was allowed to stand in contact with solid potassium hydroxide for several days. After decanting, the liquid was fractionated at atmospheric pressure. The large middle fraction, which was obtained, was fractionally distilled again at 10 mm. pressure. The final middle portion, which was retained, had a conductivity in the range of $0.6\text{--}2.0 \times 10^{-7}$ ohm $^{-1}$ cm. $^{-1}$.

Et $_4$ N $^+$ I $^-$ and Pr $_4$ N $^+$ Br $^-$ were synthesized from the proper alkyl halides and tertiary amines by standard procedures. The other quaternary ammonium salts were commercial products. Each salt was recrystallized at least twice from a suitable solvent and dried to constant weight in a vacuum oven at 60°.

The bridge, cells and procedure of the conductance measurements have been described previously.² The temperature of the oil thermostat was maintained at $25.00 \pm 0.02^\circ$ by an electronic relay.

The following data for dimethylformamide at 25° were used in the calculations: dielectric constant, 36.71; viscosity, 7.96×10^{-3} poise; density, 0.9443 g./ml.

Results and Discussion

The experimental results,⁴ representing the combination of data from either two or three independent series of solutions for each salt, are shown graphically in Fig. 1. Values of the limiting equivalent

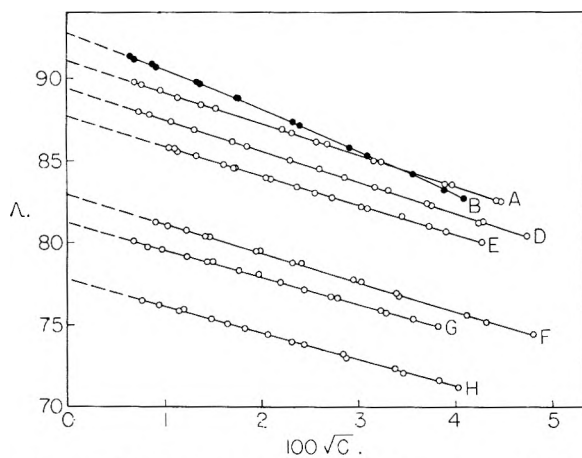


Fig. 1.—Plots of Λ versus \sqrt{C} for some quaternary ammonium salts in dimethylformamide at 25°: A, Me $_4$ N $^+$ I $^-$; B, Me $_4$ N $^+$ Br $^-$; D, Et $_4$ N $^+$ Br $^-$; E, Et $_4$ N $^+$ I $^-$; F, Pr $_4$ N $^+$ Br $^-$; G, Pr $_4$ N $^+$ I $^-$; H, Bu $_4$ N $^+$ I $^-$.

conductances obtained by the linear extrapolation of a large plot of Λ versus \sqrt{C} for each salt may be found in Table I together with other data pertinent to the comparison of the experimental and the theoretical slopes. Because the slope of each plot was found to be more negative than that calculated by the Onsager equation, the Shedlovsky extrapolation method⁵ was employed for determining better limiting equivalent conductance values. Shedlovsky plots for the quaternary ammonium bromides and iodides may be found in Fig. 2. Data pertinent to the limiting equivalent conductances, dissociation constants and degrees of

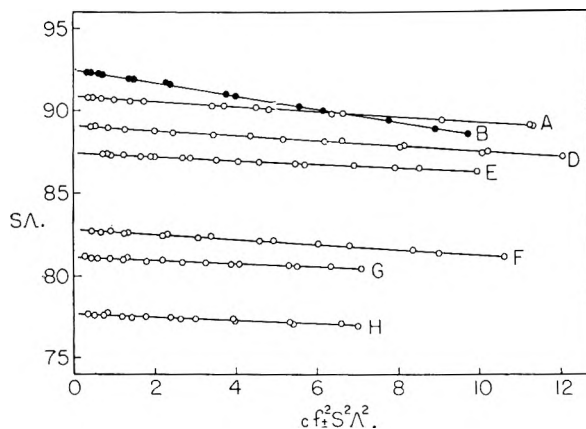


Fig. 2.—Plots of the Shedlovsky extrapolation equation for some quaternary ammonium salts in dimethylformamide at 25°: same as that given for Fig. 1.

dissociation of the quaternary ammonium salts based on the Shedlovsky method are presented in Table II.

TABLE I

TEST OF ONSAGER'S EQUATION FOR SOLUTIONS OF SOME QUATERNARY AMMONIUM BROMIDES AND IODIDES IN DIMETHYLFORMAMIDE AT 25°

Salt	Λ_0 , ohm $^{-1}$ cm. 2	Exptl. negative slope (S ϵ)	Theor. negative slope (S τ)	$S_{\epsilon} - S_{\tau}$ 100 S τ
Me $_4$ NBr	92.7	215	165	30
Me $_4$ NI	91.0	190	164	16
Et $_4$ NBr	89.3	188	163	15
Et $_4$ NI	87.5	175	162	8
Pr $_4$ NBr	82.8	174	158	10
Pr $_4$ NI	81.1	163	157	4
Bu $_4$ NI	77.7	160	155	3

TABLE II

LIMITING EQUIVALENT CONDUCTANCES, DISSOCIATION CONSTANTS AND DEGREES OF DISSOCIATION OF SOME QUATERNARY AMMONIUM BROMIDES AND IODIDES IN DIMETHYLFORMAMIDE AT 25° BY THE SHEDLOVSKY METHOD

Salt	Λ_0	K	θ at 0.001 N
Me $_4$ NBr	92.5	0.027	0.973
Me $_4$ NI	90.9	.069	.988
Et $_4$ NBr	89.2	.062	.987
Et $_4$ NI	87.5	.082	.991
Pr $_4$ NBr	82.8	.081	.991
Pr $_4$ NI	81.1	.12	.993
Bu $_4$ NI	77.7	.12	.993

It may be observed that the degree of dissociation, θ , for each salt in a $1 \times 10^{-3} N$ dimethylformamide solution is rather high, although, for a common anion, it tends generally to increase slightly with increasing size of the quaternary ammonium cation. Furthermore, the iodides are dissociated in all cases to a greater extent than the corresponding bromides. The dissociation constants for Pr $_4$ NI and Bu $_4$ NI are essentially equal to 0.13 which is the value previously reported for sodium bromide,² but they are less than the infinite dissociation constants of potassium bromide, and potassium and sodium iodides in this solvent.

The data in Table III show that the difference between the limiting equivalent conductances of bromide and iodide salts having a common cation is

(4) Complete tables of experimental data may be obtained upon request from the Department of Chemistry, University of Kentucky.

(5) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

$1.6 \pm 0.1 \text{ ohm}^{-1} \text{ cm.}^2$ for each of five pairs of salts. This constant difference not only substantiates the Kohlrausch law of independent ion migration in this solvent, but also attests to the general consistency of the results. Assuming a constant ionic conductance for an anion irrespective of the cation with which it is associated, the limiting cationic conductances can be arranged in the following series of increasing conductance: $\text{Bu}_4\text{N}^+ < \text{Pr}_4\text{N}^+ < \text{Na}^+ < \text{K}^+ < \text{Et}_4\text{N}^+ < \text{Me}_4\text{N}^+$. The positions of the sodium and potassium ions in this series, indicating that their effective sizes and ionic conductances closely approximate that of the tetra-*n*-propylammonium ion, constitute strong evidence that these ions are rather highly solvated in dimethylformamide. This may account in part for the potassium and sodium salts being dissociated to such a large extent.

