

THE JOURNAL OF PHYSICAL CHEMISTRY

(Registered in U. S. Patent Office)

28th NATIONAL COLLOID SYMPOSIUM, TROY, N. Y., JUNE 24-26, 1954

Allan Kahn and Donald R. Lewis: The Size of Sodium Montmorillonite Particles in Suspension from Electro-optical Birefringence Studies.....	801
Robert O. French, Milton E. Wadsworth, Melvin A. Cook and Ivan B. Cutler: The Quantitative Application of Infrared Spectroscopy to Studies in Surface Chemistry.....	805
J. Fred Hazel and George L. Schnable: Colloidal and Surface Phenomena in the Preparation of Cathode-ray Screens..	812
C. R. Adams and W. O. Milligan: Electron Diffraction Studies in the System BeO-In ₂ O ₃	817
F. P. Price, W. D. Bellamy and E. J. Lawton: Effect of High Velocity Electrons on Dry Dextran.....	821
Harold L. Greenwald and George L. Brown: The Unusual Viscosity of Water Solutions of Alkylaryl Polyoxyethylene Ethanols.....	825
Ernst A. Hauser: Morphological Studies of Reclaimed Elastomers.....	829
Ruth R. Benerito, W. S. Singleton and R. O. Feuge: Surface and Interfacial Tensions of Synthetic Glycerides of Known Composition and Configuration.....	831
C. F. Hiskey and T. A. Downey: The Colloid Error of Indicators.....	835
B. Roger Ray, Edwin O. Davisson and Henry L. Crespi: Experiments on the Degradation of Lipoproteins from Serum.....	841
J. L. Shereshefsky and Maurice E. King: Monolayers of Bovine Plasma Proteins.....	847
Joseph Parker and J. L. Shereshefsky: Monolayers of Some Synthetic Polymers.....	850
J. W. Williams and Winifred M. Saunders: Size Distribution Analysis in Plasma Extender Systems.....	854
M. B. Epstein, A. Wilson, C. W. Jakob, L. E. Conroy and J. Ross: Film Drainage Transition Temperatures and Phase Relations in the System Sodium Lauryl Sulfate, Lauryl Alcohol and Water.....	860
Sydney Ross and Harold F. Schaeffer: Non-soap Thickeners of Lubricating Oils. I. Sedimentation Volumes.....	865
Donald Graham: The Characterization of Physical Adsorption Systems. II. The Effects of Attractive Interaction between Adsorbed Molecules.....	869
L. H. Reyerson and Robert A. Brand: The Heats of Sorption of Bromine on Silica Gel.....	873
John H. Gross and Walter H. Bauer: Water Vapor Sorption by Aluminum Soaps.....	877
G. J. Young and F. H. Healey: The Physical Structure of Asbestos.....	881
F. H. Healey and G. J. Young: The Surface Properties of Chrysotile Asbestos.....	885
F. H. Healey, J. J. Chessick, A. C. Zettlemoyer and G. J. Young: The Heats of Immersional Wetting of Rutile and Graphon in Organic Liquids.....	887
W. O. Milligan and C. R. Adams: An Analytical Expression for Cumulative Pore Volumes and Pore Size Distributions.....	891
T. H. James and W. Vanselow: Coöperative and Competitive Adsorption in the Photographic Process.....	894
Carroll L. Lloyd and B. L. Harris: Binary Liquid Phase Adsorption.....	899
Norman Hackerman and Sarah Jane Stephens: The Adsorption of Sulfate Ions from Aqueous Solutions by Iron Surfaces.....	904
Robert S. Hansen and Bert H. Clampitt: The Apparent Adsorption of Some Aliphatic Compounds from Aqueous Solutions as Inferred from Hydrogen Overvoltage Measurements.....	908
* * * * *	
A. W. Martin: Determination of the Formula of an Oxide of Polonium.....	911
Charles B. Hurd and Stephen H. Laning: Studies on Silicic Acid Gels. XVIII. The Action of Sodium Hydroxide on the Gel.....	914
Rex Neihof: The Preparation and Properties of Strong Acid Type Collodion-base Membranes.....	916
John B. Ockerman and Farrington Daniels: α -Radioactivity of Some Rocks and Common Materials.....	926
NOTE: N. W. Luft: Thermodynamic Functions of HCl and Cl ₂	928

THE JOURNAL OF PHYSICAL CHEMISTRY

(Registered in U. S. Patent Office)

W. ALBERT NOYES, JR., EDITOR

ALLEN D. BLISS

ASSISTANT EDITORS

ARTHUR C. BOND

EDITORIAL BOARD

R. P. BELL

R. E. CONNICK

S. C. LIND

E. J. BOWEN

PAUL M. DOTY

H. W. MELVILLE

G. E. BOYD

J. W. KENNEDY

W. O. MILLIGAN

MILTON BURTON

E. A. MOELWYN-HUGHES

Published monthly by the American Chemical Society at 20th and Northampton Sts., Easton, Pa.

Entered as second-class matter at the Post Office at Easton, Pennsylvania.

The *Journal of Physical Chemistry* is devoted to the publication of selected symposia in the broad field of physical chemistry and to other contributed papers.

Manuscripts originating in the British Isles, Europe and Africa should be sent to F. C. Tompkins, The Faraday Society, 6 Gray's Inn Square, London W. C. 1, England.

Manuscripts originating elsewhere should be sent to W. Albert Noyes, Jr., Department of Chemistry, University of Rochester, Rochester 3, N. Y.

Correspondence regarding accepted copy, proofs and reprints should be directed to Assistant Editor, Allen D. Bliss, Department of Chemistry, Simmons College, 300 The Fenway, Boston 15, Mass.

Business Office: American Chemical Society, 1155 Sixteenth St., N. W., Washington 6, D. C.

Advertising Office: Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y.

Articles must be submitted in duplicate, typed and double spaced. They should have at the beginning a brief Abstract, in no case exceeding 300 words. Original drawings should accompany the manuscript. Lettering at the sides of graphs (black on white or blue) may be pencilled in, and will be typeset. Figures and tables should be held to a minimum consistent with adequate presentation of information. Photographs will not be printed on glossy paper except by special arrangement. All footnotes and references to the literature should be numbered consecutively and placed in the manuscript at the proper places. Initials of authors referred to in citations should be given. Nomenclature should conform to that used in *Chemical Abstracts*, mathematical characters marked for italic, Greek letters carefully made or annotated, and subscripts and superscripts clearly shown. Articles should be written as briefly as possible consistent with clarity and should avoid historical background unnecessary for specialists.

Symposium papers should be sent in all cases to Secretaries of Divisions sponsoring the symposium, who will be responsible for their transmittal to the Editor. The Secretary of the Division by agreement with the Editor will specify a time after which symposium papers cannot be accepted. The Editor reserves the right to refuse to publish symposium articles, for valid scientific reasons. Each symposium paper may not exceed four printed pages (about sixteen double spaced typewritten pages) in length except by prior arrangement with the Editor.

Remittances and orders for subscriptions and for single copies, notices of changes of address and new professional connections, and claims for missing numbers should be sent to the American Chemical Society, 1155 Sixteenth St., N. W., Washington 6, D. C. Changes of address for the *Journal of Physical Chemistry* must be received on or before the 30th of the preceding month.

Claims for missing numbers will not be allowed (1) if received more than sixty days from date of issue (because of delivery hazards, no claims can be honored from subscribers in Central Europe, Asia, or Pacific Islands other than Hawaii), (2) if loss was due to failure of notice of change of address to be received before the date specified in the preceding paragraph, or (3) if the reason for the claim is "missing from files."

Subscription Rates: to members of the American Chemical Society, \$8.00 for 1 year, \$15.00 for 2 years, \$22.00 for 3 years; to non-members, \$10.00 for 1 year, \$18.00 for 2 years, \$26.00 for 3 years. Postage free to countries in the Pan American Union; Canada, \$0.40; all other countries, \$1.20. Single copies, current volume, \$1.25; foreign postage, \$0.15; Canadian postage \$0.05. Back issue rates (starting with Vol. 56): non-member, \$1.50 per issue, foreign postage \$0.15, Canadian postage \$0.05; \$12.50 per volume, foreign postage \$1.20, Canadian postage \$0.40; special rates for A.C.S. members supplied on request.

The American Chemical Society and the Editors of the *Journal of Physical Chemistry* assume no responsibility for the statements and opinions advanced by contributors to THIS JOURNAL.

The American Chemical Society also publishes *Journal of the American Chemical Society*, *Chemical Abstracts*, *Industrial and Engineering Chemistry*, *Chemical and Engineering News*, *Analytical Chemistry*, and *Journal of Agricultural and Food Chemistry*. Rates on request.

THE JOURNAL OF PHYSICAL CHEMISTRY

(Registered in U. S. Patent Office) (Copyright, 1954, by the American Chemical Society)

VOLUME 58

OCTOBER 18, 1954

NUMBER 10

THE SIZE OF SODIUM MONTMORILLONITE PARTICLES IN SUSPENSION FROM ELECTRO-OPTICAL BIREFRINGENCE STUDIES

BY ALLAN KAHN AND DONALD R. LEWIS

• *Publication No. 44, Exploration and Production Research Division, Shell Development Co., Houston, Texas*

Received March 5, 1954

The size of sodium montmorillonite particles in aqueous suspension was determined from electro-optical birefringence "decay curves." Five suspensions, each of a narrow particle-size range, were prepared from a batch of sodium montmorillonite by means of a Spinco Model L ultracentrifuge. The electro-optical birefringence behavior of these suspensions was determined at a weight concentration of 0.05% sodium montmorillonite. On the assumption that the particles are oblate spheroids in which the major axis is much larger than the minor axis, the semimajor axes of the particles were found to range from 2500 to 12,300 Å.

Introduction

In the study of aqueous clay suspensions, the determination of the size and shape of the clay particles is of great importance. Of the numerous techniques available for the measurement of the size and shape of colloidal particles, the electro-optical birefringence technique has been chosen for several reasons. First, external forces are applied to the suspension for only a fraction of a second during measurement. Second, in addition to determining the rotational diffusion constant of the particles, information about the electrical properties of the particles may be obtained.

Benoit¹ and O'Konski and Zimm² have described methods for orienting colloidal particles in a suspension by applying a rectangular voltage pulse and observing the rate of orientation. O'Konski and Zimm used a repeated rectangular voltage pulse; Benoit used a single rectangular voltage pulse, which is also the type used in the present study. At the end of a pulse the applied voltage decreases to zero and the particles return to random orientation. The rate of relaxation for this return to random orientation may be used to determine the major dimension of the particle.

Benoit has applied electro-optical birefringence methods to measure the size of particles of tobacco mosaic virus, thymonucleic acid and vanadium pentoxide. In this paper, the application to sodium montmorillonite is discussed.

(1) H. Benoit, *Ann. phys.*, [12] **6**, 561 (1951).

(2) C. O'Konski and B. Zimm, *Science*, **11**, 113 (1950).

Theoretical

A suspension of sodium montmorillonite is normally optically isotropic. When an electric field is applied the suspension behaves optically like a uniaxial crystal and becomes birefringent. The birefringence is attributed to the orientation of the particles under the influence of the electric field.³ Upon removal of the field, the particles return to random orientation and the birefringence decays. The rate of decay is given to a good approximation¹ by

$$\frac{\Delta n}{\Delta n_0} = e^{-sDt} \quad (1)$$

where Δn_0 is the initial value of the birefringence and Δn is the value at time t . D is the rotational diffusion constant.

On the basis of a great deal of qualitative evidence, the montmorillonite particle is considered to be disc-shaped (an oblate spheroid).^{4,5} Then according to Perrin's formula for oblate spheroids in which the major axis is much larger than the minor axis⁶

$$a^3 = \frac{3}{32} \frac{kT}{\eta D} \quad (2)$$

where a is the semimajor axis of the particle and η is the viscosity.

(3) C. E. Marshall, *Trans. Faraday Soc.*, **26**, 173 (1930).

(4) C. E. Marshall, "The Colloidal Chemistry of the Silicate Minerals," Academic Press, Inc., New York, N. Y., 1949, p. 69.

(5) O. J. Kelley and B. T. Shaw, *Proc. Soil Sci. Am.*, **7**, 58 (1942).

(6) A. E. Alexander and P. Johnson, "Colloid Science," Vol. 1, Oxford University Press, New York, N. Y., 1949, p. 386.

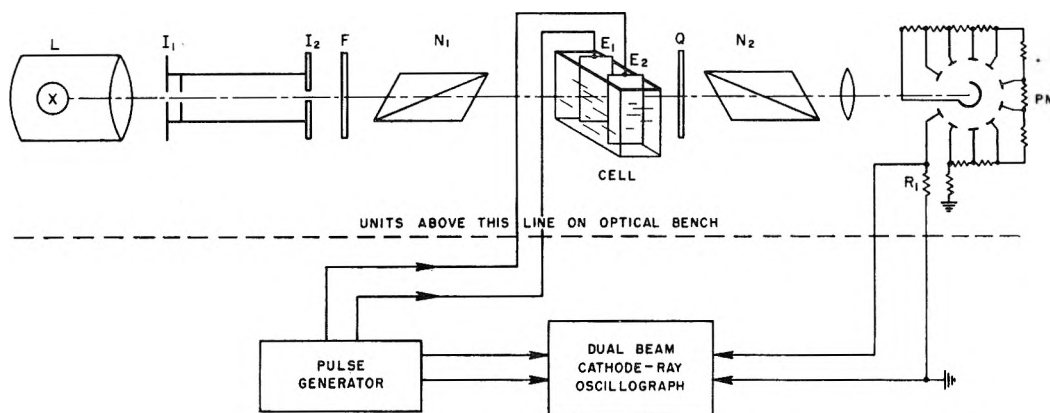


Fig. 1.—Schematic arrangement for single-pulse operation.

The quantitative determination of birefringence is based on well-known optical principles.⁷ When the suspension is in an electric field it acts as a uniaxial crystal with its optic axis parallel to the field so that a beam of plane-polarized light entering the suspension perpendicular to the field becomes elliptically polarized. For the greatest convenience in the interpretation of results, the light entering the suspension is plane-polarized at 45° to the electric field. The light emerging from the suspension is passed through a quarter-wave plate, the principal axes of which are also at 45° to the electric field. The light emerging from the quarter-wave plate is found to be plane-polarized but at an angle θ from the original plane of polarization.

$$\theta = \frac{\pi}{\lambda} d(\Delta n) \quad (3)$$

where λ is the wave length of light used, d is the thickness of the birefringent layer and Δn is the birefringence, which equals the refractive index parallel to the electric field minus the refractive index perpendicular to the electric field.

Experimental

Optical Equipment.—The general arrangement of the optical equipment in our investigations was similar to that usually used in the investigation of the Kerr effect. As shown schematically in Fig. 1, a beam of light was collimated into a narrow pencil, passed through a filter F, which transmitted a narrow wave length region, and then into a Nicol prism N_1 , which plane-polarized the beam of light. After traversing the cell which contained the suspension made birefringent by an electric field the beam was no longer plane-polarized but was elliptically polarized. The quarter-wave plate Q, with its axes also at 45° to the direction of the electric field, again rendered the light beam plane-polarized. The light beam finally emerged from the second Nicol prism N_2 and was detected by the photomultiplier tube PM.

All the equipment shown in Fig. 1 above the dashed line was mounted on an optical bench. The light source L was a 12-ampere 6-volt projection lamp which was powered by a storage battery. While the lamp was being operated the battery was simultaneously charged from a battery charger so that the principal function of the battery was that of a voltage regulator for the lamp. The lens on the lamp housing focused the image of the filament at infinity so that a beam of parallel light emerged from the lamp. The light beam was collimated into a narrow pencil by means of irises I_1 and I_2 . The iris I_1 was a Rapax No. 1 camera shutter unit, without any lens, which contained an iris diaphragm so that it would be used to interrupt the beam of light. I_2 was a simple multiple-leaf iris diaphragm. The filter F was a Baird interference filter with its transmission peak at 5466 Å.

(7) S. Procopiu, *Ann. phys.*, [10] 1, 213 (1924).

The polarizer prism N_1 had a 9-mm. aperture. The cell was made of optical glass with accurately flat parallel faces which had been annealed to be as strain-free as possible. The two electrodes E_1 and E_2 , which were immersed in the clay suspension, were made from sheets of platinum $1/16$ inch thick and 10 mm. wide in the direction parallel to the propagation of the light. The quarter-wave plate Q was designed for use at 5461 Å. The analyzer prism, N_2 was of exactly the same type as the polarizer prism. A 931-A photomultiplier tube PM was used to detect any light which passed through the analyzer. The signal from the photomultiplier tube went to one channel of a dual-channel oscilloscope.

The two polarizing prisms N_1 and N_2 and the quarter-wave plate Q were mounted in worm-gear-driven mounts which permitted complete rotation of their optical axes. The position of any of these optical components was determined by means of a mechanical counter which was coupled to the driving shaft of the worm gear. One unit on the mechanical rotation counter corresponded to 0.2° of arc.

Electronic Equipment.—The basic components of the electronic equipment are also shown in Fig. 1. The pulse generator produced a single rectangular voltage pulse by using a circuit which operated in the manner described by Reich.⁸ The maximum voltage of the peak of the pulse was approximately 100 volts. The voltage gradient in the cell was controlled by varying the distance between the electrodes. Five pulse widths from 2 to 200 milliseconds were available.

The pulses which were generated were all of one polarity with respect to ground. A succession of pulses of the same polarity, if applied to the cell, would cause a net transfer of montmorillonite from the suspension to the anode. The equivalent of reversing the polarity of the pulse was accomplished by means of a switching arrangement which automatically reversed the role of the two electrodes E_1 and E_2 . A time delay of 10 seconds was provided from the time of initiation of the pulse until the switching of the relay units, which reversed the polarity of the electrodes. This permitted the recording of the pulse and response on the face of the oscilloscope to be completed without any possibility of transient voltages being injected into the pulse or response by the switching of the electrodes.

A z-axis intensity modulation permitted timing "pips" to be imposed on the trace across the oscilloscope. This was provided by a signal from an audiooscillator which passed through a wave shaper and was then amplified before being applied to the z-axis of the oscilloscope.

Materials.—The montmorillonite was obtained from a sample of bentonite from Clay Spur, Wyoming, specially selected to be free of accessory minerals.⁹ The montmorillonite was converted to the sodium form in an ion-exchange column, similar to the one described by Lewis.¹⁰ This material contained a wide variety of particle sizes and was separated into a series of fractions, each of a narrow particle-size range, by a Spinco Model L ultracentrifuge. Five

(8) H. J. Reich, "Theory and Application of Electron Tubes," McGraw-Hill Book Co., Inc., New York, N. Y., 1937, p. 360.

(9) This material was provided through the courtesy of Baroid Sales Division, National Lead Company, Houston.

(10) D. R. Lewis, *Ind. Eng. Chem.*, 45, 1782 (1953).

particle-size fractions were obtained. These were labeled, in order of decreasing size, R₁, R₂, R₃, R₄, R₅.

Experimental Method. Calibration.—The polarizer and quarter-wave plate were set up at 45° to the plane of the electrodes. The analyzer could then be set at any position and the trace on the dual-channel oscilloscope from the phototube (response trace) was positioned to coincide with the signal trace corresponding to zero voltage between the electrodes. The apparatus was calibrated by rotating the analyzer and determining the vertical displacement of the response trace as a function of analyzer position. If the analyzer was initially crossed with the polarizer, the displacement of the trace on rotation of the analyzer was found to be accurately proportional to sin² θ. This indicated that the displacement on the oscilloscope was directly proportional to the intensity of light striking the phototube.

Birefringence Curves.—With the suspension in the cell, the voltage pulse was applied to the electrodes. The rise in voltage of the pulse simultaneously triggered the sweep of the oscilloscope which was common for both channels. A permanent record of the traces on the oscilloscope was made by means of a camera attachment.

Results

All the samples were run at a weight concentration of 0.05% sodium montmorillonite. Preliminary experiments showed that this was below the concentration range where the calculated value of

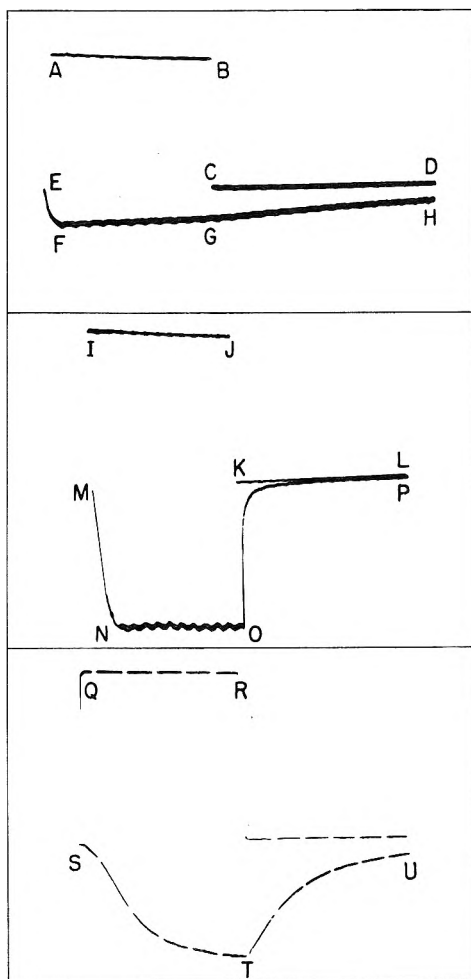


Fig. 2.—Birefringence curve of sample R₁: voltage pulse, ABCD; birefringence curve, EFGH. Distance AB corresponds to 192.5 milliseconds.

Fig. 3.—Birefringence curve of sample R₅: voltage pulse, IJKL; birefringence curve, MNOP. Distance IJ corresponds to 192.5 milliseconds.

Fig. 4.—Birefringence curve of sample R₃. Distance QR corresponds to 10.3 milliseconds.

D, the rotational diffusion constant, is a function of the concentration.

The marked effect of particle size on the birefringence decay curve is shown in Figs. 2 and 3. In Fig. 2, the decay curve GH of the largest size fraction R₁ is shown. At H, 274 milliseconds after the field has been removed, the sample still has 62% of the birefringence at G.

In Fig. 3, taken with the smallest size fraction, R₅ in the cell, 62% of the initial birefringence has been reached after the field has been off for only 4 milliseconds.

In Fig. 4, the time scale for an R₅ fraction has been expanded so that the decay curve may be obtained more precisely. The discontinuities in the oscilloscope traces of Fig. 4 are caused by the timing signals. The time interval between two successive discontinuities is 2 milliseconds.

The value of D may be obtained from a curve such as that in Fig. 4 and the calibration curve. From equation 1

$$\log \Delta n = \log \Delta n_0 - \frac{6}{2.303} Dt$$

From equation 3, for a given wave length of light and thickness of birefringent material

$$\theta = K \Delta n \text{ where } K \text{ is a constant}$$

$$\therefore \log \theta = \log \theta_0 - \frac{6}{2.303} Dt$$

Therefore, a plot of θ versus t on semilogarithmic paper should yield a straight line of slope 2.61 D. From equation 2, the value of a, the semimajor axis of the particle, may now be obtained. In Fig. 5, θ is plotted against t on semilogarithmic paper for section TU of Fig. 4. The deviations from linearity are undoubtedly due to the fact that the sample actually contained a range of particle sizes. The calculated value of D is based on the straight line which is drawn through the first four points.

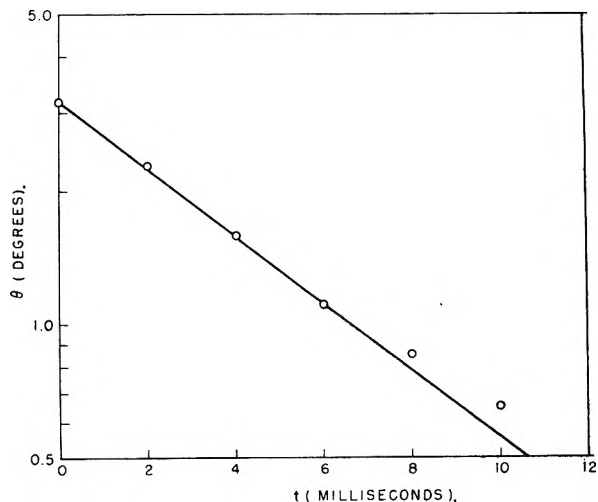


Fig. 5.—Semilogarithmic plot of birefringence decay curve TU of Fig. 4.

The results on the various size fractions of sodium montmorillonite are presented in Table I.

It can be seen from Table I that the semimajor axis of the particles in each of the fractions is very large in comparison to the equivalent spherical radius. However, the values of the equivalent

TABLE I
PARTICLE-SIZE DATA ON FRACTIONS OF
SODIUM MONTMORILLONITE

Values of D obtained from suspensions containing 0.05% by weight of sodium montmorillonite.

Fraction	Equiv. ^a spherical radius, Å.	% by wt. of total sodium mont- morillonite	D , sec. ⁻¹	a , Å.
R ₁	>1380	27.3	0.23	12,300
R ₂	810-1380	15.4	0.40	10,300
R ₃	400-810	17.0	7.9	3,800
R ₄	230-400	17.9	17	3,000
R ₅	70-230	22.4	29	2,500

^a Calculated from speed and duration of centrifugation, from data given in Technical Manual for Ultracentrifuge Model L, Specialized Instruments Corporation, Belmont, California.

spherical radius were obtained at an initial sodium montmorillonite concentration of about 1% and not at 0.05%. On the basis of published data on asymmetric large molecules¹¹ and some unpublished data from this Laboratory, it is still unlikely that the equivalent spherical radius of the particles would be more than twice as large as those given.

There is less than a factor of five difference between the semimajor axis values of the R₁ and R₅ fractions. This is confirmed qualitatively also by inspection of electron micrographs of these sam-

(11) Reference 6, p. 276.

ples.¹² The electron micrographs show, however, that the particles of the R₁ fraction are considerably thicker than the particles of the R₅ fraction.

In addition to the size data obtainable from the "decay curves," the electro-optical birefringence "rise curves," such as the portion ST of Fig. 4, might be expected to yield information about the electrical properties of the sodium montmorillonite particles. Benoit¹ has derived equations for "rise curves" on the assumption that the orientation of the particles in the electric field was due solely to some combination of permanent and induced dipoles in the particles. It was not found possible to fit our data to any of these equations.

DISCUSSION

HERBERT L. DAVIS.—Have you considered or measured the effect of pH, of cations and anions, and of substances known to produce marked effects on the clay slips used commercially? This excellent technique might provide useful information on the magnitude and influence of charge and hydration, as these influence viscosities, plasticities and other properties of clay dispersions. Comparable systems with sodium hydroxide, silicate or phosphate would be relevant. Additions of cationic materials such as barium chloride, aluminum chloride or quaternary compounds might produce notable effects of academic and practical interest.

ALLAN KAHN.—Up to the present we have only used pure materials in our measurements. We hope however to be able to use this birefringence technique to study the interaction of clays with materials such as you mentioned.

(12) Electron micrographs were prepared by Dr. Thomas F. Bates Dept. of Mineralogy, Pennsylvania State University, State College, Pennsylvania.

THE QUANTITATIVE APPLICATION OF INFRARED SPECTROSCOPY TO STUDIES IN SURFACE CHEMISTRY

BY ROBERT O. FRENCH,¹ MILTON E. WADSWORTH, MELVIN A. COOK AND IVAN B. CUTLER

Department of Metallurgy, University of Utah, Salt Lake City, Utah

Received March 5, 1954

A vacuum die was constructed which represents a modification of one previously proposed by Schiedt. Several features were added which contribute to the ease and speed of assembly and disassembly of the die proper. It is possible to form a clear window of KBr or KI in such a die using a total pressure of 20 tons on a disk 22 mm. in diameter. Essentially the technique involves the grinding of a known quantity of the solid under investigation with a known amount of KI or KBr. A weighed portion of this sample may then be compressed in the evacuated die, forming a clear matrix through which the solid in question is uniformly disseminated. It is possible by this means to prepare sample disks with reproducible thickness and uniform distribution. This technique was applied to the study of the surfaces of solids having large surface area. The variation in hydroxyl groups on the surface of Wyoming bentonite was shown to vary uniformly depending upon the pH of the solution from which the sample was taken. Organic flocculants adsorbed on the surface of clays were also detected by this means. This application is of fundamental importance in the study of flocculation. Some results for the adsorption of oleic acid on fluorite and ammonia on silica-alumina catalysts are reported in this article.

Recent fundamental studies carried out at the University of Utah concerning flocculation clearly emphasized the need of a direct means for the investigation of the surfaces of solids. Particularly suited to such a study is infrared spectroscopy providing certain conditions are satisfied. The detection of surface effects requires that the solids have large surface areas and that the particles themselves be less than approximately one micron in diameter to minimize light scattering. In addition, the solid sample must be suspended uniformly and reproducibly in some matrix for mounting in the infrared spectrometer.

Several techniques have been used in the past to study solids quantitatively. Barnes, *et al.*,² employed an internal standard in each Nujol mull studied to determine the cell thickness. Dinsmore and Smith³ used metal spacers accurately to gage specimen thickness for the study of natural and synthetic rubber. Sands and Turner⁴ prepared solid samples by placing the solid between sheets of mica, silver chloride or polyethylene.

Of particular interest is the work of Stimson and O'Donnell⁵ in which solid samples were thoroughly mixed with finely ground KBr. Disks were then pressed out in an evacuated die. This technique provided a convenient method for reproducibly mounting solid samples. Schiedt⁶ has also demonstrated the improved transmittancy of solids suspended in this way, and has compared the transmittancy of several salts for possible use as suspension matrices. It is this latter technique that was employed in this study.

Vacuum Die

A die was constructed which is a modification of one previously developed by Schiedt. The essential changes include an external vacuum chamber with a vacuum tight plunger operating through a Garloc graphite-impregnated packing. The seal is made by two opposing 60° cones

which force the packing against the shaft. The total stroke is approximately three inches which permits application of the vacuum chamber to dies of various design. The bottom of the chamber is a circular 1/2 inch polished steel plate with a center pin for centering of the die proper. The vacuum seal between the upper and lower sections of the vacuum housing is maintained with silicone vacuum grease. The die itself consists of three essential internal parts: (1) the die plunger, (2) the die body and (3) the die anvil. The die body and anvil are held together by means of the external portion of the die which screws down until its shoulder presses against the upper surface of the die body. This pressure forces the mirror finished faces of the die body and anvil together. The end of the die plunger shaft is also mirror finished providing polished surfaces for both sides of the sample. Two holes extend through the side of the die body, permitting the rapid removal of air during evacuation. Two similar holes are also provided in the outer locking section of the die. During evacuation the bottom of the die plunger is held above the evacuation hole by means of a coiled spring.

The die plunger operates with a clearance of 0.0005 inch to minimize the loss of the sample during pressing. It has a diameter of 22 mm. with an extended portion on top of 1.5 inches in diameter to match the plunger of the vacuum chamber. It is essential that the head of the die plunger pass through the hole in the top of the outer locking section of the die to permit rapid disassembly of the die and removal of the pressed disk. Disassembled in this manner, the sample may be readily pressed out using a cylindrical section of plastic against the mirror surface of the die body. The three internal portions of the die proper must be made of high strength, deep-hardening tool steel to prevent distortion under the 20-ton load applied to the 22-mm. diameter die plunger. Details of the die construction have been presented elsewhere.⁷

Experimental Procedure

Both KBr and KI were investigated as mounting materials, and although KBr has somewhat better transmittancy, KI was chosen because of the shorter pressing time required to produce plates. Completely clear plates were formed in 5 minutes.

The transmission of C.p. KI as received can be materially improved by recrystallization, CO₂ and H₂O being the principal impurities. A saturated solution of KI was prepared, boiled and recrystallized in a steam-bath and the recrystallized KI was then heated in a vacuum furnace at 110° for 36 hours. All grinding was carried out in a Fisher mechanical agate mortar, and a large portion of recrystallized KI was ground for approximately two hours. This material was kept in a sealed bottle ready for sample preparation. All grinding operations were standardized for reproducibility. A weighed portion of previously ground solid was combined with 10 g. of ground KI. This charge was then re-ground and usually provided a uniform distribution within 20

(1) This paper comprises part of a thesis to be presented by R. O. French in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Department of Metallurgy, University of Utah. This work was supported by the Atomic Energy Commission.

(2) R. B. Barnes, R. C. Gore, E. F. Williams, S. G. Linsley and E. M. Peterson, *Anal. Chem.*, **19**, 620 (1947).

(3) H. L. Dinsmore and D. C. Smith, *ibid.*, **20**, 11 (1948).

(4) J. D. Sands and G. S. Turner, *ibid.*, **24**, 791 (1952).

(5) M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

(6) U. Schiedt, *Z. Naturforsch.*, **76**, No. 5, 270 (1953).

(7) R. O. French, M. E. Wadsworth, M. A. Cook and I. B. Cutler, Technical Report No. III, AEC Contract No. AT(49-1)-633, February, 1954, Department of Metallurgy, University of Utah.

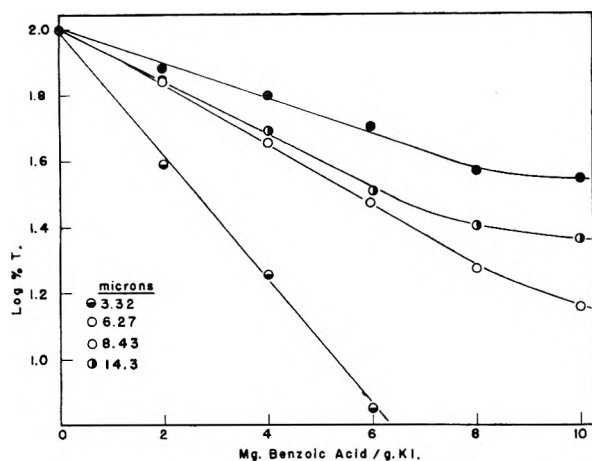


Fig. 1.—Log per cent. transmission vs. concentration for four peaks of the benzoic acid spectrum.

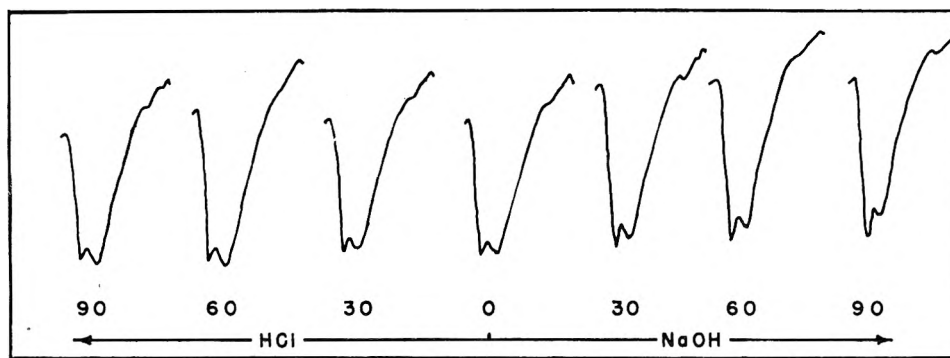


Fig. 2.—Infrared spectra of $-\text{OH}$ stretching (2.85μ) and $-\text{OH}$ hydrogen bonded (3.0μ) bands for various additions of NaOH and HCl to 1.8% suspensions of acid washed Wyoming bentonite.

minutes. From this, a carefully weighed one-gram aliquot sample was taken for pressing providing a circular plate 22 mm. in diameter and approximately 0.9 mm. thick. The use of an initial 10-gram charge materially minimized errors due to weighing and mixing. Table I lists the weight and thickness of seven consecutive plates after pressing. The average density was 94 to 96% of theoretical.

TABLE I

Sample	Wt., g.	Thickness, mm.
1	0.9958	0.889
2	.9901	.884
3	.9930	.882
4	.9931	.877
5	.9945	.874
6	.9960	.882
7	.9961	.879

It was found that the geometry or distribution of the powder in the die materially affected the type of plate produced. Improved plates were formed by packing the powder higher in the center than at the edges before pressing. This was accomplished with a plastic rod machined to the same dimensions as the die plunger but having a dome shaped bottom. This curvature was such that the center of the powder was approximately one millimeter higher than that around the edges. The plastic plunger was pressed firmly against the powdered sample by hand and rotated ten times with a smooth downward pressure. The die chamber was evacuated by means of a Cenco vacuum pump, and it was found that the vacuum should be applied slowly since the sample was distributed by the rapid outward diffusion of gases. This could be prevented by using approximately two minutes to reach maximum vacuum.

Quantitative Application

The quantitative application of the technique was first carried out using benzoic acid as a sample. Benzoic acid has a complicated spectrum between two and fifteen microns, providing many peaks at wave lengths between these limits. Samples were prepared which contained 2, 4, 6, 8 and 10 mg. of benzoic acid per gram of KI. A Perkin-Elmer Model 12-C infrared spectrometer was used for all tests and the disks were mounted in the standard sample holder which was provided with a one-fourth inch brass spacer to take up the space of the rock salt crystals normally used. Water was eliminated by passing argon through the spectrometer and through a plastic cylindrical housing between the exit window of the spectrometer source and the sample holder. This cylinder was fitted with rubber gaskets at each end and telescoped in the middle providing a simple means for installation. The assembly was held in place by the friction of the rubber gaskets. Four peaks were chosen along the entire benzoic acid spectrum to determine the applicability of the Lambert-Beer law and the per cent. transmission was determined by means of the base-line tangent method. The distance from the base line to the bottom of a peak divided by the distance from the base line to

a tangent drawn across the band tangent to the two sides of the spectrum was taken as the per cent. transmission. This technique is common and has been presented in more detail by Barnes, *et al.* The base-line method has the inherent property of self-calibration. This is essential in studies of this type because slight variations in the area of the disk observed can be normalized. Such variations are equivalent to a gain change, but ratios measured by the base-line method are unaltered. For this reason disks which were not completely clear provided satisfactory results. Figure 1 represents plots of log per cent. transmission for different concentrations of benzoic acid in KI at the four peaks chosen. These correspond to phenyl-CH stretching (3.32μ), conjugate phenyl stretching (6.27μ) and two monosubstituted phenyl bands (8.43 and 14.6μ). It is evident from these plots that the Lambert-Beer relationship applies up to 8 mg. of benzoic acid per gram of KI. This corresponds to 0.8% concentration by weight or approximately 0.2 mole per liter. Above this concentration the curves consistently deviated from the Lambert-Beer relationship.

Flocculation Studies

Fundamental studies of solid surfaces are important to the understanding of the flocculation process. Clay minerals such as kaolinite and Wyoming bentonite have flocculation and viscosity characteristics markedly influenced by pH. In general the dispersion of fine particles is due to charge repulsion between particles caused by adsorption or dissociation characteristics. This may be attributed to the dissociation of clay-OH groups in a manner similar to a weak acid or to the adsorption of $-\text{OH}^-$ ions which result in a nega-

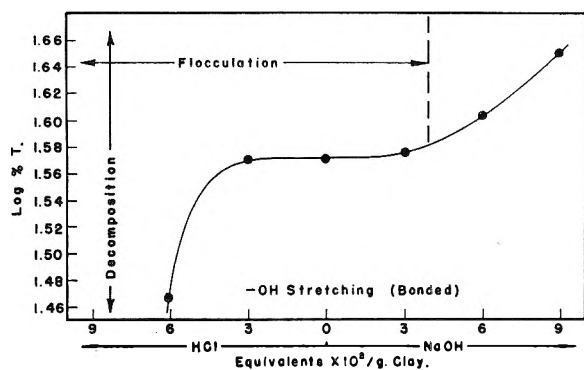


Fig. 3.—Log per cent. transmission for $-OH$ surface sites on Wyoming bentonite treated with various concentrations of NaOH and HCl.

Cook, *et al.*,⁸ have correlated the ion-exchange properties of cation exchangers quantitatively as being associated with a surface charge which in turn is dependent upon the pH of the aqueous medium in contact with the clay surface. Below a pH of 7, kaolinite flocculates rapidly without the aid of flocculants and Wyoming bentonite forms large gel-like flocs.

The purpose of this study was to observe by means of infrared spectroscopy, systematic shifts in clay- OH groups for samples removed from solutions of various pH . Wyoming bentonite as received was washed at a pH of 2 followed by centrifuging in a Sharples Super centrifuge. The clay was repeatedly rewashed with distilled water and centrifuged until the pH of the wash water was approximately 4.5. Varying amounts of NaOH and HCl were added, resulting in a titration curve typical of a dibasic acid. Several points along this curve and a point above and below the

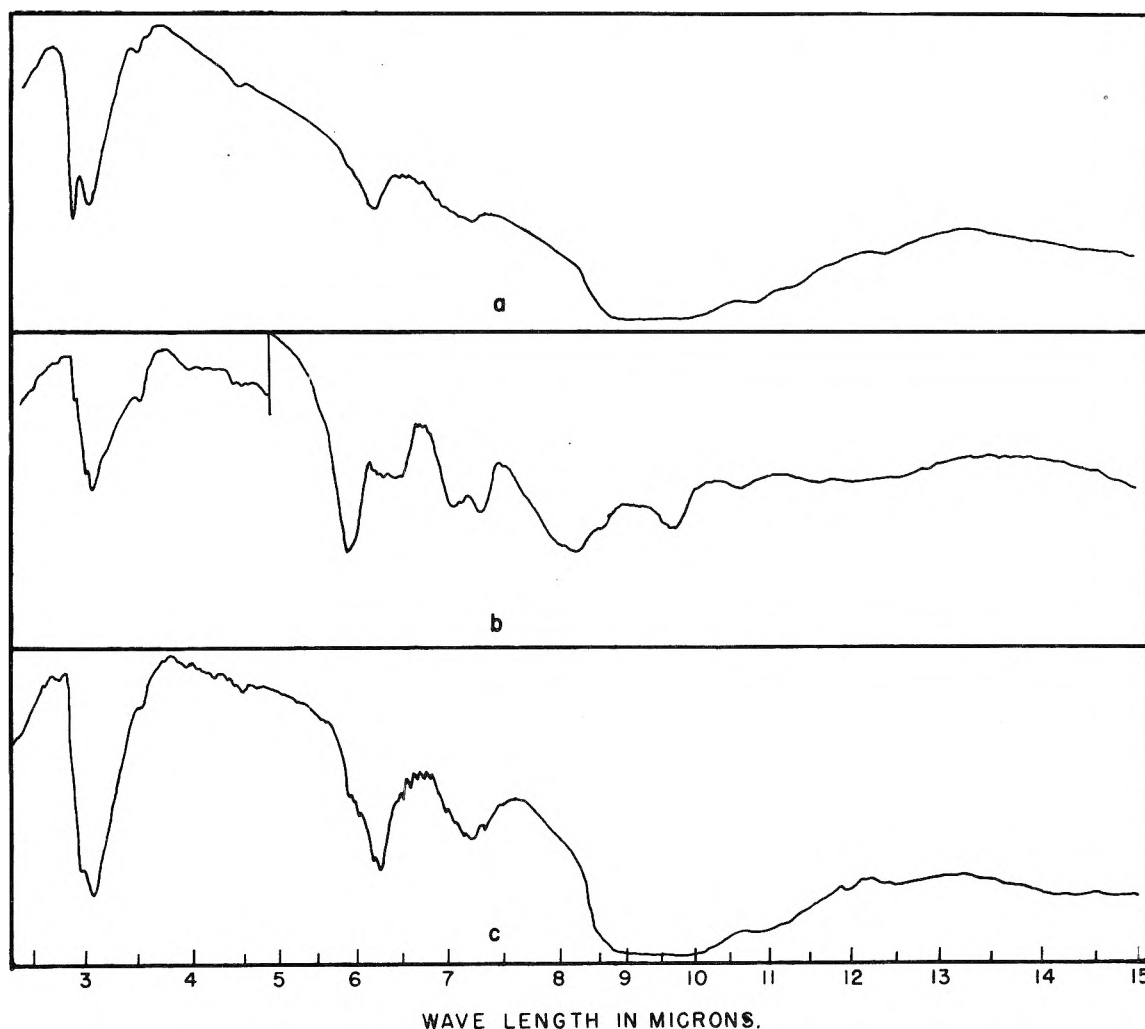


Fig. 4.—a, Acid-washed Wyoming bentonite; b, flocculent Lytron 886; c, Lytron 886 adsorbed on Wyoming bentonite.

tively charged clay surface. Either process results in the formation of a double layer characteristic of the most strongly adsorbed cations present in solution. These cations replace one another in the reverse order of their hydration energies resulting in a series commonly referred to as the lyotropic or Hofmeister series. For this reason factors contributing to flocculation and dispersion are fundamental also to the ion-exchange properties of clays.

concentration range of the curve were investigated in this study. The samples included the washed clay by itself and clay samples to which 30, 60 and 90 meq. of NaOH and HCl per gram of clay had been added. All samples were centrifuged and heated to 250° to remove physically adsorbed water. The heating was accomplished in the furnace of the differential thermal analyzer in cycles of 23 minutes. The differential thermal analysis curves of all

(8) M. A. Cook, I. B. Cutler, G. R. Hill, M. E. Wadsworth and A. G. Oblad, *THIS JOURNAL*, **57**, 1 (1953).

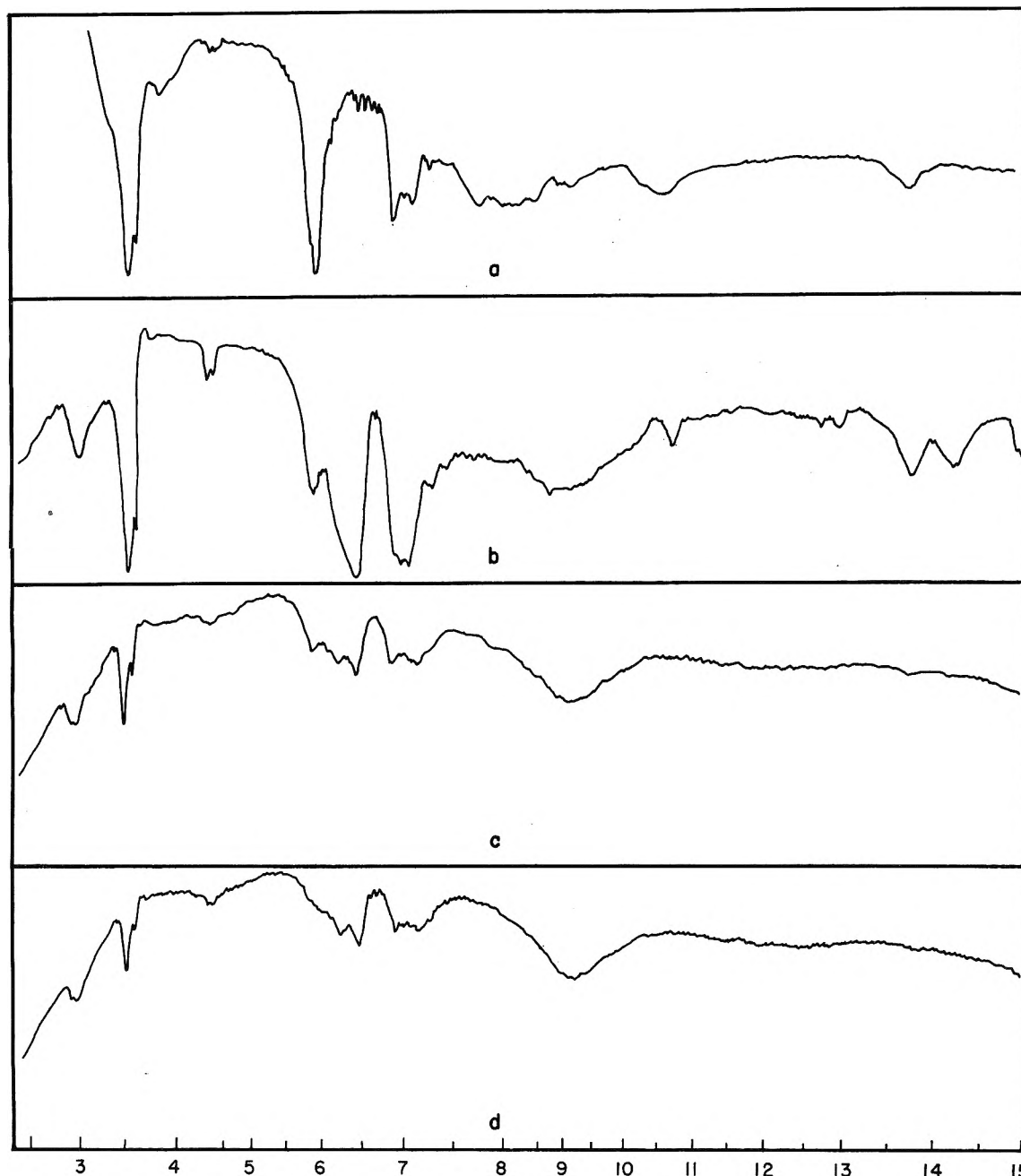


Fig. 5.—a, Oleic acid; b, sodium oleate; c, oleic acid adsorbed on fluorite, water washed; d, oleic acid adsorbed on fluorite, water and acetone washed.

samples removed indicated a large continuous drift for the clay treated with 90 meq. of HCl. This has been attributed to decomposition of the clay under extreme acid conditions.