TABLE III

LIMITING EQUIVALENT CONDUCTANCES ($\text{OHM}^{-1} \text{ CM.}^2$) OF BROMIDE AND IODIDE SALTS HAVING COMMON CATIONS IN DIMETHYLFORMAMIDE AT 25°

	Pr_4N^+	Na^+	K^+	Et_4N^+	Me_4N^+
Bromide	82.8	83.4 ^a	84.1 ^a	89.2	92.5
Iodide	81.1	81.9 ^a	82.6 ^a	87.5	90.9
Difference	1.7	1.5	1.5	1.7	1.6

^a From reference 2.

A search of the literature revealed that the limiting ionic conductances for these six cations in acetone^{6,7} fall into the same series arrangement. A closer comparison of the conductimetric behavior

(6) M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).

(7) M. J. McDowell and C. A. Kraus, *ibid.*, **73**, 3293 (1951).

of electrolytes in these two solvents produced the results which are presented in Table IV.

TABLE IV

RATIO OF THE LIMITING EQUIVALENT CONDUCTANCE OF SOME SALTS IN ACETONE^{6,7} TO THAT IN DIMETHYLFORMAMIDE² AT 25°

Salt	$\frac{\Lambda_0(\text{Acetone})}{\Lambda_0(\text{DMF})}$	Salt	$\frac{\Lambda_0(\text{Acetone})}{\Lambda_0(\text{DMF})}$
Me_4NI	2.31	Me_4NBr	2.31
Et_4NI	2.33	Et_4NBr	2.32
Pr_4NI	2.35	Pr_4NBr	2.35
Bu_4NI	2.31	KBr	2.34
KI	2.34	NaBr	2.33
NaI	2.33	KClO ₄	2.37
KNO_3	2.28	NaClO_4	2.36
NaNO_3	2.28	KSCN	2.24
		NaSCN	2.23

It may be observed from Table IV that the conductance ratio is 2.32 ± 0.09 , *i.e.*, constant within 4%, for each of the seventeen salts. This close correspondence of conductance phenomena probably results from similar solvation effects occurring in these media. If the solvating power of a medium depends upon its ability to donate electrons, the solvating powers of acetone and dimethylformamide should be somewhat comparable since both are electron donors. The observed conductance ratio of 2.32 ± 0.09 being less than the calculated viscosity ratio of 2.62 implies that the ions may be effectively greater in size in acetone than in dimethylformamide. Thus, while general solvation effects probably are quite similar in these media, the degree of solvation of ions appears to be greater in acetone than in dimethylformamide. Therefore, acetone possesses the greater basicity.

SORPTION BY ORGANIC SUBSTANCES. II. EFFECT OF FUNCTIONAL GROUPS ON AMMONIA SORPTION¹

BY A. C. ZETTMAYER, J. J. CHESSICK AND AMIR CHAND

A Contribution from the Surface Chemistry Laboratory, Lehigh University, Bethlehem, Penna.

Received December 10, 1954

A study of the sorption of NH_3 on simple organic compounds was conducted as a necessary preliminary to an investigation of complex organic systems such as proteins. The sorption of NH_3 was found to increase in the order polyethylene < hexadecylamine < hexadecylamide < dipeptide < nylon < stearyl alcohol < succinimide and monobasic acids < dibasic acids. No NH_3 sorption was found for the hydrocarbon, polyethylene. Strictly speaking the sorption by the first four nitrogen compounds was small and not vastly different; evidence indicated, however, that accessible functional groups rather than external surface area was responsible for the NH_3 uptake. Stoichiometric sorption is first approached with stearyl alcohol. Both the monobasic and dibasic acid sorb one NH_3 per carboxyl group. Stable intermediate compounds containing $1/2 \text{ NH}_3/\text{COOH}$ were formed by degassing either NH_3 treated stearic or succinic acid at 25° and 10^{-5} mm.

Introduction

Studies of the sorption of polar molecules by organic compounds such as amino acids² and proteins^{3,4} have been conducted in the past. Because

(1) Sorption by Organic Substances I. Krypton and Nitrogen on Polyethylene, Nylon and Collagen appeared in *J. Am. Chem. Soc.*, **72**, 2752 (1950).

(2) (a) W. D. Bancroft and C. E. Barnett, *THIS JOURNAL*, **34**, 449 (1939); (b) E. J. Czarnetsky and C. L. A. Schmidt, *J. Biol. Chem.*, **97**, 333 (1932).

(3) S. W. Benson, D. A. Ellis and R. W. Zwanzig, *J. Am. Chem. Soc.*, **72**, 2102 (1950).

(4) E. F. Mellon, A. F. Korn, E. L. Kokes and S. R. Hoover, *ibid.*, **73**, 1870 (1951).

of the complexity of some of these and other systems, the analysis of the results of these studies is often difficult. For example, the assignment of a definite number of sorbate molecules to a given functional group in a protein molecule is often quite arbitrary. For this reason a systematic study of the sorption of NH_3 by simple organic molecules was undertaken to lay the foundation for a current work on the sorption of NH_3 and HCl by the proteins edestin, collagen and insulin. The organics studied included an amine, amide, imide, dipeptide, alcohol and mono- and dibasic acids as

TABLE I
 AMMONIA SORPTION BY ORGANIC COMPOUNDS

Organic cpd.	T, °C.	ΣN_1 , m. ² /g.	NH ₃ Sorption		
			ml. (STP) g.	moles (g) mole (s)	Molecules NH ₃ functional group
Polyethylene	-31.6	11.1	0
Hexadecylamine	-31.6	1.7	0.88	0.01	0.01
Hexadecylamide	-31.6	18.9	4.3	.06	.06
	27		4.6	.06	
Dipeptide	-31.6	29.0	6.4	.17	.09
Nylon	-31.6	11.4	35.2	21.20	.17 ^a
Stearyl alcohol	27	..	65.6	0.79	.79
Succinimide	-31.6	..	226	1.00	1.00
Benzoic acid	27	..	180	0.98	0.98
Stearic acid	27	..	78.0	0.99	.98
			38.0 ^b	0.48	.48 Resorption
Succinic acid	27	..	370	1.96	.98
			185 ^b	0.98	.49 Resorption
<i>o</i> -Phthalic acid	-31.6	..	270	2.00	1.00
			525	4.82	2.41
<i>p</i> -Phthalic acid	27	..	265	1.96	0.98

^a Adsorption on amide groups only. ^b Resorption after evacuation at 25°.

well as the hydrocarbon, polyethylene, and a more complex organic, nylon.

Experimental

Materials.—Polyethylene was obtained from E. I. du Pont and Company, Inc., Delaware, lot No. A-8269, molecular weight about 9000. The material was recrystallized from thiophene-free benzene, dried over P₂O₅ and vacuum, and evacuated on the adsorption apparatus for several days before adsorbing gases on it.

Hexadecylamine (Armine 16D, lot No. 2942) was obtained from the Chemical Division of Armour and Co., Chicago, Illinois. The treatment of the sample was the same as for polyethylene.

Stearic acid (Lot No. 2733) was obtained from Paragon Testing Laboratories, Orange, N. J. The acid was further purified by fractional precipitation from alcohol-water solutions. Finally the pure flakes were dissolved in hot 95% alcohol and the solution was poured into distilled water with stirring. The white, granular precipitate was filtered, washed with distilled water and dried over P₂O₅ *in vacuo* for several weeks.

Succinic acid of analytical grade was manufactured by Kahlbaum, Germany. This material was further purified by recrystallization from *t*-butyl alcohol. The material was dried over P₂O₅ and vacuum, and then degassed at 80° for 24 hours at 10⁻⁶ mm. on the adsorption apparatus.

C.P. benzoic acid was supplied by J. T. Baker Co., Phillipsburg, N. J. A supersaturated solution of the acid in thiophene-free benzene was prepared and then poured into ice cold, distilled water with stirring. The acid was filtered, washed and dried over P₂O₅ under vacuum for a week before use.

Reagent grade *o*-phthalic acid was pulverized, dried over P₂O₅ in a vacuum desiccator and degassed on the adsorption apparatus before adsorption measurements were made.

Succinimide was supplied by Eastman Kodak Co., Rochester, N. Y. It was treated in the same manner as *o*-phthalic acid.

Hexadecylamide and stearyl alcohol were the products of Armour Chemical Co. and were treated like polyethylene.

The dipeptide was prepared by refluxing stoichiometric quantities of methyl stearate and ethylenediamine at 120°. The material was purified by fractional crystallization. The analysis for nitrogen on the basis of C₃₈H₇₈N₂O₂ was 4.78% calculated, 4.86% found. The compound was treated in the same fashion as polyethylene.

Nylon was obtained from E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware (Code 1152-85-B Unoriented Nylon yarn). Three grams was dissolved in 30 ml. of 85% formic acid, and the solution poured into distilled water with vigorous stirring. The fine pulp obtained was filtered on a fine muslin cloth and washed with distilled water until the wash water was neutral to litmus. The pulp was dried in air, powdered and then

dried over P₂O₅ in a vacuum for a month. The functional groups present in this sample of nylon are listed below.

NYLON ANALYSIS (AV. MOL. WT. 13,500 ± 500)

Functional Groups	Equiv./g.
Amine	35 × 10 ⁻⁶ (±3)
Carboxyl	75 × 10 ⁻⁶ (±5)
Acetyl	38 × 10 ⁻⁶
Amide	8750 × 10 ⁻⁶

The samples were degassed for a minimum of 48 hr. on the adsorption rig before measurements were made. A conventional BET apparatus was used.⁵ High purity helium was used for dead space determinations. This material was further purified before use by passing the gas through charcoal immersed in a bath at -195°. The NH₃ was high purity tank gas which was passed through anhydrous CaSO₄ before use.

Results and Discussion

The results of the NH₃ sorption studies are listed in Table I. For adsorption measurements at -31.6° the BET *V_m* values were selected as appropriate values for comparison between NH₃ uptake on the various samples. Those samples studied at 27° exhibited typical Langmuir Type I adsorption and the corresponding *V_m* values were easily obtained from the linear portion of the isotherm. This behavior is illustrated in Fig. 1 for the adsorption of NH₃ on stearic acid. Surface areas calculated from nitrogen adsorption measurements are tabulated in column 3 for a number of samples.

The sorption of NH₃ on all the simple nitrogen compounds except succinimide was generally far below that expected if each functional group adsorbed one NH₃ molecule. In the case of NH₃ uptake at -31.6° on hexadecylamide and the dipeptide fair agreement was found between areas calculated from the NH₃ and N₂ *V_m* values using the appropriate factors for the cross-sectional areas obtained from liquid densities. These results suggested that physical adsorption on surfaces which were predominantly hydrocarbon was taking place. Evidence exists, however, that absorption was responsible for the greater part of the NH₃ uptake.

(5) F. H. Healey, J. J. Chessick and A. C. Zettlemoyer, *THIS JOURNAL*, **57**, 178 (1953).

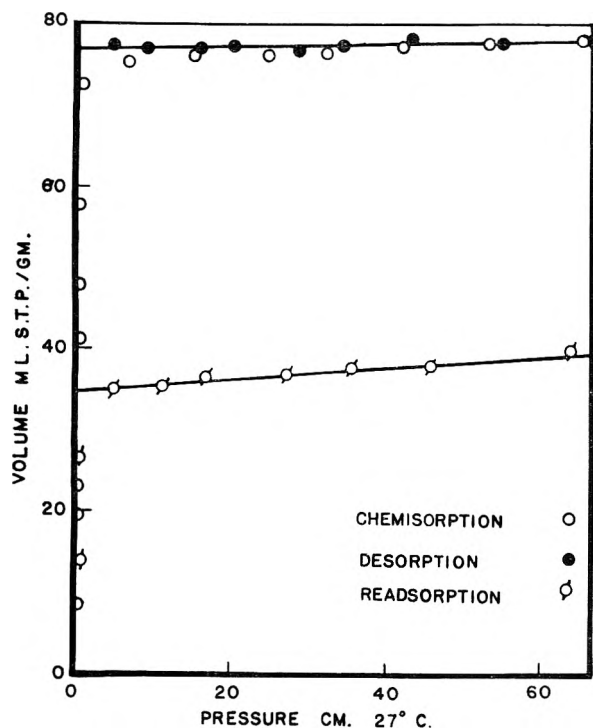


Fig. 1.—Sorption of NH_3 on stearic acid.

For example, no NH_3 adsorption was observed for the hydrocarbon polyethylene at -31.6° even though its area was $11.1 \text{ m}^2/\text{g}$. as determined by nitrogen adsorption. The polyethylene is lyophobic toward NH_3 in the same manner as paraffin wax or Graphon toward water.⁶ Furthermore, the V_m value for NH_3 on the amide at 27° , where physical adsorption is unlikely, agreed well with that obtained at -31.6° . In fact, all the nitrogen containing compounds sorbed NH_3 at 27° . This evidence was taken to indicate at least limited solubility of NH_3 into the interior of the simple nitrogen compounds at -31.6° rather than surface adsorption except in the region of surface functional groups.

The order of increasing NH_3 sorption is given by the following listing: polyethylene < hexadecylamine < hexadecylamide < dipeptide < nylon < stearyl alcohol < succinimide and monobasic acid < dibasic acid. The amine, amide and dipeptide, however, could be grouped together because the NH_3 sorption by these compounds was extremely small and not vastly different. The largest NH_3 uptake in this group amounted to about 9 NH_3 molecules per 100 amide groups in the dipeptide. The sorption results obtained with these simple compounds of nitrogen do not appear to allow a differentiation between the adsorptive capacity for NH_3 of the amino, amido and peptide groupings in complex, protein-like molecules as was hoped.

With the more complex molecule nylon the volume of NH_3 sorbed increased somewhat relative to these simple nitrogen compounds. Actually, more than 12 times as much NH_3 was sorbed as could be accommodated by the surface itself. The sorption was reversible and no strong compound formation