Five milligrams of each clay sample was pressed in a one-gram KI plate and the absorption spectrum between 2 and 4 μ was studied. Included in this region are both -OH (free) and -OH (hydrogen bonded) stretching frequencies at 2.85 and 3.0 μ , respectively. The large -OH free (2.85 μ) band may be attributed to -OH contained within the lattice of the Wyoming bentonite. Surface -OH stretching groups are not free but are hydrogen bonded. Figure 2 represents the spectra of the clay sample treated at various pH. A systematic increase in the -OH stretching (hydrogen bonded) concentration at 3.0 μ as the acidity was increased is clearly evident by comparing the relative heights of the two peaks.

The log per cent. transmission corresponding to the -OH stretching (hydrogen bonded) is plotted for each clay sample in Fig. 3. A continuous and

increased concentration in surface -OH is evidenced by lower transmission as acidity increases. The vertical dashed line represents the point of pH 7 on the titration curve. Below this pH large gel-like flocs form.

A large number of organic flocculating agents such as the Lytron polyanionic electrolytes produced by Monsanto Chemical Company, Quartec and Galactosal by General Mills, the Jaguar gums of Stein Hall Company, the glues of the Peter Cooper Corporation, plus many others are all effective flocculants to variable degrees for clay minerals. The relative effectiveness of these reagents depends upon ionic strength, foreign ions present in solution and pH effects. These flocculants flocculate not only by charge neutralization

but by physical bridging between particles. This has been demonstrated by Ruehrwein and Ward⁹ for the Lytron polymethacrylate anionic resins. One of the most effective of these flocculants is Monsanto Lytron 886 which is a heteropolymer of maleic anhydride and is anionic in character. Figure 4a is the infrared spectrum of acid washed Wyoming bentonite by itself and Fig. 4b is that for solid Lytron 886. In 4b the peak at 3.0μ is due to $-\text{OH}$ stretching (hydrogen bonded) which contributes to bonding in the solid molecular crystal. The peak at 6.0μ represents carboxyl undissociated and 6.4μ represents carboxyl ionized. The peak at 7.2μ represents C-H bending. Acid washed bentonite upon which Lytron 886 was adsorbed from solution is presented in Fig. 4c. Following contact with the Lytron 886 the clay was washed and centrifuged five times with distilled water. Several important peaks of both Lytron 886 and Wyoming bentonite superimpose, but the variations in the quantities associated with each are clearly evident. In the adsorbed state Lytron 886 possesses some undissociated carboxyl, but a large portion of the carboxyl is present in the salt form. Of particular interest is the large increase in $-\text{OH}$ stretching (hydrogen bonded) at approximately 3μ . The relatively large increase compared to the acid washed bentonite by itself illustrates the presence of hydrogen bonding in the adsorbed state. This bonding is probably fundamental to the effectiveness of flocculants of this type since it provides linkage for physical bridging between particles.

Application to Flotation

The application of infrared spectroscopy to adsorbed monolayers holds much promise in flotation studies. Considerable controversy exists as to the adsorbed reagent. A problem of particular interest in this field is the study of the adsorption of oleic acid on fluorite. Hamilton, Johns and Bradford¹⁰ have demonstrated that the application of heat (above 90°) to a fluorite pulp containing oleic acid greatly improved its floatability. Similar results were obtained where the fluorite ore was ground dry in the presence of oleic acid. Last¹¹ has demonstrated that when heated, oleic acid is so strongly adsorbed the fluorite may be repulped and floated as many as fifteen times without appreciable loss of the mineral. These results have been explained by Cook and Last¹² according to the "free acid" theory of flotation previously proposed by Cook.¹³ According to this model the effect of temperature increases the kinetic energy of undissociated oleic acid to form the activated complex for chemisorption. Undissociated oleic acid physically adsorbed by this process chemisorbs on the surface of the fluorite already covered with adsorbed water and splits out a molecule of water

thus forming a $-\text{Ca}-\text{oleate}$ surface site and a $-\text{F}-\text{H}$ surface site. These conditions are presented as being necessary to preserve electrical neutrality and at the same time produce a hydrophobic surface. By this process, therefore, calcium oleate should be observed by infrared spectroscopy.

Hand picked samples of fluorite (CaF_2) were ground wet in a porcelain ball mill for three days. The ground product was sized in a Sharples Super centrifuge and a near colloidal fraction was removed and repulped. Sodium oleate was added to the pulp which was then brought to boiling. Chemisorption of the oleate collector readily flocculated the fluorite, making it possible to wash the pulp by successive decantation. This process of repulping and decanting was carried out fourteen times using a Waring Blendor for agitation during each cycle. A portion of this washed sample was further washed and decanted three times with acetone.

Figure 5a represents the spectrum of oleic acid by itself. The peak at 3.6μ represents C-H stretching, undissociated carboxyl is evidenced at 6μ , and the C-H bending peak occurs at approximately 7μ . The $\text{C}=\text{C}$ *trans* configuration is

shown at 10.6μ , while the $\text{C}=\text{C}$ *cis* configuration occurs at approximately 13.8μ . Figure 5b is the absorption spectrum of sodium oleate. Some undissociated carboxyl is present as evidenced by a small peak at 6μ . A new peak is evident at approximately 6.4μ which corresponds to the carboxyl salt. Figure 5c is the spectrum of oleic acid adsorbed on fluorite after fourteen washings. Definite peaks for C-H stretching (3.6μ), undissociated carboxyl (6.0μ), and carboxyl salt (6.4μ) may be seen. It is interesting to note that some undissociated oleic acid is still present after fourteen washings. Of particular interest are the *trans* and *cis* $\text{C}=\text{C}$ peaks at 10.6 and 13.8μ , respectively. The *trans* absorption peak appears to be completely missing and the *cis* absorption peak only slightly evident. A comparison of the relative heights of the *trans* and *cis* peaks compared to the $-\text{C}-\text{N}$ stretching in Figs. 5a and 5b indicates that these should still be measurable if they exist. For this reason it appears that the *trans* configuration has disappeared completely or is at least greatly diminished. The *cis* configuration similarly has been reduced.

Figure 5c is similar to 5b except the fluorite has been washed an additional three times with acetone. The undissociated carboxyl (6μ) has been removed and neither the $\text{C}=\text{C}$ *trans* or *cis* bonds are measurably evident. These spectra indicate the presence of undissociated oleic acid physically adsorbed prior to chemisorption and clearly demonstrate the formation of $-\text{Ca}-\text{oleate}$ at the surface following chemisorption.

Of particular interest is the diminishing of the *trans* and *cis* $\text{C}=\text{C}$ bonds. This may possibly be explained by lateral polymerization following chemisorption. This characteristic of oleic acid may explain its outstanding properties as a collector compared to other long chain fatty acids.

Application to Catalysis

The application of infrared spectroscopy seems particularly suitable for the study of products adsorbed on catalysts. A few preliminary tests

(9) R. A. Ruehrwein and D. W. Ward, *Soil Science*, **73**, 485 (1952); and R. A. Ruehrwein, "The Interaction of Polyelectrolytes with Clay Suspensions," Central Research Laboratories, Monsanto Chemical Company.

(10) J. H. Hamilton, J. W. Johns and H. R. Bradford, "Utah Engineering Experiment Station Bulletin," No. 47, Vol. 40 (1950).

(11) A. W. Last, Thesis, University of Utah, 1947.

(12) M. A. Cook and A. W. Last, "Utah Engineering Experiment Station Bulletin," No. 47, Vol. 40 (1950).

(13) M. A. Cook and J. C. Nixon, *THIS JOURNAL*, **54**, 445 (1950).

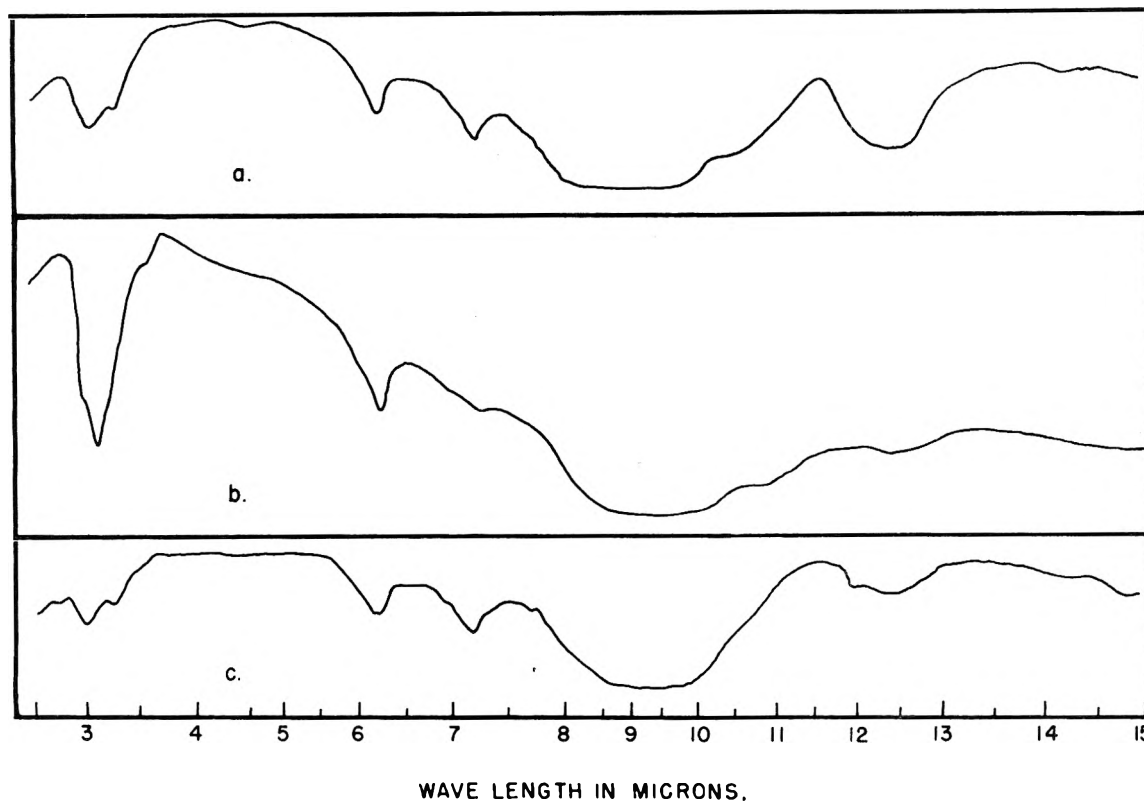


Fig. 6.—a, Ammonia on silica gel; b, Filtrol catalyst Grade 58 before adsorption; c, Filtrol catalyst Grade 58 after adsorption.

have been carried out for the adsorption of ammonia on silica gel and two silica-alumina cracking catalysts. Mapes and Eischens¹⁴ recently reported the presence of NH_3 and NH_4^+ on the surface of a cracking catalyst. The presence of $-\text{NH}_3$ was attributed to chemisorption on Lewis acid sites and the $-\text{NH}_4^+$ to either the presence of anhydrous Brönsted centers or to a reaction of residual water with the Lewis sites.

Figure 6a is the spectrum of ammonia adsorbed on silica gel. Ammonia was passed over the silica gel at room temperature. The presence of $-\text{NH}_4^+$ (bending) is evident at 7.2μ and $-\text{NH}_4^+$ (stretching) at 3.2μ . The band at 6.2μ is due to water which also shows up as $-\text{OH}$ (hydrogen bonded) at 3.0μ . It is at this latter wave length the $-\text{NH}_3$ chemisorbed should also appear.

Figures 6b and 6c are the spectra of Filtrol Catalyst Grade 58 before and after adsorption of ammonia. The $-\text{NH}_4^+$ bending and stretching frequencies are evident at 7.2 and 3.2μ , respectively. An additional change appears for the adsorption band between 12 and 13μ . After adsorption, this band is much more pronounced than before. Absorption in this region is probably due to vibrational frequencies associated with the solid lattice. This, therefore, suggests a possible change in the nature of the lattice as a result of the absorption of ammonia.

A series of tests were carried out in which Houdry Catalyst S-45 was placed in an absorption apparatus designed to weigh the catalyst while at temperature. The ammonia was produced by passing air through NH_4OH , passed over NaOH to remove water and then into the absorption apparatus. The amount of ammonia in equilibrium with the catalyst was controlled by changing the temperature for each

test and the resulting spectra are illustrated in Fig. 7. The first sample (Fig. 7a) was heated to 200° without passing ammonia over it and its spectrum gives no indication of adsorbed ammonia. Ammonia was brought into contact with samples 2, 3 and 4 (Figs. 7b, c and d) at 200 , 150 and 28° , respectively, and the corresponding weight changes were 10.8 , 25.4 and 33.2 mg. per gram of catalyst. All samples were rapidly quenched in air at room temperature and mounted as soon as possible. As with the Filtrol catalyst the $-\text{NH}_4^+$ bending and stretching frequencies were clearly evident. A systematic increase in these peaks took place as greater amounts of ammonia were adsorbed and a plot of the log per cent. transmission of the $-\text{NH}_4^+$ bending (7.2μ) frequency versus the weight gain indicated a linear relationship. The separation of $-\text{OH}$ stretching and chemisorbed ammonia will require a carefully controlled study in which all water is eliminated and each absorption peak carefully studied quantitatively. The scope of this study has been insufficient to make this distinction.

Acknowledgments.—The authors wish to thank Professor Roscoe H. Woolley of the University of Utah Engineering Experiment Station for the construction of the vacuum die used in this study. Thanks are also extended to Dr. W. Martin Fassell for his helpful suggestions in the design and construction of the die and to Dr. John R. Lewis, Head of the Department of Metallurgy, for his support.

DISCUSSION

H. GREENWALD.—Does one have to be sure that the pressed plate is of uniform density? Since the light intensity at the entrance slit varies from point to point, would not a lack of such uniformity lead to deviations from the Beer-Lambert Law?

M. E. WADSWORTH.—The plates used in this study were carefully selected for overall clarity. We did find, however, that partial blanking of a clear plate with the instrument shutter did not change the percent absorption using the base-line method of calculation. Also reproducible results were obtained for a series of several plates containing the same material in the same concentration.

(14) J. E. Mapes and R. P. Eischens, Abstract Am. Chem. Soc. 124th Meeting, Chicago, Ill., September 6-7, 1953.

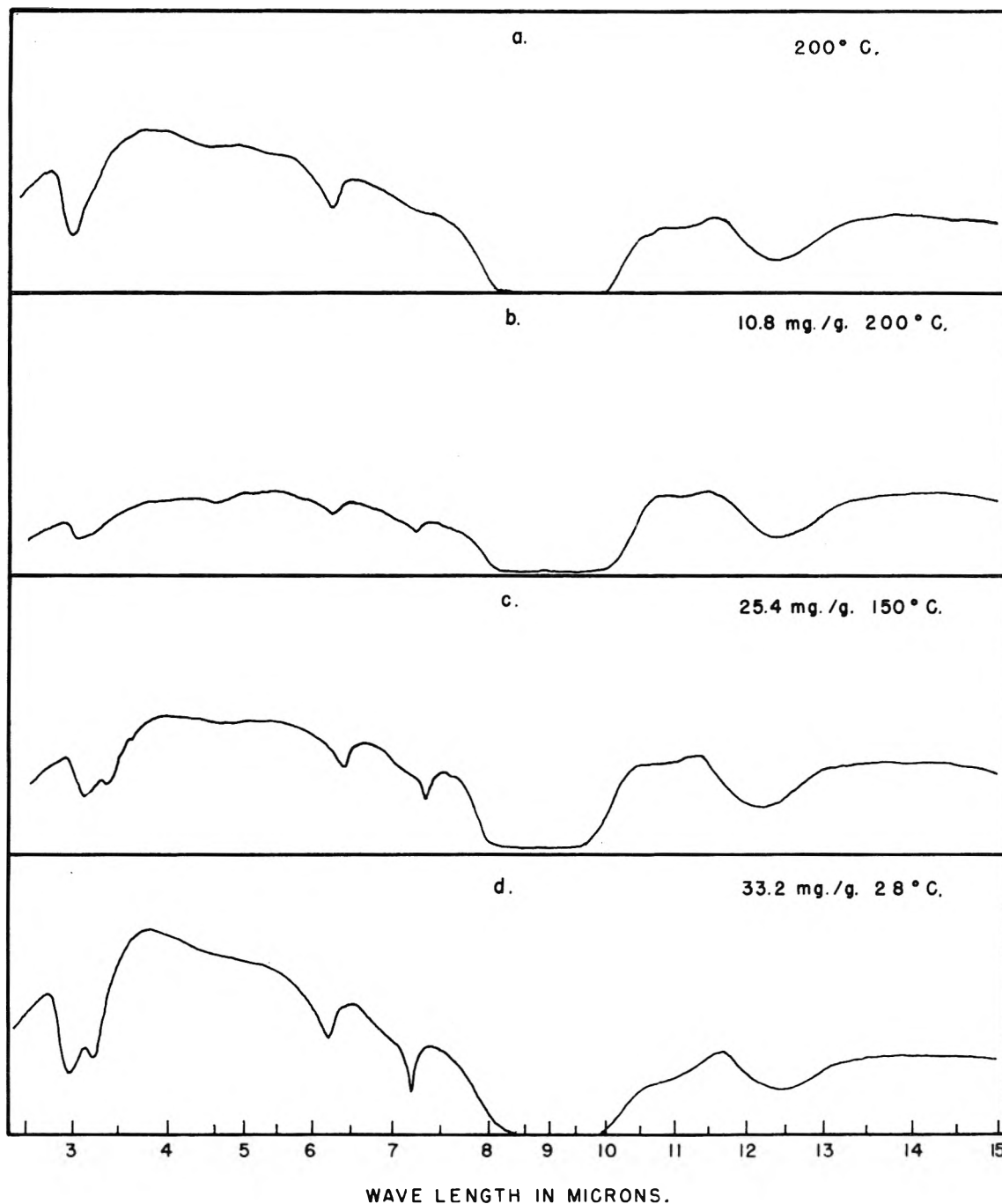


Fig. 7.—Infrared spectra for various amounts of ammonia adsorbed on Houdry catalyst S-45.

F. C. NACHOD.—We have used the KBr technique to great advantage in our Laboratories and Dr. Wiberley at Rensselaer Polytechnic Institute has had equally gratifying experiences. We have found that with suitable design of die, pressure and sieve employed, one can dispense with the vacuum and obtain clear pellets. Our preferred parameters are 5×25 mm. pellet dimensions, 10,000–15,000 p.s.i. and three minutes compression time. The deviations from Lambert's law are due to the scattering and are dependent on particle size of the substance. We have not noted any heat build-up during compression. We think that heat dissipation of any heat during compression is extremely rapid, since extremely heat sensitive substances can be investigated with this technique.

F. M. FOWKES.—Is the extinction coefficient about the same for ammonium ions adsorbed on clays and for ammonium salts (both in KI windows), or does the clay or silica

“hide” many of the adsorbed ions? Why do you expect ammonia coordinated with a cation in a Lewis acid site to adsorb at the same wave length as uncoordinated ammonia, rather than at the same wave length as ammonia coordinated with a proton?

M. E. WADSWORTH.—We have not checked our results for ammonia adsorbed on cracking catalysts with a parallel series of runs with ammonium salts. For this reason comparative absorption coefficients have not been measured.

Your question concerning the wave length of ammonia coordinated with a cation is quite pertinent and certainly one which arouses serious thought. The work of Mapes and Eischens seems to indicate the presence of absorption bands in the region of the normal water bands. We are at present attempting to determine the wave lengths associated with cation coordinated ammonia by an independent method.

COLLOIDAL AND SURFACE PHENOMENA IN THE PREPARATION OF CATHODE-RAY SCREENS

By J. FRED HAZEL AND GEORGE L. SCHNABLE

Department of Chemistry, University of Pennsylvania, Philadelphia, Pa.

Received March 6, 1954

The slow development of adhesion of phosphor powders to glass when dilute solutions of potassium silicate are used has been studied and compared to systems employing mixtures of solutions of potassium silicate and barium acetate. A decrease of zeta potentials with time has been noted for glass and phosphor powders in contact with solutions containing potassium silicate. A possible correlation of this behavior and the increase in adhesion has been discussed. A study of the effect on glass and phosphor surfaces of mixtures of potassium silicate and barium acetate in the concentration range where rapid adhesion is developed also was carried out. Sharp and simultaneous decreases in zeta potentials and flow rates of solutions through the powdered solids has been attributed to the formation of the bonding agent, silica gel, on the surfaces.

Introduction

The settling method of preparing screens of luminescent powders in glass bulbs to serve as cathode-ray tubes in black and white television sets has been employed almost universally since its inception.¹ The process gets its name from the practice of distributing a suspension of the phosphor powder on top of an aqueous layer placed in a bulb and permitting the solid particles to settle onto the glass. The aqueous medium is poured off by tilting the bulb after the particles have adhered to the glass. The time required for adhesion to develop depends in a large measure on the composition of the solution through which the particles settle. The shortest times have resulted when mixtures of potassium silicate with either alkali metal, ammonium or alkaline earth metal salts are employed. Indeed, it has been found possible to pour off the supernatant liquid within 10 or 20 minutes without disturbing the screen, depending on the concentrations of silicate and other salt.

The potassium silicate is the source of the bonding agent for holding the phosphor to the glass, but when it is used alone, adhesion develops slowly and a minimum of several hours are required before the screen can be tilted without displacement of the phosphor. Previous work involving streaming potential measurements of phosphor powders and glass surfaces in the presence of potassium silicate has revealed that this substance increases the negative zeta potentials of both these solid surfaces, indicating adsorption of silicate.² A model of the mechanism by which cations of alkali and alkaline earth metals promote adhesion between silicate coated surfaces has been developed on the basis of two observations. Ions of this type decrease the repulsion between the surfaces by lowering their zeta potentials^{2,3}; they also cause the silicate to polymerize.^{2,3} It is suggested that two silicate coated surfaces would be bonded together under these conditions. The polymerization of potassium silicates by inorganic salts can be observed macroscopically by the increase in optical density or turbidity of the systems and by gel formation.³

One of the objects of the present work was a search for a clue that might lead to an explanation of the slow development of adhesion when silicate alone is employed in the aqueous medium through

which the particles settle. To this end, changes in the system with time, as reflected by streaming potential measurements, have been observed. A second objective was an investigation of the effect on solid phosphor and glass surfaces of mixtures of potassium silicate and barium acetate in concentration ranges where rapid adhesion is developed.

Materials.—The potassium silicate solution, containing approximately 7.8% alkali calculated as K_2O and 19.5% SiO_2 , was a purified solution of $K_2O:3.92SiO_2$.⁴ Light scattering studies on this system⁵ indicate that it is stable with a molecular weight in the vicinity of 2000.