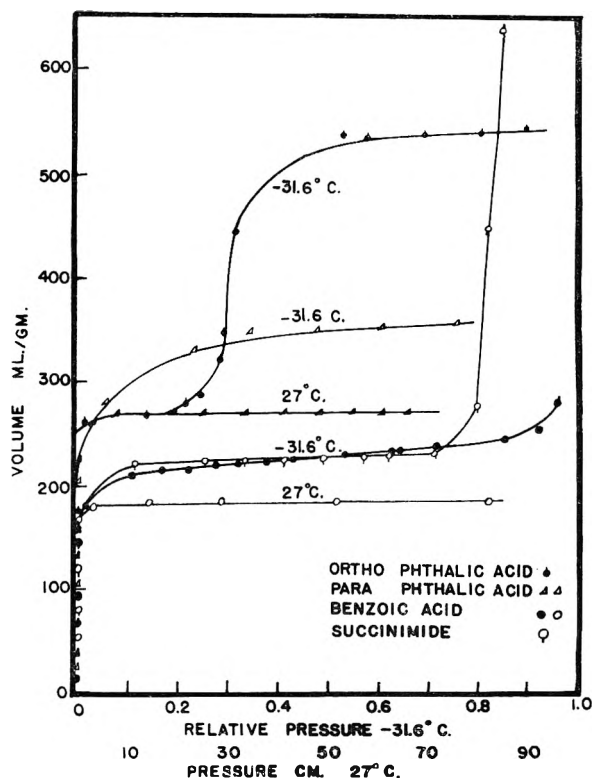


Fig. 2.—Sorption of NH_3 on various organic substances

occurred. Unlike water sorption, however, where 2 to 4 molecules sorb per amide group⁷ only 17 NH_3 molecules were taken up per 100 amide groups. This figure was calculated on the assumption that all the ammonia sorption took place on the amide groups except for the sorption of 1 NH_3 per acetyl and acid end groups. These latter groups accounted for only 7% of the total ammonia sorption. McGrew and Schneider⁸ also found that the amide groups in nylon were sufficiently basic to account for the adsorption of dye anions from solution at high pH values. They concluded that penetration did not occur with the large dye molecule but that the chain endings in which basic character resides make up amorphous areas and are not buried in the crystalline structure of the polymer. The much smaller size of the NH_3 molecule allows for limited solubility into the nylon crystallites although this sorption is undoubtedly influenced by the polar amide groups.

The first organic to approach stoichiometric NH_3 sorption was stearyl alcohol. The monobasic acids and succinamide sorbed NH_3 in a 1:1 mole ratio.

Peculiarly, the isotherm for NH_3 sorption on *o*-phthalic acid at -31.6° showed two steps: the first undoubtedly corresponded to diammonium salt formation and second to possible ammoniation of the salt as well as solution since the sorption here was somewhat greater than stoichiometric. This behavior is shown in Fig. 2. Where isotherms were obtained at the two temperatures employed, the one at -31.6° always showed slightly greater sorption indicating van der Waals adsorption or

(7) O. L. Sponsler, J. D. Bath and J. W. Ellis, *J. Phys. Chem.*, **44**, 996 (1940).

(6) G. J. Young, J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, *This Journal*, **58**, 313 (1954).

(8) F. C. McGrew and A. K. Schneider, *J. Am. Chem. Soc.*, **72**, 2547 (1950).

absorption in addition to the stoichiometric sorption found at 27°. This behavior is illustrated in Fig. 2 for benzoic and *p*-phthalic acids.

Ammonia sorption on stearic and succinic acids was also stoichiometric with formation of the mono- and diammonium salts, respectively. However, whereas the sorption was found to be completely reversible for the other acids studied, only half of the original volume of NH₃ sorbed on stearic and succinic acids could be removed by degassing at 27° for periods ranging from 12 hr. to 10 days. Sorption after the first run was completely reversible.

The intermediate obtained upon degassing sorbed NH₃ from stearic acid retained very nearly 1/2 mole of NH₃ per mole of acid. The unpurified material was stable in air, melted between 83–85°, and a Kjeldahl determination revealed 2.50% nitrogen. The increase in m.p. over stearic acid suggested stable compound formation. Further, the reversible sorption of the remaining 1/2 mole of NH₃ as well as the excellent agreement between calculated and experimentally determined nitro-

gen suggested formation of stearyl imide. However, recrystallization of the intermediate from acetone yielded a compound melting at 70°, the m.p. of stearic acid. This suggested that the semi-stable intermediate was the ammoniate, CH₃(CH₂)₁₆COOH·1/2NH₃.

To rule out more definitely the possibility of imide formation in the case of stearic acid, ammonia sorption and desorption studies were carried out on succinic acid since the imide of this acid has been characterized. As with stearic acid, a semi-stable intermediate was formed which retained 1/2 of the NH₃ initially sorbed. The m.p. of this intermediate was 160–162°; this value did not change after 14 days of storage under high vacuum. The high m.p. ruled out the possibility of imide formation. Most likely, the ammoniate was also formed with this acid.

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NOTES

BASE EXCHANGE CAPACITY OF TALC

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Although there have been extensive investigations of base-exchange capacity of kaolinite and montmorillonite,^{1–8} few data are available for the mineral talc, Mg₃Si₄O₁₀(OH)₂. The base exchange of talc has been reported as small^{7–9} but no data regarding composition, structure or particle size were obtained. In the present research, various monodisperse fractions have been prepared and their mineralogical composition and base-exchange capacities determined.

Experimental

While commercial talcs correspond to various compositions and mixtures of hydrated magnesium silicates,¹⁶ the present research is concerned with the specific mineral talc, Mg₃Si₄O₁₀(OH)₂ (31.4 MgO, 63.45 SiO₂, 4.75 H₂O). The material employed, "Yellowstone Talc," produced by the Sierra Talc and Clay Company, corresponds closely to the theoretical chemical composition of the mineral talc as

shown by chemical analysis (30.23 MgO, 62.52 SiO₂, 4.87 H₂O, 1.51 Fe₂O₃, 0.31 Al₂O₃, 0.27 CO₂, 0.15 Na₂O, 0.05 K₂O).

The raw material was initially treated with an 0.3% solution of hydrogen peroxide for several days to remove any organic impurities, and then washed and decanted from dilute hydrochloric acid to remove carbonates and other soluble impurities. This treatment was repeated several times until all foaming with H₂O₂ ceased. The talc then was ground wet in a porcelain ball mill for thirty hours to decrease the particle size which originally was about 50% greater than 20 μ.

This material was deflocculated with sodium silicate and monodisperse fractions were prepared by gravity settling and with the Sharples Supercentrifuge as described by Hauser.¹⁰ Particle size distributions were determined by the hydrometer method which has been described previously.¹¹ Any exchangeable ions initially present were removed by electro dialysis at 220 volts d.c. for several days until the cell current reached a steady low value.¹² Each fraction prepared was examined by differential thermal analysis, X-ray diffraction (powder pattern with Geiger counter spectrometer) and with the electron microscope to determine whether there was variation in structure or properties.

Base-exchange capacity was determined for the separate size fractions of the purified hydrogen-talc by pH and electrical conductivity titrations^{13–15} with sodium hydroxide. Yield point and viscosity of suspensions were determined with various additions of sodium hydroxide using a modified MacMichael viscosimeter previously described.¹⁴

Results and Discussion

As received, approximately 50% of the material is less than 20 μ, and very little material is smaller

- (1) G. W. Brindley, "Ceramics: A Symposium," A. T. Green (Ed.), British Ceramic Society, 1953, p. 15.
- (2) S. B. Hendricks, *J. Geol.*, **50**, 276 (1942).
- (3) C. E. Marshall, "The Colloid Chemistry of the Silicate Minerals," Academic Press, Inc., New York, N. Y., 1949.
- (4) S. B. Hendricks, *Ind. Eng. Chem.*, **37**, 625 (1945).
- (5) S. B. Hendricks, R. A. Nelson and L. T. Alexander, *J. Am. Chem. Soc.*, **62**, 1457 (1940).
- (6) R. E. Grimm, *J. Geol.*, **50**, 225 (1942).
- (7) S. K. Mukherjee and A. K. Ganguly, *Ind. J. Phys.*, **24**, 248 (1950).
- (8) W. P. Keeley and H. Jenny, *Soil Sci.*, **41**, 367 (1936).
- (9) W. W. Gaskins, *J. Am. Cer. Soc.*, **31**, 80 (1948).