Streaming potential measurements were made with two different glasses in the form of powders. These included Pyrex, which was ground to pass a 150-mesh screen, and a lead-free glass used in the industry.⁶ The latter was ground to pass a 100-mesh screen. A zinc sulfide-zinc cadmium sulfide powder, used in the industry (du Pont No. 1630), was the phosphor employed in the experiments. Other reagents were of reagent-grade quality.

Experimental.—Streaming potential measurements were made in the apparatus described previously.³ The powders under investigation were placed between perforated platinum electrodes using a section of rubber tubing as the cell compartment. In individual measurements, the solution was permitted to stream through the diaphragm for 15 minutes at a pressure of 40 cm. of mercury before the first potential reading was made. Four readings were taken at five-minute intervals in each case. Many of the determinations were repeated and the standard deviation was calculated for those data for which five or more zeta potential values derived from different streaming cells were available. The standard deviation was found to be less than 2.5 millivolts.

The cell constants of the packed diaphragms were determined for purposes of converting streaming potentials to zeta potentials.² A standard solution of 0.100 *N* potassium chloride was employed for this purpose, it being found that there was no appreciable surface conductance under these conditions.

Adhesion Tests.—The first test of the adhesion of phosphor to glass was conducted with potassium silicate alone. Two hundred milligrams of phosphor was mixed with 10 ml. of 10% by volume potassium silicate in a small beaker and added to 90 ml. of 10% by volume potassium silicate in a 400-ml. beaker. The phosphor powder settled to the bottom of the beaker within a few minutes. The increase of adhesion with time was measured by impinging a jet of water on the phosphor screen. A two-ml. pipet was mounted vertically over the beaker with the aperture placed 8 mm. from the screen. The other end of the pipet was connected to a water reservoir whose surface was 72 cm. above the screen. Water was allowed to impinge on the screen for a period of five seconds at the following intervals: 0.5, 4, 24 and 48 hours. The results are shown in Fig. 1. The

(4) The material is sold by the Philadelphia Quartz Company under the trade name Kasil No. 1.

(5) A. P. Brady, A. G. Brown and H. Huff, *J. Colloid Sci.*, **8**, 252 (1953).

(6) The glasses were supplied by the Corning Glass Works and designated as No. 7740 (Pyrex) and No. 9010.

(1) M. Sadowsky, *J. Electrochem. Soc.*, **95**, 112 (1949).

(2) R. Edelberg and J. F. Hazel, *ibid.*, **96**, 13 (1949).

(3) J. F. Hazel and G. L. Schnable, *ibid.*, **100**, 65 (1953).

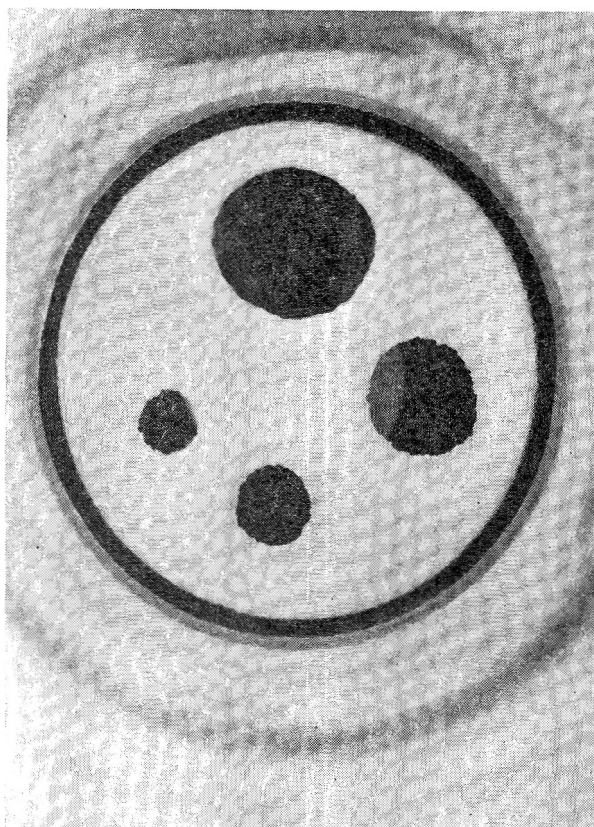


Fig. 1.—Two hundred mg. of phosphor settled in 100 ml. of 10% by volume potassium silicate. A small jet of water was allowed to impinge on the screen at the following intervals: 0.5, 4, 24 and 48 hr. (beginning at 12 o'clock and reading clockwise with increasing time). The solution was decanted after 24 hr.

black areas indicate bare glass. The above experiment was repeated using a lower concentration of potassium silicate: 200 milligrams of phosphor was mixed with 10 ml. of 6% potassium silicate and added to 90 ml. of water.⁷ A water jet was impinged on the screen with the results shown in Fig. 2. The diameters of the displaced area were 25, 22 and 20 mm. corresponding to the time intervals of 0.5, 4 and 24 hours. The increase in adhesion with time was less in this case than when the more concentrated solution was used, Fig. 1.

The next test was made with mixtures of potassium silicate and barium acetate. The more dilute solution of potassium silicate was used in this experiment. Two hundred milligrams of phosphor was suspended in 10 ml. of 6% potassium silicate by volume in a small beaker and added to 90 ml. of 0.03% barium acetate in a 400-ml. beaker. The effect of time on the adhesion was determined by allowing a jet of water to impinge on the screen after 10, 20, 30 and 210 minutes, Fig. 3.

An inspection of Fig. 3 shows that the phosphor powder adhered to the rounded edges of the bottom of the beaker (as indicated by the absence of a ring of bare glass) on impact when a mixture of potassium silicate and barium acetate was used. This was not the case when potassium silicate alone was employed and as a result the phosphor powder piled up in a thick white ring near the edge, Figs. 1 and 2. The effect of addition agents, *e.g.*, barium acetate, in promoting adhesion in this system has been discussed previously,^{2,3,8} and attributed to the lowering of the zeta potential of the solid surfaces, and to the polymerization of the adsorbed silicate.

The rapid increase in adhesion with time in the same sys-

(7) The amount of potassium silicate employed may have a marked effect on the adhesion. Indeed, it has been shown that very small amounts of this reagent cause the phosphor and glass to repel each other.⁸

(8) Wm. Stericker and J. F. Hazel, *THIS JOURNAL*, **54**, 1045 (1950).

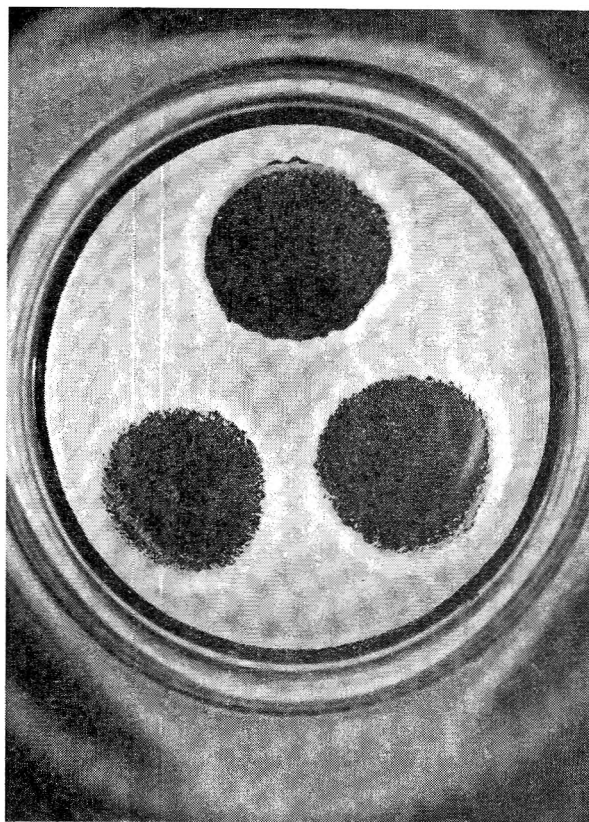


Fig. 2.—Two hundred mg. of phosphor settled in 100 ml. of 0.6% by volume potassium silicate. Jet of water impinging at 0.5, 4 and 24 hr. (reading clockwise). The picture was taken without decanting the solution.

tem, Fig. 3 (the diameter of the displaced screen decreased from 11 to 5 mm. in 3.0 hours) can probably be attributed to an increase in the degree of polymerization of the silicate with time. Figure 4 shows the effect of time on the turbidity readings obtained with a Klett-Summerson Photoelectric Colorimeter using different amounts of potassium silicate with a constant amount, 268 p.p.m., of barium acetate. Brady, Brown and Huff have shown that alkali metal and ammonium salts also cause the rapid polymerization of potassium silicate.⁵ The same authors noted a slow rate of polymerization in dilute solutions, such as are used here, of potassium silicate alone.

A 10% by volume solution was allowed to age for 24 hours in order to allow for any possible polymerization. This solution was then used for preparation of a screen following the same procedure as described under Fig. 1. Adhesion was less in this case than when the freshly prepared solution was brought in contact with the phosphor and the glass, Fig. 1. This was evidenced by the fact that the phosphor powder tended to pull away from the glass when the liquid was decanted.

Streaming Potential Studies.—The decrease of the zeta potential of glass and phosphor in contact with potassium silicate, shown in Fig. 5 also probably aids the adhesion by decreasing the repulsion between the surfaces. The decrease of negative zeta potentials with time might be attributed to changes in the properties of the potassium silicate-barium acetate mixtures with time (in the case of mixtures), to solubility of the solid, swelling of the solid, and base exchange.

A comparison of the slopes of graphs of zeta potential *versus* time for the solids in various solutions rules out the first possibility as a major cause, since the zeta potentials changed at approximately the same rate with potassium silicate alone as with potassium silicate-barium acetate mixtures.

Appreciable solubility of Corning No. 9010 glass and of the phosphor was detected by conductivity measurements. When distilled water was streamed through cells of glass or phosphor for about 10 minutes the resistance between the

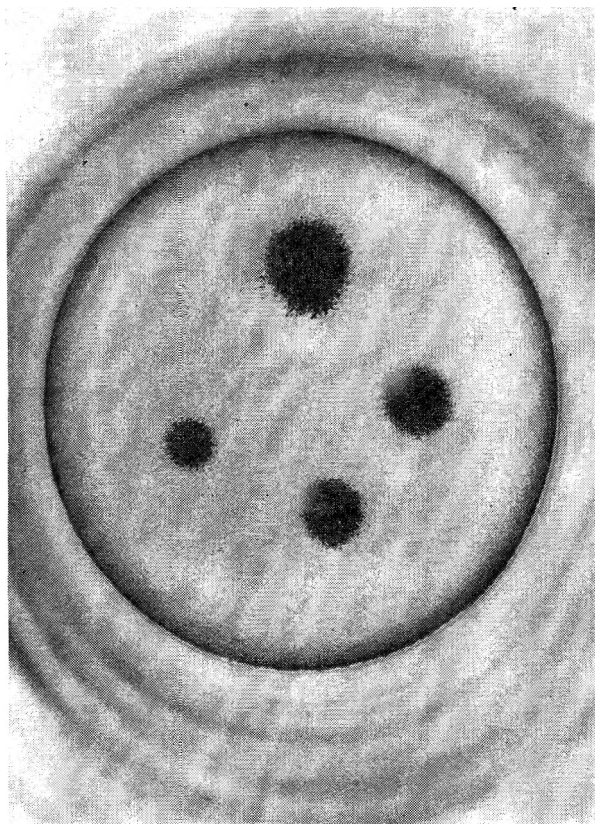


Fig. 3.—Two hundred mg. of phosphor settled in 100 ml. of 0.6% by volume potassium silicate and 268 p.p.m. of barium acetate. A jet of water was impinged at 10, 20, 30 and 210 min. (reading clockwise).

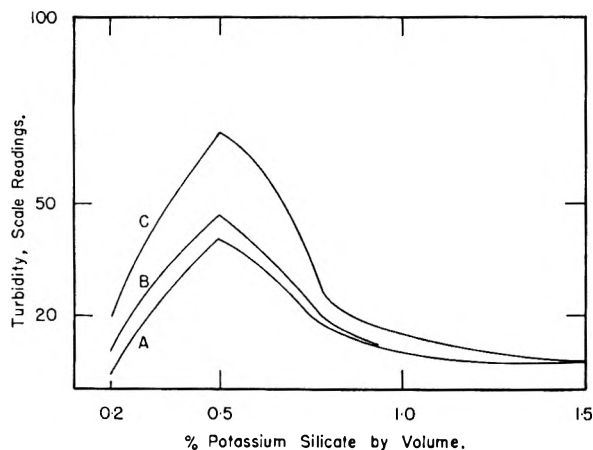


Fig. 4.—Effect of 268 p.p.m. of barium acetate on the turbidity of potassium silicate solutions: A, 15 min.; B, 30 min.; C, 24 hr.

conductance electrodes asymptotically approached a value of about 120,000 ohms. When streaming was stopped the resistance between the electrodes decreased rather rapidly. For cells of Corning No. 9010 glass the resistance decreased to about 55% of the initial value after 30 minutes, to 25% after 2 hours, and to 12% after 6 hours. With the phosphor the resistance decreased to 17% after 4 minutes and to 10% after 30 minutes. When distilled water having a specific resistance of 800,000 ohms was streamed (under 40 cm. pressure) through a cell of Corning No. 9010 glass the effluent from the cell had a specific resistance of 50,000 ohms.

The decomposition of glass by water is not a simple case of solution but a highly complex process involving the penetration of the glass by water and the subsequent decomposi-

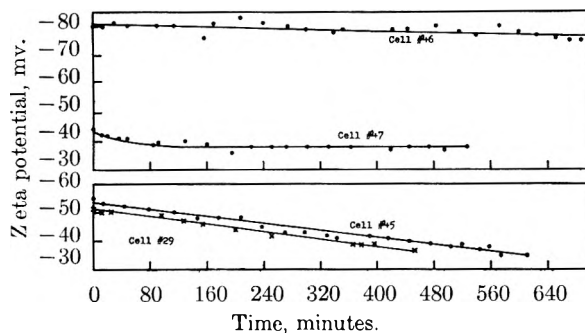


Fig. 5.—Change of zeta potentials with time: cells 45 and 29, Corning No. 9010 glass in 0.6% by volume potassium silicate and in 0.6% by volume potassium silicate plus 50 p.p.m. barium acetate, respectively; cells 46 and 47, phosphor in 0.6% by volume potassium silicate and in 0.6% by volume potassium silicate plus 200 p.p.m. barium acetate, respectively.

tion of the complex silicate mixture with formation of substances wholly different from those originally present. Decomposition of most glasses by water results in the liberation of alkali. The remaining more siliceous glass might be expected to have a lower zeta potential than the original glass. The effect of solubility on the electrokinetic properties of phosphors is not known. The slopes for the Corning No. 9010 glass are about three times as great as for the phosphor, and this is believed to be due, at least in part, to swelling of the glass.

Hubbard, Hamilton and Finn⁹ have shown that glass does swell measurably in water. Mysels and McBain¹⁰ observed that fritted Pyrex glass offered increasing hydrodynamic resistance but unchanged electrical resistance. Hubbard and Goldman state the uneven distribution of migrating ions between the inner and outer phases (the glass surface and the ambient solution, respectively) produces osmotic pressure within the surface of the glass, causing swelling and ultimate destruction of the specimen. Kanamaru, *et al.*,¹¹ investigated the apparent electrokinetic potentials of some swelling substances (including glass) calculated in the usual way from streaming potential or electroosmosis data. They found that the apparent zeta potential decreases as the swelling progresses.

Base exchange, the equivalent replacement of positive ions in the solid by cations from the solution, probably did not contribute substantially to the reduction in zeta potentials observed in the present case. This is because the rate of decrease of potential (Fig. 5) was the same in solutions containing potassium ions only as with solutions containing both potassium ions and barium ions. Willard¹² has studied the exchange between glass and aqueous solutions of K^+ , Ba^{++} and H^+ ions. In experiments extending over 330 hr. he concluded that the replacement of sodium ions in the surface by foreign ions was not as rapid as the rate of dissolution of the glass to expose new sodium.

Effect of Barium Acetate Concentration on Rates of Flow in Streaming Potential Measurements.—The zeta potentials of the phosphor and glasses in various potassium silicate-barium acetate mixtures are plotted as a function of the barium acetate concentration in Figs. 6, 7 and 8. The last points on the curves fall within, or close to, concentration ranges of reagents which promote rapid adhesion of phosphor to glass. These points are encircled and are connected to the rest of the curve with dotted lines in order to distinguish the fact that the solutions had abnormally low flow rates through the cells. While most of the solutions were cloudy, others were clear.

A number of the streaming cells which displayed abnormally low flow rates with potassium silicate-barium acetate mixtures were disassembled, the powdered material removed, and the cell reassembled without the powder but

(9) D. Hubbard, E. H. Hamilton and A. N. Finn, *J. Research Natl. Bur. Standards*, **22**, 339 (1939).

(10) K. J. Mysels and J. W. McBain, *J. Colloid Sci.*, **3**, 45 (1948).

(11) K. Kanamaru, T. Kobayashi and M. Seki, *Kolloid Z.*, **87**, 62 (1939); K. Kanamaru and T. Takada, *Z. physik. Chem.*, **A184**, 179 (1939); *Kolloid Z.*, **90**, 315 (1940).

(12) J. E. Willard, *This Journal*, **57**, 120 (1953).

with the paper discs. Flow rates of the mixtures or of distilled water through the reassembled cells ranged from about 100 to 700 ml./min. under 40 cm. pressure, in contrast to flow rates of the mixtures through the original cells of about 0.2 ml./min. and less. The possibility of low flow rates being due to the formation of silica gel on the filter paper discs or to clogging of the pores of the filter paper by colloidal silica particles from the cloudy mixtures streaming through the cells was ruled out by these experiments.

In seeking other explanations for the low flow rates it may be pointed out that these could have resulted from the formation of silica gel on the surface of the solid under test or, in the case of cloudy mixtures, to the action of the porous plug of solid as a filter for the silica particles. Since low flow rates occurred with clear solutions in several cases, the first explanation appears to be valid, *i.e.*, the potassium silicate-barium acetate mixtures caused the surfaces of the particles confined in the streaming cell to become coated with silica gel.

Salts tend to promote the polymerization of silicates and since the silicate is concentrated by adsorption on the solid surfaces, the loci of polymerization are predominately there. Because of the adsorption concentration, the formation of silica gel on the surface of the phosphor or glass could occur in potassium silicate-barium acetate mixtures which were clear. In cases where the solution was cloudy, it seems likely that the polymerization, which was evident in the bulk of the solution, would occur to an even greater extent on the surface of the solid because of the adsorption of reagents.

Discussion.—If it is assumed that silica gel coats the particles of phosphor or crushed glass, it is evident that a portion of the total pressure difference across the streaming cell is expended in overcoming the resistance to hydrodynamic flow offered by the silica gel. There are, in effect, two streaming potential cells in series, across which there is applied the total pressure difference measured by the manometer. The streaming potential resulting will be the sum of the potentials of the two cells.

The electrokinetic equation is

$$E = \zeta PDR / 4\pi\eta c \quad (1)$$

where E is the streaming potential, ζ is the zeta potential, P is the pressure difference across the cell, R is the resistance between the platinum conductance electrodes, D is the dielectric constant, η is the viscosity of the solution, and c is the cell constant of the streaming cell. Since no change in conductance occurs as silica gels set, c does not change. If E_s is the streaming potential of the conventional streaming cell and E_g is that of the silica gel, the total potential difference is their sum.

$$E_t = E_s + E_g \quad (2)$$

The sum of the pressure across the two cells under consideration is the total pressure, which is measured by the manometer.

$$P_t = P_s + P_g \quad (3)$$

Let ζ_c be the zeta potential of the streaming cell as calculated in the usual manner; ζ_s is the zeta potential of the solid under test; ζ_g is that of the silica gel.

$$\zeta_c = \frac{4\pi\eta E_t c}{P_t DR} \quad (4)$$

and

$$E_t = E_s + E_g = \frac{\zeta_s P_s DR}{4\pi\eta c} + \frac{\zeta_g P_g DR}{4\pi\eta c} \quad (5)$$

$$E_t = \frac{\zeta_s P_s DR + \zeta_g P_g DR}{4\pi\eta c} = \frac{(\zeta_s P_s + \zeta_g P_g) DR}{4\pi\eta c} \quad (6)$$

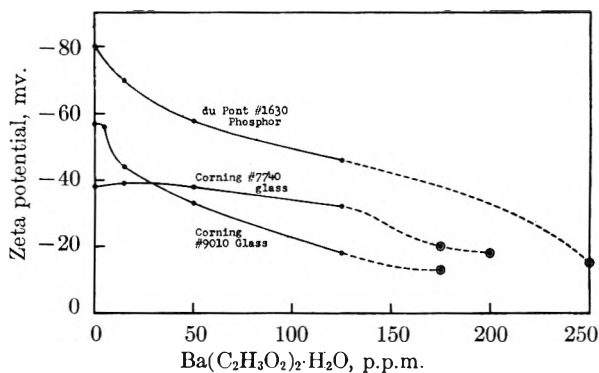


Fig. 6.—Zeta potentials of Corning No. 7740 glass, Corning No. 9010 glass and du Pont No. 1630 phosphor in 0.6% by volume potassium silicate plus barium acetate.

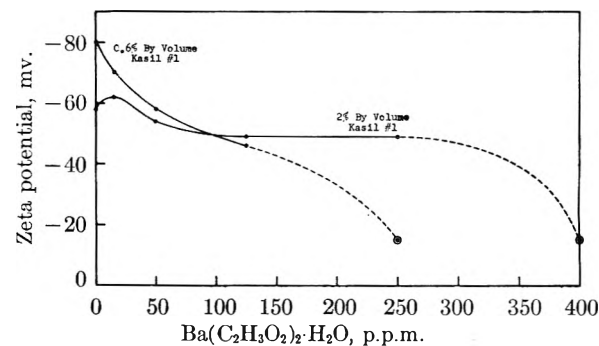


Fig. 7.—Zeta potentials of du Pont No. 1630 phosphor in potassium silicate-barium acetate mixtures.

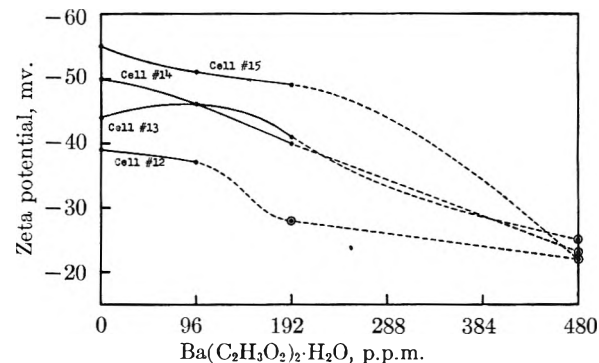


Fig. 8.—Zeta potentials in potassium silicate-barium acetate mixtures: cells 12 and 13, Corning No. 9010 glass in 8 and 10% by volume potassium silicate, respectively; cells 14 and 15, du Pont No. 1630 phosphor in 8 and 10% by volume potassium silicate, respectively.

Substituting expression 6 for E_t in equation 4 and cancelling

$$\zeta_c = \frac{\zeta_s P_s + \zeta_g P_g}{P_t} \quad (7)$$

From this equation it can be seen that if an appreciable pressure drop exists across silica gel formed in the streaming cell, the zeta potential calculated will be intermediate between that of the solid and the gel. In cases where flow rates less than about 10% of normal were observed, practically all of the pressure difference existed across the silica gel and hence the zeta potential calculated corresponded approximately to that of the silica gel.

The average of 10 zeta potentials, calculated from data obtained with streaming cells showing

abnormally low flow rates with solutions containing 0.6% by volume potassium silicate plus 175–400 p.p.m. barium acetate, was -14 millivolts. Extrapolation of the curves derived from these same streaming cells with 0.6% by volume potassium silicate plus 0 to about 150 p.p.m. barium acetate, all showing normal flow rates, yields zeta potentials averaging more than 10 mv. higher than those determined with the low flow rates.