- (10) E. A. Hauser and C. E. Reed, *THIS JOURNAL*, **40**, 1169 (1936).
- (11) F. H. Norton, "Refractories," Second Edition, McGraw-Hill Book Co., New York, N. Y., 1942, p. 589.
- (12) A. L. Johnson and F. H. Norton, *J. Am. Cer. Soc.*, **24**, 63 (1941).
- (13) W. H. East, *ibid.*, **33**, 211 (1950).
- (14) A. L. Johnson and F. H. Norton, *ibid.*, **24**, 189 (1941); *ibid.*, **25**, 336 (1942).
- (15) W. D. Kingery, *ibid.*, **34**, 242 (1951).

than 1 μ . After grinding, the particle size is considerably reduced so that about 50% is finer than 4 μ and almost 10% is finer than 0.5 μ . Fractions separated for further study are shown in Fig. 1. The mean particle sizes obtained were 0.34, 0.88, 3.8 and 9.2 μ .

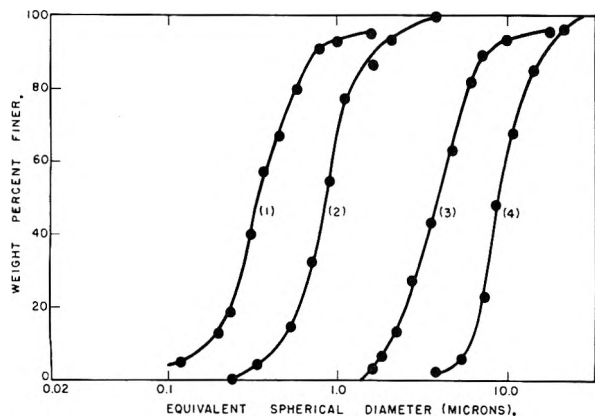


Fig. 1.—Particle size distribution of talc fractions prepared.

Differential thermal analysis gave a single endothermic peak at about 900° for each fraction. This peak is due to the mineral talc and no indication for carbonates, tremolite, chlorites or other accessory minerals¹⁶ were observed. X-Ray diffraction patterns indicated that all fractions were composed of the mineral talc and no variations between samples were observed except minor variations in intensities which were within the reproducibility of the technique used. Electron micrographs indicated that all fractions consisted of irregularly shaped plates having a mean basal plane diameter 13–20 times the thickness and about 2.5 times the equivalent spherical diameter. The diameter to thickness ratios tended to be higher for the larger sized particles. No accessory minerals were observed in the electron micrographs.

The results thus far described indicate that the fractions obtained were all composed essentially of the mineral talc, having similar structural and physical properties with the exception of particle size.

Results of pH and electrical conductivity titrations are shown in Fig. 2. In both curves, a break occurs at an end-point corresponding to the base-exchange capacity in the same way as for kaolin except that the base-exchange capacities found are lower. Also, as indicated in Fig. 3, the viscosity (and similarly yield point) of talc suspensions decreased markedly once the base-exchange capacity has been exceeded, indicating that talc suspensions can be deflocculated in the same way as kaolin, except that the base-exchange capacity is considerably lower. Base-exchange capacities found for the various particle size ranges are collected in Fig. 4. The values reported are determined with the precision of ± 0.1 – 0.2 meq./100 g., and it is apparent that there is no trend of increasing base-exchange capacity with small particle sizes.

The base-exchange capacity of kaolinite has most commonly been considered due to “broken bonds”

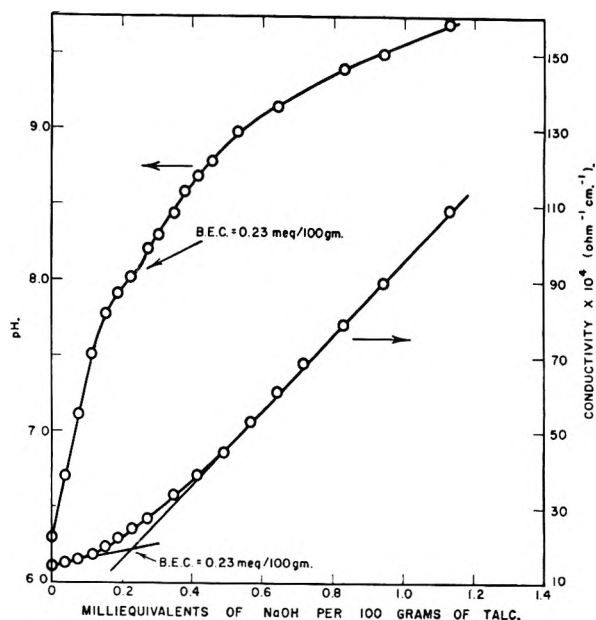


Fig. 2.—Titration of a hydrogen-talc fraction with NaOH.

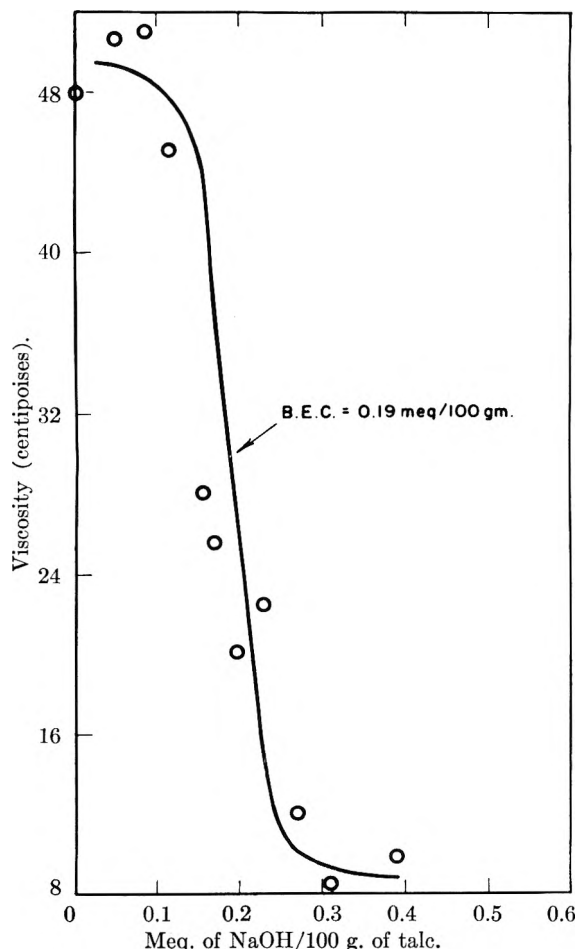


Fig. 3.—Variation of the apparent viscosity of a hydrogen-talc with additions of NaOH.

at the edges of particles. If a particle is broken normal to the basal plane, two new edges are formed with unsatisfied positive and negative charges. Under moist conditions, hydroxyl ions are likely to be picked up at positive points, and hydrogen ions

(16) J. A. Pask and M. F. Warner, Univ. Cal. Inst. Eng. Research, Tech. Report, Series No. 18, No. 4, February 27, 1953.

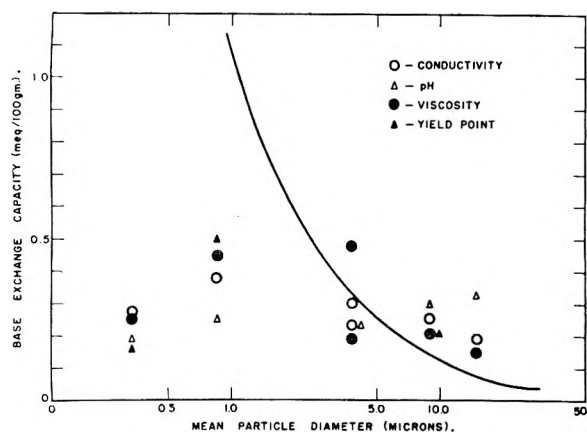


Fig. 4.—Base-exchange capacity of talc fractions. Solid line is for the equation base exchange = $1.2/D$.

are likely to be picked up at unsatisfied oxygen ions giving hydroxyl groups so that the whole particle is bound by oxygen or hydroxyl ions. Hydroxyl ions attached to Si probably dissociate at neutral pH giving $\text{Si-O}^-\text{H}^+$ where H^+ is exchangeable. A similar process is less probable with Al-OH groups but has apparently been assumed by some authors (and would be even less likely for Mg-OH). Calculation of the possible base-exchange capacity of talc due to SiOH dissociation can be made from the particle shapes observed in the electron micrograph.¹ This leads to the result that exchange capacity = $1.2/D$, as shown in Fig. 4. It is apparent that these experimental results cannot be reconciled with the "broken bond" theory.

In contrast to the "broken bond" theory, Sampson and Schofield, as cited by Brindley,¹ suggest that the hydroxyl groups of kaolinite do not dissociate appreciably at neutral pH, and that the base-exchange capacity is mainly or entirely due to isomorphous replacements of Al for Si in the tetrahedral sheet leading to a negative charge on the particle which is counteracted by exchangeable cations. Recent work by Robertson, Brindley and Mackenzie¹⁷ involving very careful chemical analyses of kaolin clays and their base-exchange capacity leads to the same conclusion. This conclusion, it may be noted, is not incompatible with a change in exchange capacity with particle size since the amount of isomorphous substitution may be greater in the smaller particles (and, in fact, be the factor that limits their size). East¹³ has made a similar suggestion that disorder in the crystal lattice may lead to active exchange positions.

In considering the mechanism responsible for base exchange in these materials, the most striking experimental fact is that kaolin has a normal base exchange capacity in the range from 1 to 6 meq./100 g., which is found to vary with particle size and grinding, while talc has a base-exchange capacity of 0.2-0.4, which is independent of particle size and grinding, and pyrophyllite (which has the same structure as talc except that Al^{+3} ions replace Mg^{+2} ions in the layer) has a reported base exchange capacity of 4.0, which is markedly increased by grinding.¹⁶ The most significant variation in struc-

ture between these materials is the change from Mg^{+2} having an ionic radius of 0.78 Å. to Al^{+3} having an ionic radius of 0.57 Å. combined structurally with Si^{+4} having an ionic radius of 0.39 Å. While Al^{+3} is capable of isomorphous substitution for Si^{+4} in the tetrahedral silica layer, leading to a net negative charge, Mg^{+2} is much too large and no excess negative charge would be expected.

Consequently, the results found here are in good agreement with an extension of the hypothesis of Schofield and Sampson,¹ and Robertson, Brindley and Mackenzie¹⁴ that base-exchange capacity in kaolin is due to isomorphous replacement of Al^{+3} in the silica sheet, since in the case of talc with layer Mg^{+2} ions, this is not feasible.

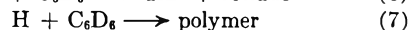
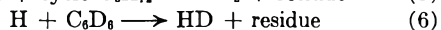
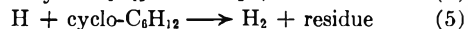
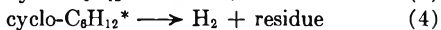
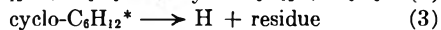
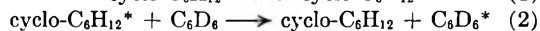
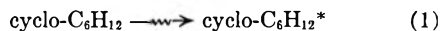
THE MECHANISM OF HYDROGEN FORMATION IN RADIOLYSIS OF CYCLOHEXANE

BY ROBERT R. HENTZ

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Received January 3, 1955

Burton and Patrick¹ in study of the radiolysis of cyclohexane and benzene- d_6 mixtures postulate an excitation transfer from the 3.6 e.v. state of benzene- d_6 to cyclohexane with subsequent decomposition of the cyclohexane to yield hydrogen in an elementary process. Their results can be explained with the original reaction scheme proposed without the necessity for this additional postulate, if r_3/r_4 for the spectrum of excited states produced is independent of benzene- d_6 concentration.



G is the 100 e.v. yield in pure cyclohexane

G' is the 100 e.v. yield in the mixture

ϵ_B and ϵ_C are the electron fractions of benzene- d_6 and cyclohexane, respectively

N_B and N_C are the mole fractions of benzene- d_6 and cyclohexane, respectively

$$k = k_2/(k_3 + k_4)$$

If a steady-state concentration of excited cyclohexane is assumed, the kinetics give

$$G_3' = \frac{G_3\epsilon_C}{1 + kN_B}; \quad G_4' = \frac{G_4\epsilon_C}{1 + kN_B}$$

$$G_5' = \frac{G_5'k_5N_C}{k_5N_C + (k_6 + k_7)N_B}$$

$$G'(\text{H}_2) = G_4' + G_5'$$

$$G'(\text{HD}) = \frac{G_3'k_5N_B}{k_5N_C + (k_6 + k_7)N_B}$$

$$\rho = \frac{G'(\text{H}_2)/N_C}{G'(\text{HD})/N_B} = \frac{k_5(1 + G_4/G_3)}{k_6} + \frac{(k_6 + k_7)G_4N_B}{k_6G_3(1 - N_B)}$$

The value of ρ increases monotonously with increasing N_B as experimentally observed¹ and approaches infinity with infinite slope as $N_B \rightarrow 1$. If $G_4 = 0$ or the relative rates of 5, 6 and 7 are independent of the mole fractions, ρ would be a constant.

(17) R. H. S. Robertson, G. W. Brindley and R. C. Mackenzie, *Amer. Mineral.*, **39**, 118 (1954).

(1) M. Burton and W. N. Patrick, *This Journal*, **58**, 421 (1954).

The equation for ρ may be written in linear form

$$\rho = aN_B/(1 - N_B) + c$$

Least squares analysis of the data of Burton and Patrick¹ gives $a = 0.80$ and $c = 3.7$. The standard deviation of ρ is 0.6. If their first result is discarded, values of $a = 0.78$, $c = 4.4$, and $\sigma = 0.3$ are obtained. Taking the latter and a value for $(k_6 + k_7)/k_8 \leq 8.3$.¹

$$G_4/G_3 \geq 0.094$$

$$k_6/k_8 \leq 4.0$$

Thus, at least 8.6% of the excited cyclohexane molecules that decompose yield hydrogen in an elementary process, and the rate constant for H₂ formation by hydrogen atom attack on cyclohexane is less than 4.0 times that for HD formation from benzene-*d*₆.

In a communication to the author Professor Burton stated that the mechanism of this paper should be substituted for Burton and Patrick equation 15 and its discussion.

ISOTOPIC EXCHANGE REACTIONS OF AMERICIUM¹

By THOMAS K. KEENAN, ROBERT A. PENNEMAN AND JOHN F. SUTTLE

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Received January 17, 1955

Exchange studies have been reported by others for two transuranium elements, neptunium² and uranium.³⁻⁵ These workers showed that exchange takes place between Np(IV)-Np(V), Np(V)-Np(VI) and U(IV)-U(VI). This note reports results of an investigation of exchange between various americium valence states.

The element americium exhibits three well-defined valence states in solution; the simplest aqueous species are Am⁺⁺⁺, AmO₂⁺ and AmO₂⁺⁺. Both AmO₂⁺⁺ and AmO₂⁺ are reduced in perchloric or nitric acid solution by effects of Am²⁴¹ α -radiation at zero-order rates of $\sim 5\%$ and $\sim 2.5\%$ per hour, respectively.⁷ The ion AmO₂⁺ can also disproportionate.⁸ However, the disappearance of AmO₂⁺ *via* the disproportionation path is not appreciable at low acidities, low americium concentrations, and at room temperature.