The abrupt change in zeta potentials accompanied by the sharp decrease in flow rates, together with the fact that the numerical values of the corresponding zeta potentials appear to be independent of the nature of the original solid surfaces, suggest that the latter were coated with silica gel.

Acknowledgment.—The experimental work on streaming potential measurements was supported by a grant from the Philco Corporation.

DISCUSSION

CHARLES B. HURD.—Have you tried changing the pH of the potassium silicate-phosphor suspension because of the statement that the silicate polymerized (condensation poly-

merization) especially under the influence of Ba^{++} ion. Since a great deal of work has been done on the setting of silicic acid gels and since the setting due to condensation occurs much more rapidly in the pH range of 7, I thought lowering the pH by addition of an acid, would promote this condensation polymerization.

J. FRED HAZEL.—The screens can be made by reducing the pH of the potassium silicate using weak acids, *e.g.*, acetic and phosphoric, ammonium salts and acid salts, *e.g.*, potassium hydrogen carbonate and primary and secondary phosphates. It is desirable not to reduce the pH below about 6–8. In an acid medium adhesion is poor. Figure 3 in the preprint is inverted.

HERBERT L. DAVIS.—Is it not probable that the charge factors in these systems could be favorably influenced by other cations than barium? Many years ago we demonstrated the redispersion of silica to produce stable sols in acid solutions, and believe this emphasizes the charge factor in precipitation and gel formation. It seems possible that very tiny additions of a quaternary or other strongly sorbed cation (even possibly a basic dye to tint the picture) might give good firm adhesion. Alternatively, a pre-coating of the bulb surface with very dilute cationic-active substances (as zephiran chloride) might speed the adsorption of the phosphor, but irregular series phenomena may enter as discussed by Dr. Ross, who used quaternary compounds to prevent adhesion of particles to glass vessel walls in sedimentation tests.

ELECTRON DIFFRACTION STUDIES IN THE SYSTEM BeO-In₂O₃¹BY C. R. ADAMS² AND W. O. MILLIGAN*The Rice Institute, Houston, Texas**Received March 5, 1954*

Electron diffraction patterns have been obtained for a series of eleven dual oxide, heat-treated (2 hr., 500°) gels in the system BeO-In₂O₃. The gels were the identical ones previously studied by X-ray diffraction methods, gas adsorption and electron microscope techniques, and which exhibited two composition zones of (a) mutual protection against crystallization, (b) enhanced adsorptive capacities, (c) enhanced water surface areas, and (d) enhanced differential and integral heats of adsorption. The electron diffraction patterns exhibit enhanced line broadening in the same two composition zones. The positions of the diffraction lines are identical with those from well-crystallized In₂O₃, and the observed broadening is interpreted as indicating the presence of extremely small crystals within the dual zones of mutual protection. The secondary particles (aggregates), as viewed in the electron microscope, consist of several crystallites. The number of crystallites per aggregate increased rapidly in the two composition zones. The enhanced surface properties, occurring in the zones of mutual protection, are attributed primarily to the smaller crystal size. From a comparison of the water surface area with the geometrical area of the primary crystallite, it is deduced that more than half of the crystallite surface is accessible to water vapor. The electron diffraction pattern of BeO, as a separate phase, is detectable at a concentration as low as 60 mole % BeO in gels heat-treated at 600°.

Introduction

In previous reports from this Laboratory systematic X-ray diffraction³ and sorption-desorption⁴ studies of the dual hydrous oxide system BeO-In₂O₃ demonstrated the existence of two composition zones of mutual protection⁵ against crystallization. These composition zones showed enhanced adsorptive capacities, water surface areas, and differential and integral heats of adsorption. In a more recent report,⁶ a detailed high magnification electron microscope study of the secondary particle (aggregate) size in this system showed that the zones of mutual protection do not result from variation in secondary particle size. In an effort to elucidate the structure of these secondary particles, a systematic electron diffraction study was carried out on this system. It is the purpose of this paper to report the results obtained.

Experimental

The electron diffraction patterns were taken in a Philips electron microscope using 100-kv. electrons. The photographic densities were obtained from the plates by the use of a Moll microphotometer and a "Photopen" recorder. The photographic densities were converted to relative electron intensities and transferred to large graph paper. The incoherent scattering was obtained by drawing in a smooth curve and the structure-sensitive diffraction peaks obtained by subtracting.

In Fig. 1 are plotted, on a relative intensity basis, the coherent scattering patterns for the system heat-treated for 2 hours at temperature levels of 500 and 600°.

It will be noted in Fig. 1 that enhanced line broadening occurs at compositions corresponding to the two previously observed zones of mutual protection. The increased line broadening may result from smaller crystal size, or from strains and distortions. The positions of the diffraction lines are identical, within the limits of observation, with those obtained from large, well-formed crystals of In₂O₃. In the following interpretations of the observed line broadening, it is assumed that broadening from strain or distortion may be neglected, or is independent of the temperature

of heat-treatment. The assumption accounting the line broadening to crystal size effects leads to results agreeing closely with water surface areas measured previously by gas adsorption techniques.⁴ It appears reasonable that the line-broadening may be interpreted on the basis of crystal size.

To obtain a measure of the crystallite size from line broadening one must know the instrumental broadening due to the particular experimental apparatus. The instrumental broadening was obtained in this case for each particular line by heating samples of pure In₂O₃ and BeO to a sufficiently high temperature to obtain single crystals large enough to see and measure in the electron microscope. In the samples employed for standardization the single crystal cubes of In₂O₃ were about 250 Å. on an edge. The single crystals of BeO tended to be plate-like and were about 250 Å. in length. In these samples the broadening due to crystal size amounted to only a few per cent. of the total broadening. The electron diffraction rings were slightly spotty in appearance.

Results and Conclusions

In Fig. 1 are shown the coherent scattering patterns for the system heat-treated at 500 and 600°. From a consideration of the patterns for the system heat-treated at 500° it is apparent that the same zones of composition which had previously shown enhanced adsorptive capacity, surface areas and differential and integral heats of adsorption, correspond to a more poorly crystalline condition. Visual inspection of the patterns suggests that the crystal size is much smaller in these regions. In a previous study with X-rays³ no pattern for BeO as a separate phase was detected in the dual gels at any heat-treatment. From an examination of the 90 mole % BeO sample heated at 500°, it is apparent that the stronger diffracting power of electrons has detected the presence of a crystalline phase of BeO. However, the crystal size is very small for the samples heated at 500° and, therefore, a complete electron diffraction study was carried out on samples heat-treated for two hours at 600°. From these latter patterns it is apparent that the BeO exists as a separate crystalline phase to as low a concentration as 60 mole % BeO, although X-ray diffraction patterns of these samples fail to show the presence of a separate crystalline phase of BeO for any samples containing In₂O₃. The apparent contradiction of these experiments is attributed to the much greater diffracting power of BeO for electrons relative to X-rays. Figure 2 shows the size of the crystallites as measured by line-broadening

(1) Presented before the twenty-eighth National Colloid Symposium which was held under the auspices of the Division of Colloid Chemistry of the American Chemical Society in Troy, New York, June 24-26, 1954.

(2) Ethyl Corporation Fellow in Chemistry at The Rice Institute, 1953-1954.

(3) L. M. Watt and W. O. Milligan, *THIS JOURNAL*, **57**, 883 (1953).

(4) W. O. Milligan and C. R. Adams, *ibid.*, **57**, 885 (1953).

(5) W. O. Milligan, *ibid.*, **55**, 497 (1951).

(6) C. R. Adams and W. O. Milligan, *ibid.*, **58**, 219 (1954).

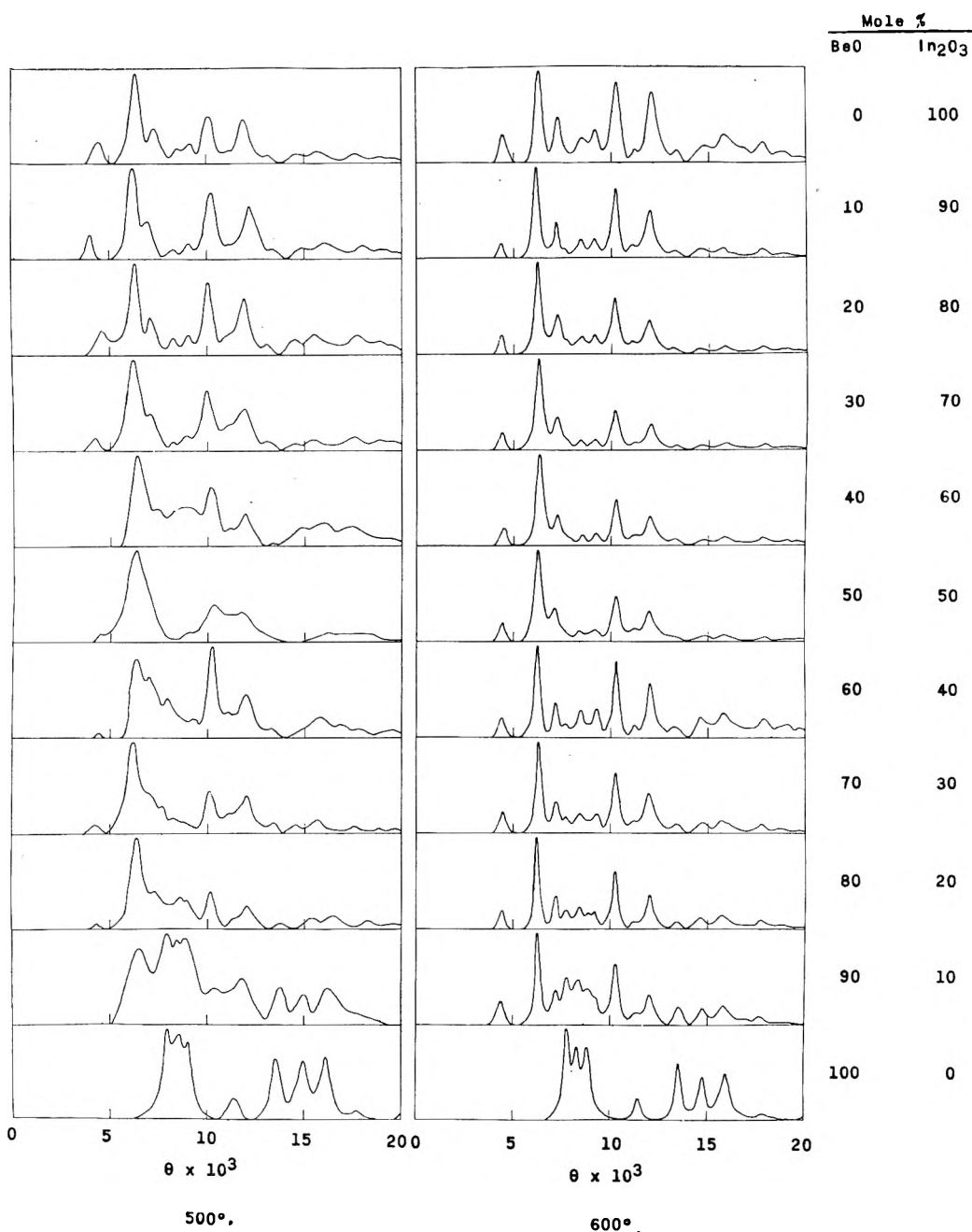


Fig. 1.—Relative coherent electron diffraction intensities for the system BeO–In₂O₃, heat-treated for 2 hr. at 500 and 600°.

for the system heated at 500° as compared⁷ to the secondary particle size. The open points give the volume average of the secondary particle diameter as measured in the electron microscope.⁶ The closed points give the edge of a crystalline cube of In₂O₃ as deduced from line broadening. The half-open circles give the diameter of a sphere of BeO. It is noted that the secondary particle size is a linear function of composition, thus indicating that the interaction has no effect on the secondary particle size. However, the crystallite size shows a decided decrease in the regions of the zones of mutual protection. It follows that the secondary particles are composed of several smaller crystallites, the number rising very rapidly in the zones of mutual protection, as shown in the top part of Fig. 2.

In Fig. 3 is shown a plot of the fraction of crystallite surface accessible to water vapor as measured by a calculation of the water surface area.⁴ It is noted that more than half of the crystallite surface is accessible to water vapor. In view of the uncertainty of the crystallite size measurements (15–20%) and a lack of a detailed knowledge of the exact shape of the crystallites, one can only conclude that most of the crystallite surface is accessible to water vapor. However, since all of the crystallite surface is not accessible to water vapor, a consideration of the packing of the crystallites in the secondary particle must account for this area which is not accessible to the water vapor. Since the water vapor does have access to a much larger area than the external area of the secondary particles,⁶ it fol-

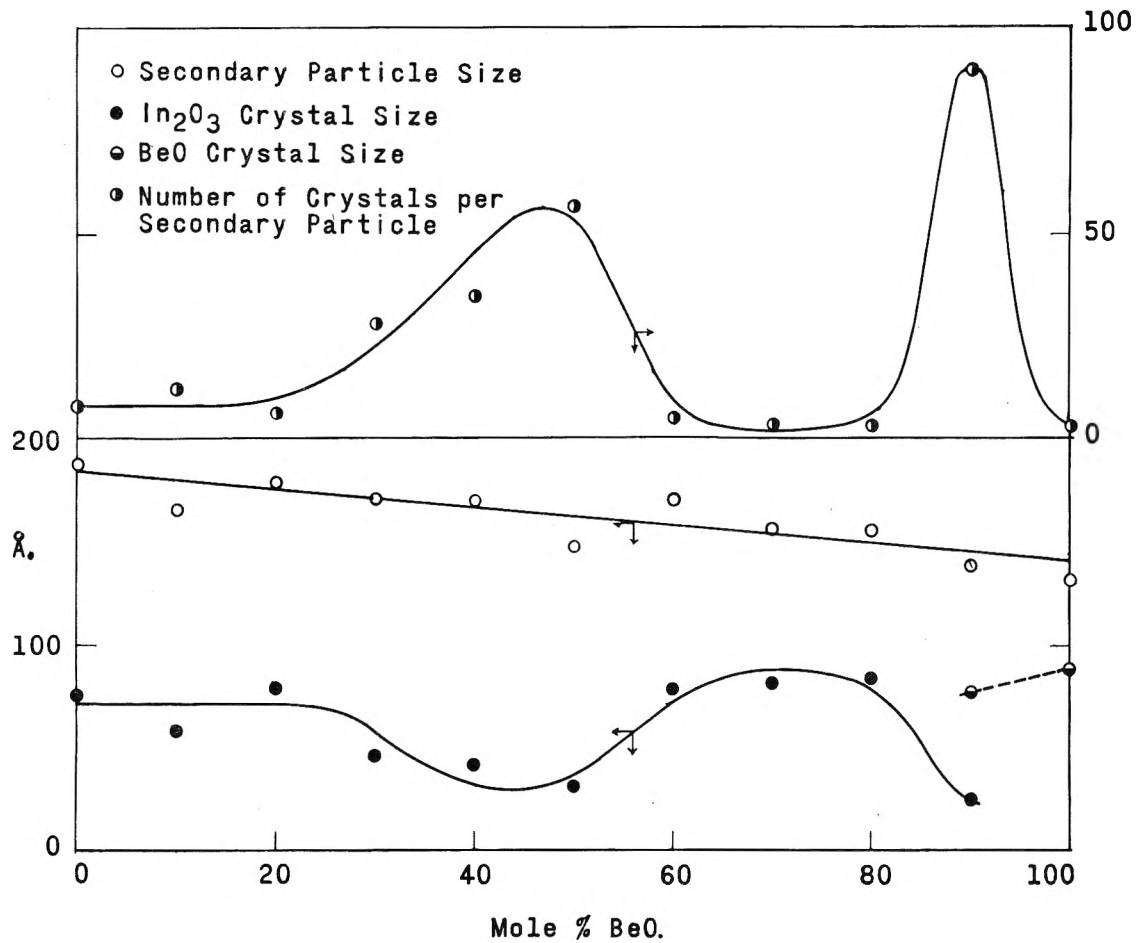


Fig. 2.—Particle sizes in the system BeO-In₂O₃. Open points are secondary particle diameters. Closed points are edges of In₂O₃ cubes. Half-open points are diameters of spheres of BeO. The top graph gives a measure of the number of crystallites per secondary particle.

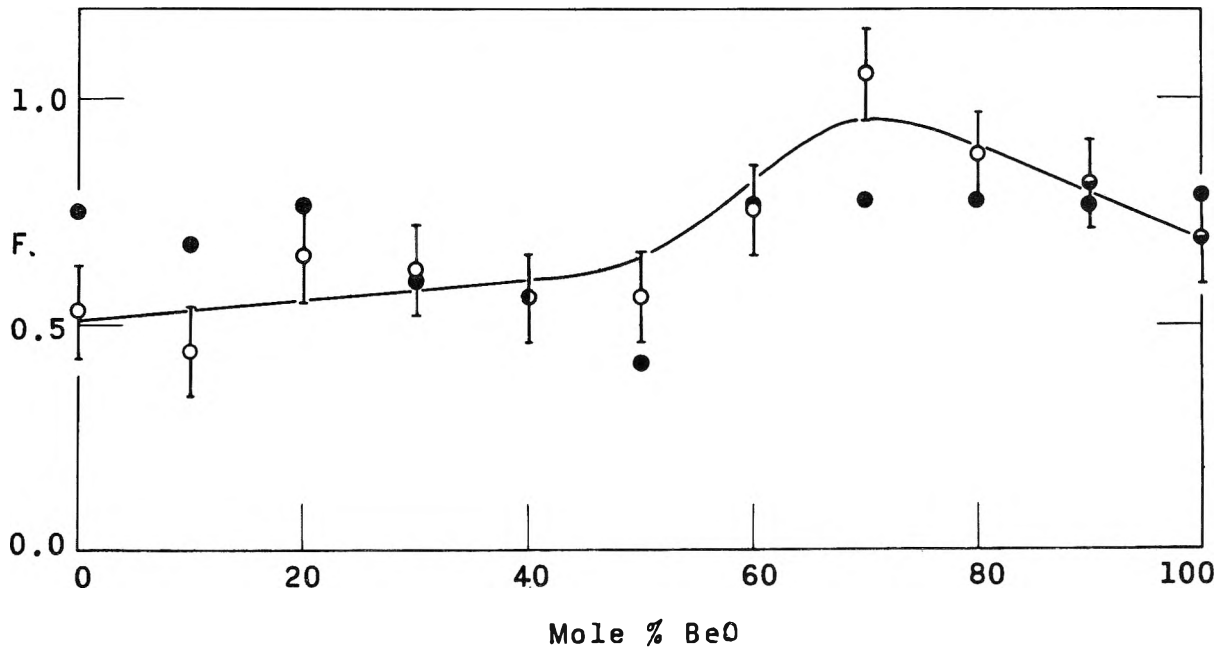


Fig. 3.—Fraction of crystallite surface area accessible to water vapor, F , as a function of composition. The closed points are the fractions available for close-packed spheres of the same size as the crystallites.

lowers that the water molecule (or OH groups) can penetrate around at least part of the area of the crystallites. The closed points in Fig. 3 give the value of the fraction of surface area available to a

water molecule for close-packed spheres of diameter equal to the crystallite size. The fair agreement indicates that the crystallites are fairly tightly packed in the secondary particles, but it would be difficult to distinguish between similar idealized models.

DISCUSSION

F. M. FOWKES.—The calculation of surface areas from weight average diameters of particles is a rather inaccurate process. It seems that more conclusions are drawn from these calculated areas (as in Fig. 3) than are justified.

C. R. ADAMS (*communicated*).—It is noted in the last paragraph of the paper that the values of areas obtained from crystal sizes are uncertain and can only be considered

approximate. For this reason the only conclusions emphasized by the authors are (a) some area inside the aggregate is accessible to water, (b) not all of crystal area is accessible, and (c) these effects are due to packing. The roughness factor values from electron microscopic data would have to be in error by several hundred per cent to invalidate the first conclusion, whereas errors of the order of one hundred per cent would be necessary in Fig. 3 to invalidate the second conclusion. The third conclusion is a natural consequence of the first two conclusions. It is obvious that the true area of the crystals would be slightly higher than areas calculated from weight average diameters since the latter are always slightly larger than areas from average diameters. This would be reflected in slightly lower values in Fig. 3, which certainly would not tend to invalidate any conclusion stated above. The idealized model of close packed spheres is not intended as a true representation but merely as an illustration of the magnitude of the effect of packing on available surface.

EFFECT OF HIGH VELOCITY ELECTRONS ON DRY DEXTRAN

BY F. P. PRICE, W. D. BELLAMY AND E. J. LAWTON

General Electric Research Laboratory, Schenectady, N. Y.

Received March 5, 1954

High molecular weight native dextran from *Leuconstoc mesenteroides* has been irradiated dry with 800-kv. peak electrons. The resulting product has been examined using light scattering, viscosity and end group analysis as investigative methods. The results indicate that irradiation produces extensive degradation accompanied by considerable branching. The efficiency of irradiation both in branching and breaking is constant in the dose range of 5×10^6 to 10^8 R.E. It is possible to produce a material of molecular weight in the clinically useful range with doses of about 5×10^7 R.E.

Introduction

It is well known that the exposure of high polymeric materials to massive doses of ionizing radiation produces extensive molecular rearrangement. At present it is difficult to predict for a given polymer whether the net result of this rearrangement will be degradation, as in the case of cellulose and many other materials, or cross-linking, as in the case of polyethylene.¹

Breaking a polymer chain is the immediate result of ionization of either an atom in the chain backbone or of an atom closely attached to the backbone. Branching on the other hand, is the culmination of a series of events initiated by an ionization somewhere within the molecule. Both branching and breaking proceed during irradiation, and therefore it is reasonable to expect that in many cases where a net degradation occurs, the resultant polymer will be more highly branched than the original material.

This paper describes the results of exposing dextran to cathode rays of 800 kv. (peak) energy. Dextran is the 1-6 polymer of α -D-glucose and is produced by specific bacteria such as the *Leuconstoc mesenteroides* during growth on sucrose. The use of this material as a plasma extender depends upon degrading the material from its initial molecular weight of several hundred million to about fifty thousand. Commercially this is now accomplished by acid hydrolysis which results in a low yield of useful product. The use of high energy cathode rays offers an alternative method for degradation with the possibility that a higher yield of usable material may be obtained.

Materials and Methods

Crude dextran, Commercial Solvents Sample N-379, was used throughout these experiments. Two-gram samples of dry dextran were irradiated after sealing into containers, $2\frac{3}{8}$ inches in diameter, of 0.003-inch thick polyethylene. The dose was accumulated at the rate of approximately 0.14 $\times 10^6$ roentgen equivalents per second.

The source of electrons was a modified 1-Mev. pressure-insulated resonant-transformer type of X-ray unit.² Number average molecular weights were calculated from analyses of end groups by a modification of the method of Somogyi.³ Weight average molecular weights were determined using light scattering techniques.

After irradiation the samples were prepared for light-scattering measurements by the following procedure: four per cent. dextran was suspended in *M/50* phosphate

buffer, pH 7.0, and heated with occasional shaking at 60° for 30 minutes. After the sample had cooled to room temperature, 4% Darco 60 and 4% Super-Cel were added. The solution was brought to a pH of 4.5 to 5.0 with *M/2* KH_2PO_4 , and then filtered through a fritted glass filter (Fine). The adjustment of the pH was necessary because the original dextran was found to have a pH of about 10. Irradiation produced a yellow-brown color which was removed by the charcoal and Super-Cel in acid, but not in neutral or alkaline solutions.

The slightly acid (pH 4.5 to 5.0) solutions were centrifuged for six hours at about 19,000 r.p.m. (26,000 *g*) at 5 to 10° in an International Refrigerated Centrifuge, Model PR-1. Ten milliliters was removed from the top of each cup by means of a pipet fitted through a large stopper to prevent the tip from going more than halfway into the cup. The withdrawn portions were placed in test-tubes which had been steamed and rinsed out in an apparatus similar to that described elsewhere.⁴ If examination of the centrifuged samples in a narrow beam of intense white light showed no visible motes, light-scattering measurements were made.