The isotope Am^{242m}, a 16.01 hour⁹ β -emitter, was used as tracer in solutions of Am²⁴¹, the common α -emitting isotope.

Experimental

All chemicals were "Analytical Reagent" grade and

(1) This work was sponsored by the Atomic Energy Commission and was carried out at the Los Alamos Scientific Laboratory in cooperation with the University of New Mexico. Some of the results were presented at the 123rd meeting of the American Chemical Society, Los Angeles, California, March 15-19, 1953.

(2) (a) J. Hindman, D. Cohen and J. Sullivan, *J. Am. Chem. Soc.*, **76**, 352 (1954); (b) **76**, 4275 (1954).

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were used without further purification. The americium was $>99\%$ pure.

The most stable aqueous state of americium is the trivalent ion. In all exchange experiments, the β -activity was initially in the (III) oxidation state only. The β -active isotope, penta- and hexavalent americium were prepared by techniques described elsewhere.⁹⁻¹¹

Trivalent americium was separated from the higher valence states by precipitation of AmF₃ with aqueous HF and LaF₃ carrier.

Procedure.—Solutions of pentavalent and β -active trivalent americium were combined and the time noted. Aliquots were removed at known later times for separation. Sealed tubes totally immersed in an oil-bath were used for runs at elevated temperatures. Following any separation, a sample of the fluoride supernatant liquid was taken for β - and α -counting to determine specific activity. Equilibrium specific activity was determined by removal and counting an aliquot of the exchanging solution without separation of the exchanging species.

Results

The data obtained from 21 experiments may be summarized as follows.

1. The exchange of Am⁺⁺⁺ and AmO₂⁺ is negligible at temperatures $\leq 100^\circ$ in acid concentrations $\leq 2.0 f$ and americium concentrations *ca.* 0.03 *f* each. The presence of incandescent or ultraviolet light or inert salt had no discernible effect. The α -reduction of AmO₂⁺ and the 16 hour half-life of the tracer made it impossible to follow this slow exchange for more than 1-2 days. The lower limit for the exchange half-time is 200 hours.

2. Exchange half-times of *ca.* 15 hours were observed between 0.03 *f* tri- and pentavalent americium under these conditions: (a) very high temperatures (*ca.* 165 $^\circ$) and acid concentrations of *ca.* 0.2 *f*; (b) moderate temperatures (*ca.* 90 $^\circ$) and acid concentrations of *ca.* 5-10 *f*. Because of reduction and rapid (acid-path) disproportionation, very rapid disappearance of pentavalent americium was noted in such media. This disappearance was too rapid to allow systematic investigation of the various kinetic parameters governing the exchange.

3. The exchange of AmO₂⁺ and AmO₂⁺⁺ was briefly investigated and found to be complete within one minute at 0 $^\circ$ in 1.0 *f* HClO₄. Americium concentrations were each 10⁻³ *f*.

Discussion

The ion Am(IV) has never been observed in solution. The quadrivalent americium ion might be expected to open a kinetic path for exchange in the system Am⁺⁺⁺-AmO₂⁺ since the neptunium exchange—which involves Np⁺⁺⁺⁺ and NpO₂⁺—proceeds at a finite rate. Lacking a corresponding Am(IV) species no analogous exchange path is apparently available to Am⁺⁺⁺ and AmO₂⁺.

It can be pointed out that under conditions where one would expect finite concentrations of Am(IV), *i.e.*, where AmO₂⁺ is disappearing very rapidly, some exchange is observed. It may be that such a system contains sufficient Am(IV) to allow exchange to take place.

The rapid exchange of AmO₂⁺ and AmO₂⁺⁺ is not surprising in view of the analogous results for the NpO₂⁺-NpO₂⁺⁺ exchange reported by Hindman, *et al.*^{2a}

(10) J. Nigon, R. Penneman, E. Staritzky, T. Keenan and L. Asprey, *This Journal*, **58**, 403 (1954).

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EXPERIMENTAL DETERMINATIONS OF THE DIFFUSION COEFFICIENTS OF GASES THROUGH WATER: NITROGEN AND ARGON¹

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Received January 24, 1955

General theoretical studies on the physiological exchange of inert gases, *e.g.*,^{2,3} as well as measurements of the permeability of tissues to inert gases,⁴ have emphasized the importance of precise measurements of the diffusion coefficients of gases through liquids. No measurements have appeared for the rare gases, and the values for nitrogen available in the literature include only the two early determinations of Hüfner⁵ and Exner⁶ for nitrogen through water, that of Tamman and Jessen⁷ for nitrogen through agar gel, and more recently those of Eggleton, *et al.*,⁸ for nitrogen through agar gel, olive oil and animal fat. In the present paper are reported the diffusion coefficients obtained experimentally for the passage through water of two gases, namely, nitrogen and argon; additional diffusion studies have been conducted with helium and sulfur hexafluoride (SF₆), but the results do not appear acceptable without further testing.⁹ The values reported for nitrogen are generally confirmatory of earlier measurements cited; so far as is known no other data have been reported for transfer of argon through water.

The apparatus of Ringbom¹⁰ with a few modifications was used. In this, a gas-saturated and a gas-free water column, introduced from either end into a capillary tube, are separated by a pure gas phase. With the gas-saturated water connected to a large reservoir and the pure water fixed as a dead end column of sufficient length, the volume of gas moving into the pure water is obtained by observing the movement of the gas-saturated water column into the displaced gas space. The rate at which this displacement occurs gives a measure of the diffusion coefficient of the gas through water, provided the tube diameter is small enough to minimize convection and that suitable temperature control is maintained.

Under these conditions, the governing equation is that of Stefan,¹¹ *i.e.*

$$D = (\pi/4a^2q^2)(V^2/t) \quad (1)$$

which, in the differential form more convenient for computing, is

$$D = (\pi/4a^2q^2)(\Delta V/\sqrt{t + \Delta t} - \sqrt{t})^2 \quad (2)$$

Here, V represents volume of gas displaced in time t , q the area at the absorbing interface, and a equal to $\alpha_T(T/273)(P/760)$, where α is the Bunsen absorption coefficient at the temperature T of the experiment; P is the partial pressure of gas under study within the gas space of the capillary tube.

To increase sensitivity Ringbom changed the relative bore of the stationary, gas-free side to about two times the bore of the saturated side, and derived the above expression in terms of the centimeters displacement, n , of the small bore meniscus, namely

$$D = k(\Delta n/\sqrt{t + \Delta t} - \sqrt{t})^2 \quad (3)$$

in which $k = (6\pi/a^2)(d_1/d_2)^4$, with d_1 and d_2 the small and large capillary diameters, respectively.

If Δn is taken in centimeters and t in hours, D will be in cm.² day⁻¹; as reported here these have been divided by 86400 to give units of cm.² sec.⁻¹.

Experimental

The apparatus as modified¹² consisted of a capillary connected through 3-way stopcocks to two reservoir flasks. The capillary was constructed by fusing together two tubes of different bore, one 3.09×10^{-2} cm. in diameter, the other 6.86×10^{-2} cm. The fine tube was 32 cm. in length and was graduated in mm.; the coarser tube was 15 cm. in length. Modifications in the original design which offered advantages in operation and minimized the possibility of diffusion through joints included the use of mercury seal stopcocks with 120° angle plug bore, and on the left reservoir a ground-glass joint with mercury well and a side arm manometer.