The clarification of water solutions for light-scattering measurements is, for some unknown reason, much more difficult than clarification of organic solvents. In this investigation, distilled water was clarified by distillation from KMnO_4 solution through a specially designed stillhead. This head consisted of a vertical Pyrex tube two feet long and two inches in diameter, closed at the top. A re-entrant take-off tube was sealed into this about two inches from the top and just below this the large column was wrapped with a nichrome heater. The condenser was sealed onto the take-off tube, thus eliminating the use of ground glass joints with their concomitant danger of introduction of small glass chips into the distillate. The long large-diameter still head allowed entrained droplets to fall out while both the heater near the top of the column and the reentrant condenser take-off above it broke the water film on the inside of the head preventing creepage of dust particles into the condenser. This apparatus consistently gave water with a 90-degree turbidity below 5×10^{-5} with dissymmetry below 1.05.

The light-scattering measurements were made in a modified Raman-type cell. The modification consisted of enlarging the upper part of the cell so that by inverting, all the solution in the light trap and the light entrance tube could be held in the top portion of the cell. This permitted addition of successive increments of relatively concentrated dextran solution to a known volume of water, thus obviating any possibility of varying solvent turbidity. The cell and the pipets used to transfer water were rinsed and shaken vigorously six times with clarified water before they were used. The cell was calibrated with solutions of the standard polystyrene distributed by P. Debye of Cornell University. Both toluene and methyl ethyl ketone were used as calibration solvents.

The concentrated, 2 to 4%, dextran solution was introduced into the cell from a graduated pipet which had a stopcock mounted on its top in the same manner as on a weighing pipet. The stopcock allowed the pipet to be used as a buret, thus minimizing reading errors and at the same time keeping the liquid out of contact with the stopcock. The concentrations of the dextran solutions were measured polarimetrically, assuming

$$[\alpha]_{25}^{5461\text{\AA}} = 235.63^\circ$$

(1) A. Charlesby, *Nature*, **171**, 167 (1953); *Plastics*, May (1953); E. J. Lawton, A. M. Bueche and J. S. Balwit, *Nature*, **172**, 76 (1953).

(2) E. J. Lawton, W. D. Bellamy, R. E. Hungate and E. Hall, *Science*, **113**, 380 (1951); *Proc. Tech. Assoc. Pulp Paper Ind.*, **34**, 113A (1951); J. A. Knowlton, G. R. Mahn and J. W. Ranfill, *Nucleonics*, **11**, No. 11, 64 (1953).

(3) N. J. Somogyi, *J. Biol. Chem.*, **160**, 61 (1945).

(4) C. Thurmond and B. Zimm, "Size and Shape of Molecules in Artificially Branched Polystyrene," ONR Report, Project No. N7 054204.

TABLE I
 EFFECT OF 800-KV. (PEAK) ELECTRONS ON THE MOLECULAR WEIGHT OF DEXTRAN

Dose (R.E.)	Ion pairs (i) per gram	M_w^a	R (Å) ^b	End groups per gram	M_n^c	M_w/M_n	$[\eta]_{R'}^f$ (cc./g.)
None	6.5×10^8	4200 ^e	3.9×10^{18}	155×10^3	420×10^1	232
5×10^6	9.0×10^{18}	34.4×10^5	943	2.06×10^{19}	29.5×10^3	11.6×10^1	...
1×10^{7d}	1.8×10^{19}	7.70×10^5	740	3.03×10^{19}	20×10^3	3.85×10^1	...
1×10^7	1.8×10^{19}	5.30×10^5	880	3.55×10^{19}	17.1×10^3	3.11×10^1	36.6
2×10^7	3.6×10^{19}	2.17×10^5	...	8.17×10^{20}	7.43×10^3	2.9×10^1	23.8
3×10^7	5.4×10^{19}	1.03×10^5	...	8.4×10^{20}	5.09×10^3	2.3×10^1	20.8
1×10^8	1.8×10^{20}	0.294×10^5	...	2.4×10^{21}	2.49×10^3	1.18×10^1	11.3

^a Weight average molecular weight determined by light scattering. ^b Root-mean-square separation of chain ends, assuming a random coil calculated from M_w . ^c Number average molecular weight determined by end group analysis. ^d Irradiated in an atmosphere of nitrogen. ^e Root-mean-square radius of gyration. ^f Limiting viscosity number.

The measurements were made on the solution from the bottom of the centrifuge tubes in which clarification had been performed. Light of 5461 Å. wave length was used.

Measurements of scattered light intensity usually were made at five concentrations and at a number of angles between 45 and 135°. If the dissymmetry, I_{45}/I_{135} , was less than 1.05, the molecular weight was calculated from the usual formula

$$Hc/\tau_{90^\circ} = (1/M) + Bc$$

where

- c = concentration in g./cc.
- τ = turbidity at 90°
- B = a constant, equal to twice the first virial coefficient in the osmotic pressure expression
- M = weight average molecular weight
- H = a constant depending on various parameters of the system. For dextran in water the refractive index increment ($\partial\mu/\partial c$) was found to be 0.14 cc./g. This leads to a value of $H = 2.07 \times 10^{-6}$.

Molecular weights were determined by extrapolating plots of c/τ_{90° vs. c to $c = 0$.

In cases where $I_{45}/I_{135} < 1.05$, the value of I_{90} was corrected to I_0 , assuming a random coil, and the molecular weight again calculated by extrapolation of c/τ_0 to $c = 0$. In these cases it was also possible to calculate the root-mean-square distance of separation of chain ends. In the case of the unirradiated dextran, a Zimm plot⁵ was made and the value of c/τ at $\theta = 0$ and $c = 0$ was determined. In this case, the root-mean-square radius of gyration in the unirradiated dextran molecule was determined from the initial slope vs. intercept ratio of the $c = 0$ line of the Zimm plot by the formula⁵

$$\frac{\text{initial slope}}{\text{intercept}} = \frac{16\pi^2\bar{R}^2}{3\lambda^2}$$

where

- \bar{R}^2 = av. square distance from center of gravity of molecule (radius of gyration)
- λ = wave length of incident light

Results and Discussion

The results of the investigation are summarized in Table I. These results show that irradiation reduces the molecular weight but not nearly to the extent indicated by the end-group analyses. Irradiation in nitrogen somewhat reduces the degradation but not markedly so. Apparently the atmospheric oxygen present in most of the irradiations has only a secondary effect.

The value of 6.5×10^8 for the molecular weight of the unirradiated dextran is subject to considerable error. The extrapolation of the Zimm plot from $\theta = 45^\circ$ to $\theta = 0^\circ$ is quite long and the intercept quite close to zero. However, it was obvious that the molecular weight was well above 4×10^8 .

Several attempts to lower the turbidity and dissymmetry by heating the solution were without effect. If the distance of 4200 Å. is taken to be the root-mean-square radius of a sphere, application of the correction factor for mean square radius to radius and use of 6.5×10^8 for molecular weight yields a density in the sphere of 1.6×10^{-3} g./cc. A random coil would be even less dense. Therefore the undegraded dextran chain must be very diffuse within its sphere of action.

Comparison of the number of end groups with the calculated number of ion pairs at each irradiation dose shows that at doses up to $6 \times 10^7 R$, there are on an average 2.1 ± 0.2 end groups per ion pair formed in the material. This implies that the end result of each ionizing act, wherever it occurs in the molecule, is the production of two reducing end groups. This is reasonable, as the polymer was irradiated in air and was dry rather than wet.

Consideration of the ring structure of this polyglucose shows that every rupture need not break the backbone of the polymer and result in degradation, for if only a bond in the cyclic monomer unit were broken, no appreciable reduction in size would result. Further, since there are twenty-two bonds in the monomer unit, five of which if excited sufficiently could result in chain scission, 4.4 ion pairs should be required to produce one chain break. In the light of these speculations, it is of interest to calculate from the data the ratio of the total number of ion pairs available per dextran molecule to the number effective in breaking the chain.

Montroll and Simha⁶ have calculated the molecular weight distributions to be expected by randomly degrading a monodisperse polymer. They derive the expression

$$\frac{M_w}{M_0} = 1 + \frac{2(1-a)[a(1+P) - 1]}{a^2(1+P)}$$

when

- M_w = weight average molecular weight
- M_0 = wt. of monomer unit = 162 for glucose
- a = av. degree of depolymerization = r_0/P
- P = no. of monomer units in original molecule
- r_0 = av. number of breaks per original molecule

In this particular case, the number of breaks per molecule (r_0) and the initial degree of polymerization (P) are so large that the formula reduces to

$$r_0 = \frac{2PM_0}{M_w} = \frac{13 \times 10^8}{M_w}, PM_0 = \text{mol. wt.} = 6.5 \times 10^8$$

(5) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

(6) E. Montroll and R. Simha, *ibid.*, **8**, 721 (1940).

The total number of available ion pairs per molecule is given by

$$i = \frac{1.7 \times 10^{12} D \times 6.5 \times 10^6}{6.06 \times 10^{23}} = 2.15 \times 10^{-3} D$$

where

D = dose in roentgen equivalents.

The calculated values of r_0 and i are given in Table II.

TABLE II

EFFECTIVENESS OF ELECTRON BOMBARDMENT IN DEXTRAN DEGRADATION

Dose (R.E.)	Total ion pairs Molecule (i)	Av. no. breaks Molecule (r_0)
5×10^6	1.08×10^4	0.0378×10^4
1×10^7	2.15×10^4	0.243×10^4
2×10^7	4.30×10^4	0.599×10^4
3×10^7	6.45×10^4	1.263×10^4
1×10^8	21.5×10^4	4.44×10^4

If i is plotted against r_0 , a fair straight line results. This line has a slope of 4.6 ion pairs/chain break, but it does not go through the origin as it should. That it does not do so may be due to the extensive degradation already produced by the smallest dose used, 5×10^6 R.E. At this dose the molecular weight had been reduced to less than 1% of its initial value. In order to have the plot pass through the origin, the value of the ion pairs per break at low doses must be much higher than that noted above. This lower chain breaking efficiency at low doses may be due to the complexity and large size of the undegraded material. However, in the dose range between 5×10^6 and 1×10^8 R.E. the chain breaking efficiency is 4.6 ion pairs/break, which is very close to the value of 4.4 predicted from bond considerations in the monomer unit. Also, it is quite close to that found for the degradation of cellulose.⁷ The evidence presented above indicates that bond rupture is entirely random and depends in no way on the strength of the bond.

Limiting viscosity numbers for several of the irradiated dextrans were determined. These are given in the last column of Table I. A plot of $\log M_w$ vs. $\log [\eta]_R$ for these samples yields a straight line which can be expressed by

$$[\eta]_R = 0.163M_w^{0.41}$$

The work of the National Bureau of Standards on acid-hydrolyzed dextrans⁸ yields the following viscosity-molecular weight relationship in water.

$$[\eta]_D = 0.091M_w^{0.51}$$

These workers showed that these materials are branched and that the value of approximately one-half for the exponent arises from branching rather than from water being an "ideal" solvent. They also state that the data will not fit a randomly branched polymer, but that the branches are short and regularly spaced along the chain. Irradiation introduces branches which probably are random both in length and spacing. Stockmayer and

Zimm⁹ have outlined a method for calculation of random branching from viscosity measurements of branched and unbranched polymers. They define a function g as

$$g = \overline{R_{0B}^2} / \overline{R_{0L}^2}$$

where $\overline{R_{0B}^2}$ and $\overline{R_{0L}^2}$ are the mean square radii of gyration of branched and linear molecules, respectively. Both values of the radius are determined for polymers of the same gross composition in "ideal" solvents. Since the viscosity can be related to the radius of gyration¹⁰ by

$$[\eta] \propto (\overline{R^2})^{3/2} / M$$

where M is the weight average molecular weight.

$$[\eta]_B / [\eta]_L = g^{3/2}$$

Also it has been shown experimentally that g is nearly independent of solvent.¹¹ If it is assumed that the short regularly spaced branches of the acid-hydrolyzed dextran have the effect merely of stiffening the chain somewhat, then for computational purposes, this material can be regarded as a linear polymer somewhat like polystyrene with its pendant phenyl groups. The random branching introduced by irradiation can then be calculated from

$$\frac{[\eta]_R}{[\eta]_D} = 1.79M^{-0.10} = g^{3/2}$$

in combination with the tables given by Stockmayer and Zimm.⁹ The results of such computations for trifunctional and tetrafunctional branching at selected molecular weights are given in Table III. Also given are the branches per ion pair calculated assuming 1.7×10^{12} ion pairs per gram per R.E.

TABLE III
BRANCHING OF DEXTRAN BY IRRADIATION

Mw	Branches/molecule		Branching efficiency (branches/ion pair)	
	Tri	Tetra	Tri	Tetra
5×10^4	4.3	1.9	0.51	0.23
10×10^4	5.0	2.1	.48	.20
50×10^4	8.2	3.0	.45	.16
100×10^4	9.5	3.7	.51	.20
	Av.		.49	.20

The figures above should be regarded as semi-quantitative only as there have been some serious and apparently valid criticisms of the theory.^{11,12} However, the figures probably are correct within a factor of two and, in spite of the quantitative uncertainty, there is no doubt that the irradiated dextran is more highly branched than is the acid-hydrolyzed polymer. The molecular weight-viscosity relationships show this unambiguously. The figures in the table indicate that branching proceeds as the degradation continues, since for a twenty-fold decrease in molecular weight the branches per molecule drop by only a factor or two. The branching efficiencies are remarkably constant at about two ion pairs per branch for trifunctional branch points only, or five ion pairs per branch for

(9) W. Stockmayer and B. Zimm, *J. Chem. Phys.*, **17**, 1301 (1949).

(10) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

(11) C. Thurmond and B. Zimm, *J. Polymer Sci.*, **8**, 477 (1952).

(12) W. Stockmayer and M. Fixman, *Ann. N. Y. Acad. Sci.*, **57**, 334 (1953).

(7) J. F. Saeman, M. A. Millett and E. J. Lawton, abstract A.C.S. Meeting, March-April, 1952; *Chem. Eng. News*, **30**, 1515 (1952).

(8) M. Wales, P. A. Marshall and S. G. Weissberg, Natl. Bur. Standards Report 1713, pp. 38-52 (1953).

tetrafunctional branch points. If the figures for branching efficiency are combined with the chain breaking efficiency of 4.6 ion pairs/break, then 2.3 branches/break are obtained for trifunctional branching and 0.9 branches/break for tetrafunctional branching. In order for the net result of irradiation to be degradation the ratio of branches/breaks must be less than unity. Therefore, the branching must be exclusively tetrafunctional. By the same argument, the value of 4.6 ion pairs per break sets an upper limit of 0.22 branch per ion pair. This must be so in spite of the fact that all the corrections to the theory of branching yield higher values of branching for given values of g .

Dextran exposed to varying doses of radiation was hydrolyzed with 1 N HCl at 100° to determine if the irradiation had affected the yield of reducing sugars as determined spectrophotometrically. The results indicate that increasing doses of irradiation decreases the total yield of reducing sugars (presumably glucose) from acid hydrolysis. There is a loss of about 6% at 10⁷ and of about 15% at 10⁸ R.E.

Conclusions.—(1) Dextran is extensively degraded by exposure to 800-kv. (peak) electrons. The initial molecular weight of several hundred million is reduced to around fifty thousand by doses of around 10⁸ R.E.

(2) Degradation is accompanied by an increase in branching. All the branch points are probably tetrafunctional.

(3) Each ionizing act wherever it occurs results in two reducing end groups.

(4) Out of five ion pairs, 1.0 produces a tetrafunctional branch, 1.1 produces a break in the chain, and the rest produce rupture of the glucose ring without either degradation or eventual branching.

Acknowledgments.—The authors wish to express their gratitude to J. S. Balwit, who carried out many of the irradiations, and to Miss M. T. Germain who did the majority of the analytical work. Thanks are also due to the Commercial Solvents Corp. and to Dr. Homer Stavely of that organization for supplying the dextran samples as well as much helpful advice.

THE UNUSUAL VISCOSITY OF WATER SOLUTIONS OF ALKYLARYL POLYOXYETHYLENE ETHANOLS

BY HAROLD L. GREENWALD AND GEORGE L. BROWN

Rohm and Haas Company, 5000 Richmond Street, Philadelphia, Pa.

Received March 5, 1954

Study of the viscosity of water solutions of three *t,t*-octylphenyl polyether alcohols at room temperature has shown that these solutions are gel-like some place in the 50-70 weight per cent. region and have positive temperature coefficients of viscosity at concentrations in the 10-20 weight per cent. region. Vapor pressure and partial molal volume data obtained with solutions of one of these compounds supports the contention of Schulman, *et al.*,³ that these molecules hydrate with one water molecule per ether linkage. A hypothesis is offered to explain the gel formation which stresses the analogy between emulsions and micellar solutions. Qualitative explanations are offered for several of the other unusual features of the viscosity behavior.

That solutions of alkylphenyl polyoxyethylene alcohols in water have unusual viscosity properties was noted by Boedeker.¹ He offered an explanation for the maximum in the viscosity-concentration curve and for the increase in viscosity with temperature at certain concentrations. The explanation embodied three factors: (1) the normal decrease in viscosity with temperature, (2) a decrease in hydration of the ether molecules with temperature, (3) coupling of incompletely hydrated molecules to form a network. No attempt was made to explain the data in terms of micelles which are now believed to exist in these solutions.²

In X-ray and optical studies of solutions of alkyl polyoxyethylene alcohols in water and petroleum ether Schulman, Matalon and Cohen³ found, except in cases of short polyoxyethylene chain lengths, evidence for lamellar, cylindrical and spherical aggregates. They also noted that in these aggregates there is one water molecule per ether linkage.

Before offering any further suggestions as to the cause of the odd viscosity behavior it seemed pertinent to make viscosity measurements on several members of the alkylphenyl polyoxyethylene ethanol family since Boedeker did not identify the compounds he worked with. In view of the observations of Schulman, *et al.*, on the hydration of the ether, vapor pressure and density measurements were also made on some of these systems.

Experimental

Materials.—*p-t,t*-Octylphenyl polyoxyethylene ethanols made by adding ethylene oxide to *t,t*-octylphenol in the presence of sodium hydroxide were used. They are identified as OPE_{*n*}, where *n* is the weight average moles of ethylene oxide condensed per mole of octylphenol. In addition to studies on three octylphenol derivatives (OPE_{7.5}, OPE_{9.7} and OPE_{12.3}) some work was done on an isoöctyl methylphenol derivative (OMPE_{9.7}) made the same way. The polyethylene glycols of molecular weights 300, 489 and 600 (HE_{6.4}, HE_{10.7} and HE_{13.2}) were commercial materials obtained from the Carbide and Carbon Chemicals Co.

Analytical data were available on only the three octylphenol derivatives and indicated for the OPE_{7.5}, OPE_{9.7} and OPE_{12.3} a water content of 0.42, 0.22 and 0.17% and a sodium sulfate content of 0.15, 0.11 and 0.12%, respectively.

Methods.—Viscosities of all solutions were determined at 12 and 60 r.p.m. spindle speeds with the Brookfield Synchroelectric Viscometer (Model LVF) made by Brookfield Engineering Laboratories, Inc., Stoughton, Mass. Data

on some solutions of low viscosity were checked with an Ubbelohde viscometer.⁴ Temperature was controlled to $\pm 1^\circ$. Except at the lower end of its range, below 0.5 poise, the roughly 1% accuracy of the Brookfield Viscometer is quite sufficient since the temperature uncertainty will usually give rise to a larger error. In order to evaluate the error at low viscosities determinations were run on Bureau of Standards viscosity standard oils. The results indicate that the viscometer gave significantly high readings in this range. Accuracy of the order of several tenths of a per cent. was probably achieved with the Ubbelohde viscometer. Flow time, *t*, in this instrument was corrected for kinetic energy by the equation

$$t(\text{cor.}) = t(\text{obsd.}) - \frac{220}{t(\text{obsd.})}$$

Viscosities were computed using the equations

$$\eta(\text{relative}) = \frac{\eta(\text{soln.})}{\eta(\text{solvnt.})} = \frac{t(\text{cor.-soln.})}{t(\text{cor.-solvnt.})}$$

Differential vapor pressure measurements were made by means of the Bremer-Frowein tensiometer⁵ (two bulbs connected by a U-tube manometer). Butyl phthalate was used as the manometer liquid. Fifty ml. of distilled water was put into one of the 200-ml. bulbs and 50 ml. of the surface active agent solution into the other. Each liquid was boiled vigorously before the system was scaled off from the pump. In some of the runs the apparatus was modified by having stopcocks in the line to the vacuum pump. In these runs the stopcocks were closed to isolate the system from the pump. In the other runs the system was sealed off. Since the pump used had a limit of about 1 mm. of mercury, some residual air was present in the bulbs. The tensiometer was immersed in a water-bath controlled to $\pm 0.1^\circ$ and manometer readings taken until equilibrium was attained. This usually took about an hour at each temperature. Since the concentration of the solution used is changed by boiling the concentration present during the experiment was determined on a 5-ml. sample removed at the end of the run. The surface active agent was determined by evaporation of the sample to dryness.

Densities were measured by using a 15-ml. suspended sinker and an analytical balance. The temperature was controlled to $\pm 1^\circ$.

Results

Results of the viscosity measurements are given in Table I. The Ubbelohde viscometer was used in the measurements on OPE_{9.7} at 10, 20 and 15.5%₀. Values for the first two concentrations are given in the tables, those for the third concentration are in poises: 25°, 0.0493; 30°, 0.0528; 40°, 0.0620; 50°, 0.0681. All of the other data were obtained with the Brookfield viscometer. Viscosities of the polyethylene glycol solutions were measured at a spindle speed of 60 r.p.m.; all of the other solutions

(1) K. Boedeker, *Kolloid Z.*, **94**, 161 (1941).

(2) J. W. McBain and S. Marsden, *J. Chem. Phys.*, **15**, 211 (1947); E. Gonick and J. W. McBain, *J. Am. Chem. Soc.*, **69**, 334 (1947).

(3) J. H. Schulman, R. Matalon and M. Cohen, *Discs. Faraday Soc.*, No. 11, 117 (1951).

(4) L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, **9**, 85 (1937).

(5) G. W. Thomson in "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, Part I, Vol. I, Second Edition, p. 185.