Water, triply distilled in glass, was degassed by boiling for 10 min. in a closed system under slightly reduced pressure and introduced while hot into the reservoir flasks and further degassed by evacuation until all bubbling ceased. The test gas was passed into the flask until the pressure inside was equal to or slightly greater than atmospheric, and the gas allowed to bubble through the water until saturation was achieved. The apparatus was placed in a large glass water-bath maintained at $25 \pm 0.05^\circ$. At the end of one hour of equilibration in the bath, the venting manometer was sealed off with mercury, and gas saturation was immediately discontinued. The capillary was first dried by passing dry gas through it, then filled with test gas saturated with water vapor by bubbling the gas through H₂O. The pressure in the capillary was then reduced by an amount sufficient to permit entry of the water column into the capillary for a suitable distance. The pure water was allowed almost to fill the coarser segment, then cut off from the reservoir. The gas saturated water column was then allowed to enter and come to rest at some point in the graduated segment of the tube, whereafter it was left confluent with its reservoir flask. The system was fully closed to prevent any effect from atmospheric fluctuation. The pressure of the test gas in the capillary was determined from the flask pressure by correcting for water vapor pressure and pressure due to the weight of the water column plus any residual differential in the heights of the Hg of the side arm manometer following final closure of its external arm.

For analysis, plots were made of the displacement of the free meniscus in cm. *vs.* \sqrt{t} , and the slopes of the region beyond the initial equilibration determined by the method of least squares.

Results and Discussion

Calculations based on twelve trials with N₂ (99.58% N₂; 0.42% O₂; 0.02% CO₂) gave for the

(12) To be described in greater detail in Research Report from Naval Medical Research Institute, Bethesda, Maryland.

(1) The opinions contained herein are the personal ones of the authors and do not necessarily reflect those of the Navy Department or the Naval Service at large.

(2) R. E. Smith and M. F. Morales, *Bull. Math. Biophys.*, **6**, 125 (1944).

(3) M. F. Morales and R. E. Smith, *ibid.*, **10**, 191 (1948).

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(5) G. Hüfner, *Ann. physik. Chem.*, **60**, 134 (1897).

(6) F. Exner, *Physik*, **155**, 321 (1875).

(7) G. Tamman and V. Jessen, *Z. anorg. allgem. Chem.*, **179**, 125 (1929).

(8) P. Eggleton, S. R. Elsdon, J. Fegler and C. O. Hebb, *J. Physiol.*, **104**, 129 (1945).

(9) The highly improbable value of $D = 10.37 \pm 0.815 \times 10^{-3}$ cm.² sec.⁻¹ was obtained for He, while the experimental value for SF₆ of $D = 4.51 \pm 0.97 \times 10^{-5}$ also appeared too high for immediate acceptance.

(10) Von A. Ringbom, *Z. anorg. allgem. Chem.*, **238**, 94 (1938).

(11) J. Stefan, *K. Akademie Wissensch. Wiener Berichte*, **77**, (II) 371 (1878).

diffusion coefficient $D = 2.246 \pm 0.106 \times 10^{-5}$ cm.² sec.⁻¹.

Eleven trials using argon (>99.5% pure) gave $D = 1.463 \pm 0.138 \times 10^{-5}$ cm.² sec.⁻¹.

The ratio $D_{\text{nitrogen}}/D_{\text{argon}} = 1.53$ conforms grossly to the inverse ratio of the square roots of the respective molecular weights = 1.2. The coefficient obtained with N₂ agrees quite closely with the experimental value obtained by Hüfner⁵ at 22° (i.e., $\bar{D} = 2.12 \times 10^{-5}$), when the latter is corrected for temperature by a factor 1.145, derived empirically from the data of Tamman and Jessen⁷ on diffusion of N₂ through agar as a function of temperature.

When corrected for partial pressure of water vapor the absolute coefficients of the latter authors give for N₂ at 25°, $D \times 10^5 = (1.56/86400)(760^2/736.2) = 1.92$, which is still somewhat lower than

the values obtained in the present study. A calculation of D from the Stokes-Einstein formula would give for N₂ at 25° the value $D \times 10^5 = 1.55$, assuming a molecular radius of 1.575 Å.¹³ A similar calculation using Hill's¹⁴ values for radii as $r^*/2 = 2.085$ Å. for N₂ and 1.915 Å. for argon gives $D_{N_2} \times 10^5 = 1.171$ and $D_A \times 10^5 = 1.275$ which does not alter the previous conclusion.

Summary.—Using a slightly modified Ringbom apparatus, measurements have been made of the diffusion of argon and of nitrogen into pure water at 25°; the respective coefficients of diffusion calculated from the data are $D \times 10^5 = 1.463 \pm 0.138$ and 2.246 ± 0.106 cm.² sec.⁻¹.

(13) Taken as 1/2 molecular diameters based on van der Waals equation ("Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., 29 Ed. Cleveland, Ohio, 1945, p. 2581).

(14) T. L. Hill, *J. Chem. Phys.*, **16**, [4], 399 (1948).

COMMUNICATION TO THE EDITOR

ON FIRST ORDER TRANSITIONS IN ADSORPTION SYSTEMS

Sir:

It has been demonstrated in several cases^{1,2} that gas-solid adsorption systems can have discontinuous adsorption isotherms on a short-time basis and completely continuous isotherms on a long-time basis. It is the purpose of this communication to comment on the above phenomenon.

For a discussion of total or thermodynamic equilibrium in an adsorption system, the following partial equilibria will be introduced: (a) gas-kinetic—the concentration of gas molecules on or near the surface of the solid until, over a small time interval, kinetic equilibrium subsists (number of molecules striking surface of solid \cong number leaving). (b) Swelling³—the adjustment or response (swelling) of the solid to the adsorptive stresses of the surroundings. (c) Thermal—the establishment of uniform temperature throughout the solid component after dissipation of the heat introduced by a heater or liberated as heat of adsorption.

When there are simultaneous, time independent kinetic, swelling, and thermal equilibria, total (thermodynamic) equilibrium is said to exist.

It is conjectured that the establishment of kinetic equilibrium is a short-time process (seconds, minutes); i.e. it is postulated that entering gas molecules quickly come to equilibrium with their surroundings, but these same surroundings are themselves changing (in the thermal and swelling senses). Thus, the rapidly established kinetic equilibrium will be reversibly displaced as the

system approaches a state of swelling and thermal equilibrium.

There is evidence that the establishment of thermal equilibrium can be a long-time process (minutes, hours),^{4,5} particularly so in the absence of a significant gas pressure in the system.⁴

As to swelling equilibrium, the swelling rate is usually greatest at low coverage and decreases with increasing coverage. Since the establishment of swelling equilibrium requires the dissipation of adsorptive stresses by a bulk (not merely surface) response³ of the solid component, it will generally be a slow process.

In a system in which kinetic equilibrium has been established and in which the approach to swelling and/or thermal equilibria is slow, it is possible to observe, on a short-time basis, reasonably complete adsorption-desorption reversibility (both adsorption and desorption points fall on the same curve) even though the system is not in total equilibrium. It is suggested that the discontinuous isotherms—with adsorption-desorption reversibility—mentioned above are probably exemplifications of such a state of partial equilibrium. It has been argued elsewhere³ that adsorption systems in total (thermodynamic) equilibrium are not likely to exhibit first order transitions.

Finally, it is asserted that for adsorption systems with isothermal surroundings the only unambiguous test of total equilibrium is the time independence, on a long-time basis, of the pertinent system variables (usually pressure and temperature).

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