TABLE I
 VISCOSITY OF SOLUTIONS (IN POISES)

Compound	Temp., °C.	Weight per cent. in water									
		10	20	30	40	50	60	70	80	90	100
OPE _{7.5}	25	1.03 ^a	1.87	2.76	3.73	5.00	76-58 ^{a,b}	266-82 ^{a,b}	4.3	3.2	2.64
	30	0.38 ^a	1.47	2.07	2.61	3.5	54-40 ^{a,b}	184-65 ^{a,b}	2.53	2.38	2.15
	40	0.22-0.18 ^a	0.70 ^a	1.02	1.4	1.72	44-29 ^{a,b}	120-47 ^{a,b}	1.68	1.50	1.25
	50	ca. 0.08 ^a	27-0.20 ^a	0.45 ^a	0.60	0.76	3.5-1.7 ^{a,b}	3-1.4 ^{a,b}	0.81	0.75	0.76
OPE _{9.7}	25	0.0244 ^c	.107 ^c	.77-0.85	4.9-5.5	Gel	8.93	5.3	3.9-3.4	2.84	2.67
	30	.0247 ^c	.119 ^c	.82	4.1	30-15 ^b	5.6	3.59	2.44	2.28	2.16
	40	.0280 ^c	.127 ^c	.57	2.04	3.25	2.58	2.0-1.76	1.41	1.4	1.31
	50	.0325 ^c	.121 ^c	.38	0.80	1.12	1.08	0.92-1.07	0.81	0.76	0.75
OPE _{12.3}	25	ca. 0.03	.02-0.07	.23	1.83	Gel	Gel	Gel	3.87	3.1	4.12 ^a
	30	ca. .03	ca. 0.06	.19	1.39	Gel	Gel	4.5	2.9	2.9-2.5	2.37
	40	ca. .03	ca. .05	.13	0.95	Gel	Gel	2.4-2.1	1.63	1.43	1.44
	50	ca. .03	ca. .05	.08-0.11	0.62	Gel	Gel	1.09	0.87	0.84	0.81
OMPE _{9.7}	25	0.05	0.14	1.22	6.12	10.60	8.14	6.40			
HE _{6.4}	25	.03	.04	0.05	0.07	0.09	0.15	0.24	.40	.47	0.62
	50	.03	.03	.03	.04	.07	.08	.10	.16	.23	0.25
HE _{10.7}	25	.03	.04	.05	.07	.09	.17	.30	.31	.63	1.00
	50	.03	.03	.04	.05	.06	.09	.13	.14	.22	0.38
HE _{13.2}	25	.03	.04	.06	.09	.11	.22	.37	.51	.86	1.29
	50	.03	.03	.04	.05	.07	.10	.17	.20	.30	0.41
OPE _{9.7} in	25	.07	.34	1.51	4.15	6.42	6.45 ^b	4.67 ^b	3.11 ^b	2.55	
1 M NaCl	50	.14 ^a	.32	0.50	0.64 ^b	0.78 ^b	0.89	0.90 ^b	0.85 ^{a,b}	0.85 ^a	
OPE _{9.7} ^{a,b} in	25	.07	.40	2.38	9.02	10.14	8.81	5.55	3.96	3.11	
1 M CaCl ₂	50	.17	.42	0.66	0.93	1.15	1.15	1.10	0.94	0.90	

^a System was cloudy (all CaCl₂ solutions were cloudy). ^b Small air bubbles present (all CaCl₂ solutions contained bubbles). ^c Ubbelohde viscometer used.

 TABLE II
 SPECIFIC VOLUME OF SOLUTIONS AT 25° (ML./G.) AND
 PARTIAL MOLAL VOLUME OF WATER IN OPE_{7.5} SOLUTIONS (ML.)

Compound	Weight per cent. in water										
	0	10	20	30	40	50	60	70	80	90	100
OPE _{7.5}	1.0029	0.9949	0.9871	0.9792	0.9728	0.9643	Viscous	Viscous	0.9472	0.9461	0.9511
OPE _{9.7}	1.0029	.9934	.9842	.9749	.9662	Gel	0.9490	0.9432	.9387	.9391	.9416
OPE _{12.3}	1.0029	.9931	.9815	.9713	.9605	Gel	Gel	.9351	.9314	.9312	.9331
HE _{6.4}	1.0029	.9859	.9708	.9552	.9390	0.9244	0.9122	.9029	.8965	.8929	.8914
OPE _{9.7} in 1 M NaCl	0.9632	.9584	.9543	.9498	.9453	.9411	.9373	.9343	.9310	.9367	.9416
OPE _{9.7} in 1 M CaCl ₂	0.9260	.9251	.9241	.9228	.9222	.9217	.9210	.9228	.92609416
\bar{v} for H ₂ O in OPE _{9.7}	18.0	18.0	18.0	18.0	18.0	...	17.8	17.7	16.9	16.6	16.5

were measured at both 12 and 60 r.p.m. Values in the table are an average of those obtained at the two speeds except where the values differed from the average by more than 5%. In this case both values are given, the 12 r.p.m. being first.

Inspection of Table I indicates a number of interesting things. In the neighborhood of 50-70% surface active agent the solutions gel or have abnormally high viscosities. As the temperature is increased the extent of this abnormality decreases. The viscosity of the polyethylene glycol solutions increases monotonically with weight per cent. Except for OPE_{7.5}, the solutions of the surface active agents have a low or positive temperature coefficient of viscosity at concentrations below 20 or 30%. Except in the region of abnormal viscosity there is no large effect of rate of shear between 12 and 60 r.p.m. in the Brookfield viscometer. Salts lower the viscosity of the solution in the gel region preventing the formation of a gel, and raise the viscosity of the more dilute solutions. The viscosity of

OMPE_{9.7} is very close to that of OPE_{9.7} except in the 50% solution. In the region below 40% the higher molecular weight surface active agent has a lower viscosity than those of lower molecular weight.

Densities were measured at 25° only and were converted to specific volumes which are recorded in Table II. No measurements were made on gels or very viscous systems. Solutions of the surface active agents have a minimum specific volume in the region 80-90% which is displaced to lower concentrations by the presence of salts. The partial molal volume, obtained by a graphical method, of water in OPE_{9.7} solutions had a maximum rate of change between 70 and 80%.

The difference in vapor pressure between water and OPE_{9.7} solutions was converted to the ratio of vapor pressure of the solution to vapor pressure of water and recorded in Table III. Inaccuracy, presumably due to residual air in the flasks, is particularly obvious in the solutions of very high and very

low relative pressures. It readily can be seen that at concentrations below about 75% of OPE_{9,7} the ratio of vapor pressures is close to unity (the critical micelle concentration for this material is about 2×10^{-4} molar). Above 75% the vapor pressure ratio drops rapidly.

TABLE III

RATIO OF VAPOR PRESSURE OF OPE_{9,7} SOLUTIONS TO VAPOR PRESSURE OF WATER

Temp., °C.	20.0	25.0	30.0	35.0	40.0	45.0	50.0
Concn. of OPE _{9,7} , %							
100			-0.09				0.01
ca. 99.9			.24				
93.2	0.63	0.66	.68	0.70			
92.3	0.65	.65	.68	.71			
86.2		.84	.85	.89	0.89		
84.0		.82	.83	.86	.88		
80.1			.81	.86	.88	0.91	0.92
73.3		.99	.99		.98		0.99
ca. 40	1.05	1.06					
34.5		1.00		1.00			1.00
29	1.02	1.02			1.01		1.01
10	0.99	0.99	.99	0.99			

Discussion

Accepting suggestion of Schulman, *et al.*,³ that the ether linkages are each hydrated with one water molecule the composition of the hydrates are: 77.8% OPE_{7,5}, 76.7% OPE_{9,7} and 75.7% OPE_{12,3}. Thus the vapor pressure and, to a lesser extent, the partial molal volume data on OPE_{9,7} confirm this idea.

In considering the abnormal viscosity-concentration curve, particularly the gel, of the surface active agents there is noted a distinct qualitative similarity to the viscosity behavior of an emulsion. In the latter case as the per cent. of internal phase is increased the viscosity increases until, in many cases, the system becomes rigid and then phase inversion occurs accompanied by a decrease in viscosity. If the emulsion droplets are uniform spheres they will be in the close packed configuration at 74% by volume. If the system is labile with respect to inversion then inversion will occur at this volume fraction for at higher amounts of inner phase interfacial tension furnishes a driving force for inversion.

Calculation of the weight per cent. of surface active agent necessary to give 74 volume per cent. of hydrated micelles of surface active agent results in values ranging from 59 to 57 weight per cent. for the three octylphenyl polyethylene oxides. This is somewhat higher than the onset of the gel region in the cases of OPE_{9,7} and OPE_{12,3} but is in good agreement for the OPE_{7,5}. Combining these observations with the knowledge that the HE_n solutions exhibit no abnormality leads to the following hypothesis:

At concentrations below the viscosity maximum (and above the very low critical micelle concentration) the system consists of micelles of hydrated OPE_n molecules in a continuum of water saturated with non-micellar OPE_n. As the volume concentration increases to the point at which there is but

a thin layer of water between the micelles, flow becomes hindered. Occurrence of considerable rigidity at a concentration below 74 volume per cent. of complex suggests that either the micelles interact strongly or are not spherical or that the micelle immobilizes some water in addition to that linking the ether chains. If the micelles are not spherical it is probable that they are also not highly asymmetric since rigidity is achieved not far from the close-packing volume.

Considering now the situation at the high in OPE_n end of the composition range, there must be explained the increase in viscosity upon the addition of water to the pure OPE_n. If the water links OPE_n molecules together, the viscosity should increase with increasing water content in general. It is noted that in OPE_{12,3} the 90% solution is less viscous than the pure material. This could be due to the same insoluble material causing this solution to be cloudy. Viscosity will increase with water content at a rate dependent on the chain length and the degree of order introduced. When the water content exceeds the amount necessary for the hydration of the ether linkages pockets of water start to form in the system. This development will also increase the viscosity since this amounts to having water suspended in the hydrated OPE_n. Going in this direction high viscosity is obtained at a comparatively low volume per cent. of free water because of the high viscosity of the medium and the strong interaction between water pockets.

Salts or higher temperature inhibit the formation of a gel by decreasing the hydration of the ether links furnishing more water phase and making it easier to deform micelles. This same factor, decreased hydration of the ether oxygens can produce the observed positive temperature coefficient of viscosity and increased viscosity with salt concentration of the more dilute solutions since the released secondary binding forces can account for increased micelle-micelle interactions. Except for the introduction of micelles this is similar to the ideas of Boedeker.¹ Although the vapor pressure data are not good enough to give an accurate value for the heat of dilution of OPE_{9,7} at high concentration they do indicate a value in the neighborhood of one kilocalorie per mole of water.

The inverse order of viscosity and molecular weight in the solutions below 40% are presumably due to differences in the interactions between the micelles. Quite possibly these differences are due to shape and size factors. It is doubtful that the viscosities of the intermicellar solution, due to differences in the critical micelle concentrations, would have so large an effect.

Absence of a gel region among the solutions of OMPE_{9,7} may be attributed to the methyl group on the benzene ring interfering with close packing in the micelle. This lack of close packing would then produce a less rigid micelle making for easier flow.

Acknowledgment.—The authors wish to thank Mrs. Jean K. Beemer for having made many of the measurements reported here and Professor Louis P. Hammett for some helpful discussions.

DISCUSSION

H. L. GREENWALD.—Certain of the ideas discussed in this paper are similar to those given in a paper on the viscosity of water-sodium caprylate-alcohol systems by A. N. Bose and J. Misra [*Kolloid Z.*, **133**, 108 (1953)].

HERBERT L. DAVIS.—Do you have any evidence for or against the interplay of hydrophil-hydrophobe areas in these gel formations? Martin Fischer gave many examples of a continuous gradation of *A* in water to water in *A*, with gel structures often appearing. He further applied such simple chemical systems to the understanding of more complex biological forms. Whereas many gels seem to have the brush-heap structure, is it correct to apply the term gel to systems whose rigidity seems to depend on firm adhesion between micellar spheres? In view of Dr. Ross' paper is it appropriate to consider the factors of dilution, salt addition, etc., as bringing the hydrophil-hydrophobe surfaces into such a balance as now appears requisite for gel formation? There is evidence that blood clotting (including

hemophilia) may involve such balances or lack of them in forming the most important gel in the world.

H. L. GREENWALD.—The explanation for the gels observed in the systems we discussed is based principally on geometric factors. Some of the other observations utilized the concept of adhesion between micelles and here it is indeed appropriate to consider the factors of dilution, salt, etc. If by a brush-heap structure you envisage the entanglement of very asymmetric micelles these would lead to rigidity at lower volume fractions and this may be the case in some of the alkali soap solutions.

F. M. FOWKES.—The low viscosities of alkylaryl polyoxyethylene ethanols in aqueous calcium chloride may result from the complex of calcium chloride with polyoxyethylene chains as described by Todd Doscher about three years ago. Has this been taken into consideration?

H. L. GREENWALD.—Since the data on viscosities of the sodium chloride solutions are quite similar to those of the calcium chloride solutions the effect of the complex does not seem to be very important.

MORPHOLOGICAL STUDIES OF RECLAIMED ELASTOMERS¹

BY ERNST A. HAUSER

*Massachusetts Institute of Technology, Cambridge, Massachusetts**Received March 5, 1954*

The morphology of natural and synthetic elastomers has been the object of extensive studies since 1944. So far, however, this work has not included studies pertaining to the morphology of reclaimed elastomers. In the present study the samples were prepared by a method similar to that used for morphological studies of natural and synthetic elastomers. To obtain satisfactory pictures of the morphological condition of the reclaimed elastomers, certain changes in the type of dispersion medium were essential. Since all the reclaimed elastomers had originally been vulcanized, and since all of these subjected to morphological studies contained compounding ingredients, it is understandable why their morphology differed from that of any crude and unvulcanized product.

Introduction

Just about ten years ago, in July, 1944, to be exact, morphological studies of pure natural and synthetic elastomers were first reported.² At that time electron micrographs of fibers and films obtained from Hevea rubber were described and discussed. Two characteristic types of structures were observed, namely, one which bears numerous "fluid" nodules and one which consists of branched networks of beaded fibers. It could also be ascertained that these two types are characteristic of the sol and the gel fractions, respectively. The effect of incorporating Channel Black into Hevea rubber during milling was also investigated. If milled Hevea rubber was subjected to vulcanization in solution, a cross-linked network of fine fibers similar to those obtained from the gel fraction of Hevea rubber could be observed. Guayule rubber, Cryptostegia, and several synthetic elastomers, like GR-S and Neoprene, also were investigated.

Soon thereafter the use of the Ultropak microscope for similar studies was reported for the first time.^{3,4} Although the magnification offered by the Ultropak microscope is much lower than that which can be obtained with the electron microscope, ample proof was nevertheless offered that it can be used advantageously for morphological studies of elastomers.⁵⁻⁹

The study of the morphology of reclaimed natural and synthetic elastomers, or mixtures of both, has not been satisfactory so far. This is due to the fact that the reclaiming process does not eliminate the combined sulfur, and for this reason dispersion of the reclaim is extremely difficult. The use of appropriate solvents and of a new technique in making the preparations has now made it possible to study the morphology of such samples.

(1) Presented at the 28th National Colloid Symposium, which was held under the auspices of the Division of Colloid Chemistry of the American Chemical Society, at Troy, New York, June 24-26, 1954.

(2) C. E. Hall, E. A. Hauser, D. S. le Beau, F. O. Schmitt and P. Talalay, *Ind. Eng. Chem.*, **36**, 634 (1944).

(3) E. A. Hauser and D. S. le Beau, *India-Rubber J.*, **110**, 169 (1946); **111**, 453 (1946).

(4) E. A. Hauser and D. S. le Beau, J. Alexander's "Colloid Chemistry," Vol. VI, Reinhold Publ. Corp., New York, N. Y., 1946, p. 1174.

(5) D. S. le Beau and E. A. Hauser, *Rubber Age*, April (1946).

(6) E. A. Hauser, *Kolloid Z.*, **110**, 78 (1948).

(7) E. A. Hauser and D. S. le Beau, *This Journal*, **53**, 274 (1949); **54**, 256 (1950).

(8) E. A. Hauser, *Rubber Age*, May (1950).

(9) E. A. Hauser, *Kautschuk und Gummi*, **6**, 120 (1953); **7**, WT13 (1954).

Important Rubber Reclaiming Processes^{10,11}

The "Neutral" Process.—This term is usually applied to any method yielding a reclaim which is relatively neutral in contrast to reclaim which is acid or alkaline. This process is primarily used for reclaiming old tires. The fiber present in the tires is destroyed in a digester by the use of metal chloride, which accelerates defiberization; this is a slower process than devulcanization. The use of metal chlorides produces reclaims which are chemically neutral and less "tacky" and less "nervy" than comparable alkali reclaims. Certain reclaiming oils and reclaiming catalyst compositions are also used to perform proper reclamation of the scraps involved.

The Alkali Process.—The alkali process was invented by Arthur H. Marks, who received U. S. Patent 635,141 in October, 1899.¹⁰ He subjected the ground, vulcanized rubber to treatment in a 3% solution of caustic soda at high temperatures for a considerable length of time and under conditions which prevented the evaporation of the solution.

In Marks' day modern vulcanization accelerators were not yet known and for that reason the amount of sulfur used to obtain vulcanization was considerably larger than it is today. This of course is a fact which affects any morphological study, because the smaller amounts of sulfur now in use will permit the most important aspects of the morphology of the unvulcanized rubber to remain unchanged.

Other reclaiming processes, as for example the solution process, the open-kettle process, the Lancaster process, the Gibbons process, and the "high-temperature water" process, will not be discussed here because their application has come to be of secondary importance.

Morphological Studies of Reclaimed Elastomers

The reclaimed elastomer must first be milled between two tightly set calender rolls rotating at the same rate. As soon as a very thin smooth sheet forms it should be withdrawn from the mill. Then an unfolded piece of the sheet is placed in a solution composed of 50% benzene and 50% toluene, the amount of the elastomer never exceeding 1% by weight. This dispersion should be kept under constant agitation up to the moment the preparation is made on the fine wire screen.³⁻⁹ A few drops of the dispersion in the organic solvent are then placed on the surface of water in a Petri dish. Since the reclaimed elastomers have the tendency to agglom-

(10) J. M. Ball, "Reclaimed Rubber," Rubber Reclaimers' Assoc., Inc., New York, N. Y., 1947.

(11) D. S. le Beau, J. Alexander's "Colloid Chemistry," Vol. VII, Reinhold Publ. Corp., New York, N. Y., 1950, p. 569.

erate, it is necessary to be very careful since agglomeration would spoil any morphological study. The fine wire screen must first be cleaned of all impurities by igniting it briefly over a Bunsen burner; it is then immersed quickly into the water and pulled up with its flat surface toward the drop of the elastomer dispersion. Immediately thereafter the wire screen is dried by holding it with tweezers on filter paper, thus accelerating solvent evaporation; it is then placed on a microscope slide and may be subjected to investigation at once.

A whole tire reclaim which was originally composed of 60% natural rubber and about 40% of the synthetic elastomer GR-S, obtained by the "neutral" process, reveals the formation of very fine threads or bands. The compounding ingredients used in mixing the elastomers are clearly noticeable.

The morphology of a light-colored tire carcass reclaim which was obtained by the alkali process shows the formation of fairly thick bands only. Film formation is also quite pronounced. This is indicative of the combination of natural and synthetic elastomers. The uniform distribution of compounding ingredients can be clearly observed.

In direct contrast thereto, a grey natural rubber inner tube reclaim, also made by the alkali process, reveals that film formation is more pronounced than that observed when studying the morphology of the synthetic elastomers or their mixture with reclaimed natural rubber. Besides this, however, the preparation also shows the formation of beaded fibers comparable to those which have been found with unvulcanized natural rubber.

A red natural rubber tube reclaim made by the alkali process also reveals some film formation, but particularly the building up of strong fibers and very fine threads with a few beads.

Reclaim made from grey mechanical goods by the alkali process reveals many thin fibers and extremely fine threads carrying a few nodules. This offers a clear indication that one is dealing here with an elastomer reclaim made from natural rubber.

This characteristic is even more pronounced when investigating a black natural rubber tube re-

claim, also made by the alkali process. Its morphology reveals the formation of very fine threads interspersed with very fine nodules.

The morphology of butyl rubber tube reclaim, a copolymer of isobutylene and isoprene, also shows some film formation but primarily very fine threads interspersed with nodules. From a strictly morphological point of view this product reveals the presence of an isoprene polymer.

Conclusions

Reclaimed rubber, both natural and synthetic, or intimate mixtures of these, cannot be classified as devulcanized products. It is possible to study only the morphology exhibited by the truly dispersed part of the reclaimed elastomer. The reclaim obtained by the "neutral" process revealed a morphology more comparable to many unvulcanized synthetics than any other. This is explainable on the basis of the combination of natural rubber and GR-S. The pure natural rubber reclaim samples showed a morphology which is most similar to vulcanized natural rubber samples. As far as the pure synthetic elastomer reclaim samples are concerned, the butyl rubber tube shows a morphology most similar to the natural rubber vulcanizates which have so far been investigated. This is explainable if the chemical composition of this synthetic product is borne in mind. In all probability the fully dispersed fractions have not yet lost all of the morphology which pertains to the crude raw material.

Acknowledgment.—The author wishes to express his most sincere thanks to the Midwest Rubber Reclaiming Company, East St. Louis, Illinois, and to its Director of Research, Dr. Desiree S. le Beau, for supplying him with all the samples of reclaimed elastomers used in this work and for the most valuable advice he has received. Thanks are also due Mr. Winglok So for his assistance in the experimental work.

SURFACE AND INTERFACIAL TENSIONS OF SYNTHETIC GLYCERIDES OF KNOWN COMPOSITION AND CONFIGURATION^{1,2}

BY RUTH R. BENERITO, W. S. SINGLETON AND R. O. FEUGE

Southern Regional Research Laboratory,³ New Orleans, Louisiana

Received March 5, 1954

For a better understanding of the fundamental theory and practical applications of fat emulsions, a precise knowledge of the surface tension at various temperatures and the interfacial tensions against water of pure synthetic glycerides was desired. The semi-micro method originally designed by Ferguson was selected and modified slightly. From the surface tension-temperature data, enthalpy and entropy changes in the surface formation were calculated, and equations were developed by the least squares method. For the simple triglycerides containing an even number of carbon atoms the variation of enthalpy and entropy changes with the number of carbon atoms per acid radical is shown graphically. Synthetic glycerides of known configuration were selected to show the effects of degree of unsaturation, degree of esterification, and *cis-trans* isomerism on the surface phenomena.

The surface tension against air and the interfacial tension against water of various glycerides of known composition and configuration are of considerable interest in the preparation of fat emulsions for intravenous injections. The literature contains few values of surface tensions of simple triglycerides⁴ and no values for the interfacial tensions of pure triglycerides. Most values contained in the literature are for the surface phenomena of natural oils or fats in which the distribution of fatty acid radicals is not definitely established and the content of minor constituents is variable.

This study has been motivated by the following objectives: (1) to determine the effects of chain length, degree of esterification, degree of unsaturation and configuration on both the surface tensions and interfacial tensions of synthetic glycerides and (2) to make quantitative measurements at various temperatures on samples of pure glycerides of known configuration, which samples were available only in very small quantities. If surface tension is accurately determined on pure compounds, it can serve as an index of the relative forces of intermolecular attraction for the compounds.

From the surface tension-temperature data for the various glycerides, the entropies, latent heats and enthalpies of the liquid surface formation can be calculated.

Experimental

Materials.—Some of the glycerides used in this investigation were obtained from a commercial source. The others were prepared in the laboratory. The triacetin, tributyrin, tricaproin and tricaprylin were obtained as Eastman Grade from Distillation Products Industries.⁵ They were redistilled prior to use. Tripalmitin, tristearin, tripelargonin, and triolein were prepared in the laboratory by interacting the appropriate fatty acid and glycerol under conditions described by Feuge, *et al.*⁶ Trielaidin was prepared

from methyl oleate by isomerizing the latter with the aid of selenium, purifying the resulting elaidate, and converting it to the triglyceride.⁷ Trilinolein was prepared by the method of Lundberg and Chipault.⁸ The monostearin and monopalmitin were prepared as described in a previous publication.⁹ The 1,2-dipalmitin was separated by solvent crystallization from the reaction products formed in the preparation of monopalmitin. 1,2-Diaceto-3-olein and 1,2-diaceto-3-stearin were prepared by acetylating 1-monolein and 1-monostearin, respectively, with acetyl chloride in the presence of pyridine.¹⁰ The 1,3-dioleo-2-palmitin was prepared by acetylating 1,3-diolein with palmitoyl chloride, the diolein being obtained by molecular distillation and fractional crystallization from mixed oleins.

All of the glycerides prepared in the laboratory were purified by recrystallization from solvents, even in those instances where no mention is made of fractional crystallization. The liquid and unsaturated materials were stored under an inert gas at refrigerator temperatures.

Analytical data on the various glycerides used in the experiments are recorded in Table I.

TABLE I
ANALYTICAL DATA OF THE GLYCERIDES

Compound	Characteristics of the glycerides			M.p., °C.
	Mol. wt., calcd.	Sapon. value Calcd.	Found	
Triacetin	218.20	771.4	773.0	...
Tributyrin	302.36	556.6	555.0	...
Tricaproin	386.50	435.5	437.4	...
Tricaprylin	470.70	357.6	360.4	...
Tripalmitin	807.30	208.5	207.4	65.4
Tristearin	891.46	188.8	186.7	72.5
Triolein	885.41	190.1	191.1	4.6
Trielaidin	885.41	190.1	191.1	42.0
Trilinolein ^a	879.41	191.4	194.6	-13.5
1,2-Diaceto-3-olein	440.62	381.9	...	-18.3
1,2-Diaceto-3-stearin	442.62	380.3	...	48.6
1-Monostearin	358.55	156.5	155.8	81.8
1-Monopalmitin	330.50	169.8	170.0	77.0
1,3-Dipalmitin	568.90	197.2	197.0	71.5
1,3-Dioleo-2-palmitin	873.36	192.7	185.2	7.8
Tripelargonin	512.81	328.2	327.0	8.5

^a Wijs iodine value 166.2 (theoretical 173.2).

Apparatus and Method.—The surface and interfacial tensions were determined by the method which was first

(1) Presented before the twenty-eighth National Colloid Symposium which was held under the auspices of the Division of Colloid Chemistry of the American Chemical Society in Troy, New York, June 24-26, 1954.

(2) This investigation was supported by funds from the Office of Surgeon General, U. S. Army.

(3) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(4) P. Walden, *Z. physik. Chem.*, **75**, 555 (1910); F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

(5) These products are named merely as part of the exact experimental conditions. It does not constitute an endorsement of them over those of other manufacturers.

(6) R. O. Feuge, E. A. Kraemer and A. E. Bailey, *Oil & Soap*, **22**, 202 (1945).

(7) R. O. Feuge, M. B. Pepper, Jr., R. T. O'Connor and Elsie T. Field, *J. Am. Oil Chemists' Soc.*, **28**, 420 (1951).

(8) W. D. Lundberg and J. R. Chipault, "Ann. Report Hornell Inst.," Univ. Minn., 1947-1948.

(9) W. S. Singleton and E. J. Vicknair, *J. Am. Oil Chemists' Soc.*, **28**, 342 (1951).

(10) R. O. Feuge, Audrey T. Gros and E. J. Vicknair, *ibid.*, **30**, 320 (1953).

TABLE II
SURFACE TENSIONS AND CHANGES IN ENTHALPY AND ENTROPY OF SURFACE FORMATION

Compound	Temperature, °C.					<i>a</i>	<i>b</i> or ΔS , ergs/deg.	ΔH , ergs
	20	40	60	80	100			
Triacetin	35.15	33.12	31.09	29.06	27.03	37.18	0.10150	64.89
Tributyrin	27.98	26.39	24.80	23.21	21.57	29.57	.07955	51.28
Tricaproin	26.32	25.16	24.00	22.84	21.68	27.48	.05797	43.30
Tricaprylin	25.68	24.44	23.19	21.95	20.68	26.93	.06252	44.00
Tripalmitin ^a	(27.69)	(26.41)	(25.13)	23.85	22.57	28.97	.06403	46.45
Tristearin	(29.61)	(28.26)	(26.90)	25.54	24.18	30.96	.06778	49.46
Triolein	28.71	27.34	25.95	24.56	23.17	30.10	.06933	49.03
Triolein	(25.78)	(24.38)	22.98	21.58	20.18	27.18	.06986	46.25
Trilinolein	20.28	19.70	19.13	18.56	17.99	20.85	.02867	28.68
1,2-Diaceto-3-olein	21.88	20.82	19.75	18.69	17.62	22.95	.05330	37.50
1,2-Diaceto-3-stearin	(30.13)	(28.27)	26.40	24.53	22.66	32.00	.09338	57.50
1-Monostearin	(23.35)	(22.17)	(21.00)	(19.82)	18.64	24.52	.05876	40.56
1-Monopalmitin	(26.16)	(24.79)	(23.45)	22.12	20.78	27.46	.06678	45.69
1,3-Dipalmitin	(24.93)	(24.00)	(23.07)	22.15	21.23	25.85	.04625	38.48
1,3-Dioleo-2-palmitin	26.49	25.60	24.72	23.83	22.94	27.38	.04442	39.51
Tripelargonin	24.25	23.12	21.99	20.86	19.73	25.38	.05650	40.81

^a Values enclosed in parentheses are hypothetical for temperatures below the melting point of the glyceride.

proposed by Ferguson,¹¹ and later modified by him,¹² and then by Nevin, *et al.*¹³ It was believed by the present authors that this method, which is a semi-micro modification of the more tedious and time consuming capillary rise method, would give more reliable values for interfacial tensions than those obtained by the ring method or drop weight method. This conclusion was based on the work of Hauser, *et al.*¹⁴ The method consists of measuring the pressure required to flatten into a plane surface a meniscus formed at the open end of a horizontal capillary tube, the meniscus being formed by the oil for surface tension measurements and by water for interfacial tension measurements. Values for surface and interfacial tension were calculated from the pressure required and the linear dimensions of the system. Typically, surface tensions were determined by introducing a sample into the capillary, attaching this capillary to the system, and allowing thermal equilibrium to become established. Sufficient air pressure was then applied to force the meniscus to a plane surface. To obtain interfacial tension data, the water was introduced at the open end of the capillary while the meniscus of the oil was still planar. The pressure was released momentarily to draw the water in, and then again increased until the meniscus formed by the water flattened to a plane surface.

The temperature of the system, held constant to within $\pm 0.1^\circ$, was read by means of a calibrated thermocouple. A 10-power eyepiece was used to observe the transition of the meniscus to a plane surface, indicated by a maximum reflection of light. Distilled water was used in the manometer and to adjust the air pressure within the system. The manometer was read to 0.001 mm. by means of a cathetometer. The capillary tubes used were of uniform bore, and the radii were determined accurately to within ± 0.001 mm. All capillaries used were approximately 0.05 cm. in diameter. As a check on the accuracy of the apparatus and method, the surface tension of triple-distilled water was determined in several capillary tubes at several temperatures up to 75° . The values obtained were within ± 0.08 dyne/cm. of those reported by Harkins and Brown.¹⁵

The surface and interfacial tensions of the various glycerides were determined repeatedly on several samples in several different capillary tubes. The average values reported are believed to be precise to ± 0.15 dyne/cm.

Results and Discussion

Surface Tension.—The method of least squares was applied to the surface tension-temperature

(11) Allan Ferguson, *Proc. Phys. Soc.*, **36**, 37 (1923).

(12) Allan Ferguson and S. J. Kennedy, *ibid.*, **44**, 511 (1932).

(13) C. S. Nevin, P. M. Althouse and H. O. Triebold, *J. Am. Oil Chemists' Soc.*, **28**, 325 (1951).

(14) E. A. Hauser, H. E. Edgerton, B. M. Holt and J. T. Cox, Jr., *This Journal*, **40**, 973 (1936).

(15) W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 449 (1919).

data to obtain linear equations of the form, $\gamma = a - bt$, where γ is the surface tension in dyne/cm., t the temperature in $^\circ\text{C}$., and a and b the least square factors. In Table II are recorded the calculated surface tensions at various temperatures together with the constants a and b and the change in enthalpy of the surface, ΔH . These values for surface tension enclosed in parentheses in Table II are hypothetical in that they are for temperatures below the melting point of the glyceride involved.

Surface tension is a fundamental thermodynamic property, and represents the work required to increase the surface area of the liquid by one square centimeter. If the process is to be carried out under isothermal conditions and reversibly, a quantity of heat, Q , will be required to maintain isothermal conditions. This quantity can be calculated by use of the following equation, where T is the temperature in $^\circ\text{K}$. and ΔS the change in entropy.

$$-\frac{\partial \gamma}{\partial T} = \frac{Q}{T} = \Delta S$$

The change in entropy, ΔS , for the formation of 1 square centimeter of surface is equal to the negative value of the temperature coefficient of the surface tension; *i.e.*, the numerical values for b tabulated in Table II are equal to ΔS . The change in enthalpy of the surface, ΔH , when the surface is expanded by 1 square centimeter is the sum of the free surface energy change, γ , and the latent heat, Q . For a given compound both ΔH and ΔS are constants over the temperature range investigated, and Q varies linearly with temperature.

Figure 1 is a plot of the changes in entropies and enthalpies as a function of the number of carbon atoms per acid radical in the simple triglycerides of the saturated fatty acids containing an even number of carbon atoms.

For the various simple triglycerides of the saturated fatty acids containing an even number of carbon atoms, the values for ΔS and ΔH and the values for surface tension at a given isotherm vary with the number of carbon atoms per acid radical. These values pass through a minimum as the length

of the carbon chain is increased. A similar variation has been observed in the melting point of at least some triglycerides as the number of the carbon atoms in one or two of the fatty acid radicals is increased from two to eighteen in multiples of two.^{16,17} The values for ΔS and ΔH for tripelargonin, which contain an odd number of carbon atoms per acid chain, are displaced from the curves plotted in Fig. 1.

The data in Table II give an indication of the effect of certain other factors like degree of unsaturation, *cis-trans* isomerism, and degree of esterification. A comparison of the data for tristearin and triolein shows that the introduction of a single double bond per acid radical lowers the surface tension approximately 1 dyne cm^{-1} while the ΔS and ΔH values remain practically unchanged. However, the introduction of a second double bond, not conjugated, as in trilinolein, lowers the surface tension, ΔS , and ΔH values markedly. The *trans* isomer, trielaidin, has a surface tension of 3 dynes cm^{-1} lower than that of the *cis* isomer, triolein. The values for 1-monopalmitin and 1,3-dipalmitin are about equal, and both are lower than that for tripalmitin.

Interfacial Tension.—Interfacial tensions of the glycerides which are liquid at room temperature were measured at $25 \pm 0.1^\circ$. Interfacial tensions of the higher melting glycerides were measured at $75 \pm 0.1^\circ$. These values were reproducible and constant over a period of several hours. In the case of some of the lower melting glycerides, where there was negligible diffusion across the interface at the higher temperatures, values of interfacial tension were obtained at both 25° and 75° . The values obtained are recorded in Table III. In one case where the interfacial tension was

TABLE III
INTERFACIAL TENSIONS AGAINST WATER OF THE GLYCERIDES

Compound	Interfacial tensions, dyne cm^{-1}	
	25°	75°
Triacetin	3.33	
Tributyryn	11.90	
Tricaproin	18.56	17.32
Tricaprylin	14.60	14.16
Tripalmitin		11.01
Tristearin		10.43
Triolein	14.61	(13.47) ^a
Trielaidin		11.56
Trilinolein	13.16	
1,2-Diaceto-3-olein	7.46	
1,2-Diaceto-3-stearin		2.90
1,3-Dioleo-2-palmitin	14.50	12.26
Tripelargonin	20.16	

^a Value obtained immediately after introduction of water phase.

not constant at the higher temperature, the first reading obtained a few seconds after the interface was formed is recorded in parentheses in Table III. Values for interfacial tension are relatively insensitive to changes in temperature.

Interfacial tensions of the mono- and diglycerides

(16) A. E. Bailey, "Melting and Solidification of Fats," Interscience Publishers, Inc., New York, N. Y., 1950, p. 161.

(17) F. L. Jackson and E. S. Lutton, *J. Am. Chem. Soc.*, **74**, 4827 (1952).

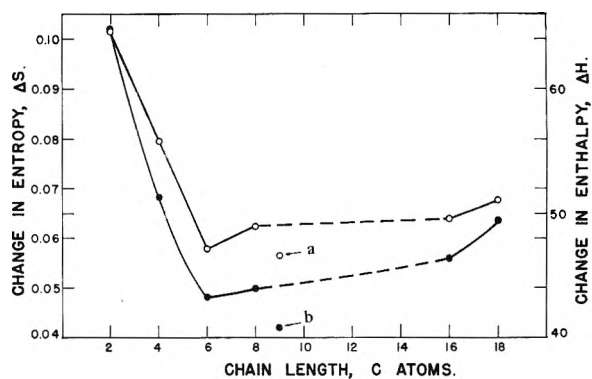


Fig. 1.—Changes in entropy (open circles) and in enthalpy (closed circles) of the simple triglycerides of saturated fatty acids containing an even number of carbon atoms. Points (a) and (b) refer to tripelargonin.

could not be determined because of extensive diffusion across the interface.

Since values for the interfacial tensions of pure glycerides had not been reported previously, the apparatus was standardized by measuring the interfacial tension of methyl laurate at 25° . Also, the interfacial tensions of several refined oils previously reported in the literature were made. The interfacial tension values of the natural oils determined by the method used in this investigation checked with those previously reported by use of the capillary rise and drop weight methods. However, the interfacial tension of refined cottonseed oil determined by this method was lower than that reported previously by use of the ring method at 75° . This difference may be due to the fact that the interfacial tension of triolein was not constant at the higher temperature, but its value increased with time. Cottonseed oil, a major portion of which is the glycerides of oleic acid, may be expected to undergo the same changes. Some of the interfacial tensions at 75° , therefore, may not be as reliable as the ones at lower temperatures.

The lowest interfacial tensions were noted in the aceto compounds. The lowering of the interfacial tension per two aceto groups introduced into tristearin and triolein were 7.53 and 7.15 dyne cm^{-1} , respectively. If we assume the lowering of interfacial tension per one aceto group to be approximately 3.6 dyne cm^{-1} , the calculated value for triacetin is 3.8 dyne cm^{-1} . The actual experimental value for the interfacial tension of triacetin at 25° is 3.3 dyne cm^{-1} .

A comparison of the interfacial tensions at 75° with the structures of the fatty acid chains in the series tristearin, triolein, trilinolein and trielaidin, yields an interesting observation. The interfacial tensions of tristearin and triolein, 10.4 and 13.5 dyne cm^{-1} , respectively, are the farthest apart in this series. Also, the fatty acid chain structures of these two compounds are the most dissimilar, tristearin having straight fatty acid chains of eighteen effective carbon atoms, and triolein, with structure of the *cis*-type, having an effective chain length of ten carbon atoms. Similarly trielaidin, with the *trans*-type structure giving it an effective chain length of seventeen, is more similar to tristearin than it is to triolein, and its interfacial

tension is only 1.1 dyne cm.⁻¹ greater than that of tristearin. The interfacial tension of trilinolein could not be obtained at 75° due to its diffusion into water at elevated temperatures. However, its interfacial tension at 25° is only 1.4 dyne cm.⁻¹ lower than that of triolein. If we assume that the interfacial tension of trilinolein at 75° would be approximately 12 dyne cm.⁻¹, based on the temperature coefficient of the interfacial tension of triolein, it can be said that the interfacial tension of the trilinolein is closer to that of triolein than it is to that of tristearin. Trilinolein, the *cis*-type isomer, has a chain structure more like triolein than tristearin.

DISCUSSION

HERBERT L. DAVIS.—In regard to the request for suggestions as to the composition of an acceptable lipid emulsion for intravenous administration, would it not be well to

attempt to copy the one nature depends on? The evidence now indicates that chylomicrons contain about 85% triglycerides, 5% cholesterol and esters, 5% phospholipids, and 5% proteins. There is reason to believe that the colloidal stability of this emulsion depends on serum albumin and globulins, lecithin, and possibly the monoglycerides produced at the interface. Frazer had shown these monoglycerides produced in the gut are sufficient to stabilize the emulsion formed there, and that about two-thirds of ingested triglycerides pass the intestinal wall in this form. On mixing with the lymph and blood, chylomicrons pick up proteins, and the persistence of the monoglycerides as transient emulsifiers in the blood appears inevitable. Mixed emulsifiers practically always give more stable emulsions than single ones. Others have shown that physiologically available emulsifiers suffice to reduce the interfacial tension between intestinal fluids and fats to such low values as to make possible spontaneous emulsification. In view of the reversibility of the lipolysis reaction, it is relevant to inquire why any triglyceride emulsion will not promptly change to the equilibrium state of about 60% free fatty acid, and whether such reactions may not explain some aberrant reactions to these emulsions?

THE COLLOID ERROR OF INDICATORS¹BY C. F. HISKEY² AND T. A. DOWNEY*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York**Received March 5, 1954*

A spectrophotometric investigation of the interaction between octadecyltrimethylammonium ion and methyl orange is reported. This study was made over a pH range from zero to twelve and with a variation of the quaternary salt concentration from 10^{-6} to 10^{-2} molar. The spectral data are quantitatively interpreted in terms of an association reaction between the quaternary salt and the basic form of the methyl orange. This interaction increases the acid ionization constant of the methyl orange by approximately 6.2 *pK* units. Evidence is presented for the submicellar units in concentrations as low as 10^{-6} molar. These data are discussed in relation to the Corrin-Harkins method for determining the critical micelle concentration, with indicator dyes.

Introduction

This report describes a spectrophotometric study of the interaction between the cationic quaternary salt octadecyltrimethylammonium chloride and the simple azo dye, methyl orange. The study was made for the purpose of developing a more quantitative treatment of such interactions than had been possible hereto.

It has been known for more than thirty years that indicator dyes have their colors altered when present in solution along with soaps or detergents.^{3,4} The phenomenon, presumably, is caused by the preferential adsorption of one form of the indicator molecule on the detergent micelles with consequent displacement of the acid-base equilibrium in favor of this form.

Fajans⁵ investigated the effect of dye adsorption on ionic surfaces. He found that if salts of eosin were added to a halide solution during titration with silver ion, there was no adsorption on the silver halide until the silver ion was in excess. Once it was in excess, the adsorption of the silver eosinate took place immediately with a change in color of the dye due to its electrical distortion.

Somewhat later Deutsch⁶ described striking examples of effects on indicators when adsorbed at oil-water interfaces. For example, when water and benzene were shaken together after the addition of nearly colorless rhodamine, the temporary emulsion was colored a bright pink. The color disappeared again as soon as the liquids separated. In this way he produced color shifts of as much as one pH unit.

In 1934, Hartley⁷ studied the effects of anionic, cationic and non-ionic detergents on a large number of dyes. He demonstrated that the greatest color changes occur when the charge on the detergent is opposite to that on the indicator ion. He later used this phenomenon in the determination of the total concentration of anionic and cationic detergents in solution, by titration with a known solution of detergents of opposite sign in the presence of brom phenol blue. Subsequently, Sheppard

and Geddes⁸ investigated changes in the absorption spectrum of pinacyanol chloride in aqueous solution to which the cationic detergent cetylpyridinium chloride was added. Their study which was preliminary in nature, was greatly extended by Harkins and colleagues,⁹ whose investigations led them to develop a method¹⁰ for determining the critical micelle concentration of detergents utilizing the spectral changes produced in various dye solutions. Their method consisted of adding varying quantities of the detergent to a solution containing a fixed amount of the indicator dye. In the vicinity of the critical micelle concentration there was reported to be an abrupt change in the color of the indicator. For example, they reported that if they took a 10^{-4} molar solution of the sodium salt of 2,6-dichlorophenolindophenol and made it 3×10^{-4} molar with hydrochloric acid the color would change from blue to red. On the addition of sufficient cationic soap to produce micelles the color changed back to blue.

The apparent simplicity of the above methods of producing color changes suggested the possibility of making a more quantitative treatment of the effect. With that object in mind a preliminary qualitative survey was made to decide what area should be investigated. A choice was finally made of octadecyltrimethylammonium chloride as the detergent and methyl orange as the indicator. The reasons for these choices are as follows.

First, this quaternary compound is the salt of a strong base and a strong acid. Consequently it will have little effect on the pH of a buffered solution and therefore a large variation of concentration can be made. Secondly, its micelles will be stable and positively charged throughout the whole practical range of pH values which we might choose to study. In addition, this particular detergent has a very long hydrocarbon tail which gives it a very low critical micelle concentration in aqueous solutions. Thus extensive studies of color change effects might be made at exceedingly low molar concentrations. As the study was to be spectrophotometric in character this would mean that the interference from turbidity would be held to a minimum. Finally, it was found that this compound could be obtained commercially with a relatively high degree of purity.

(1) The data contained herein were part of the thesis presented by T. A. Downey to the Chemistry Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the M.S. degree, June, 1953.

(2) International Biochemical Corporation, Brooklyn 20, N. Y.

(3) A. Jariach, *Biochem. Z.*, **134**, 177 (1922).

(4) A. Gutbier and H. Brintzinger, *Kolloid Z.*, **41**, 1 (1927).

(5) K. Fajans and O. Hassel, *Z. Elektrochem.*, **29**, 495 (1923)

(6) D. Deutsch, *Z. physik. Chem.*, **136**, 353 (1928).

(7) G. S. Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

(8) S. E. Sheppard and A. L. Geddes, *J. Chem. Phys.*, **13**, 63 (1945).

(9) M. L. Corrin, H. B. Klevens and W. D. Harkins, *ibid.*, **14**, 480 (1946).

(10) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 679 (1947).

The reasons for choosing methyl orange as the first dye to be studied are several. In the first place, the dye possesses a relatively simple structure, in spite of the fact that it has a very high absorptivity. This high absorptivity makes it possible to use relatively dilute solutions of the dye. There is the additional fact that there is an extensive literature on the interactions of this dye with a great many substances. This provides many opportunities for making comparison with our results.

Experimental

Reagents.—The octadecyltrimethylammonium chloride was prepared from a sample of Armour "Arqual 18," which is a 50% solution of the quaternary salt dissolved in isopropyl alcohol. The quaternary salt was precipitated from this solution by the addition of ethyl acetate. The precipitate was thoroughly washed with ethyl acetate and then vacuum dried for 16 hours. When assayed potentiometrically for chloride a value of 98.5% purity was found. This value was used as the purity of the quaternary salt although it might be a little low due to the solubilizing effect of the quaternary ammonium ion upon the silver chloride precipitate. In any event, a small error in the concentration of this material will not affect the main conclusions derived herein.

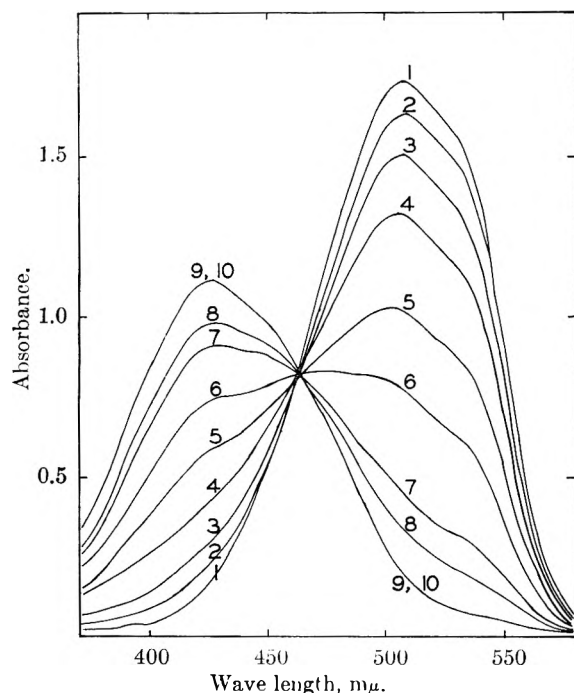
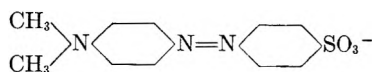


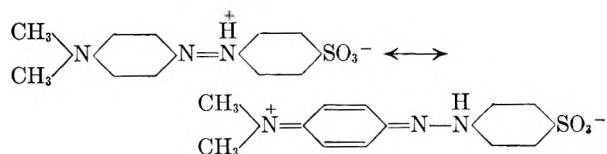
Fig. 1.—Absorption spectra of methyl orange solutions to which various amounts of octadecyltrimethylammonium chloride have been added; concn. of M. O. = 2.04×10^{-5} M, pH 1.1; concn. of quaternary salt $\times 10^6$ M: 1 = 0.0; 2 = 3.6; 3 = 7.2; 4 = 14.4; 5 = 28.8; 6 = 57.6; 7 = 144; 8 = 288; 9, 1640; 10 = 5070.

The methyl orange in this study was Merck and Co., A.C.S. grade and was used without further purification. In alkaline solution methyl orange is yellow and exists in the anionic form



On the addition of acid below a pH of 3 the color deepens to a red. The azo nitrogen atom takes on a proton and the dipolar ion is then formed as a resonant hybrid of the two structures.¹¹

(11) I. M. Kolthoff, "Acid-Base Indicators," The Macmillan Co., New York, N. Y., 1937.



Other reagents used in these studies were reagent grade and used without further purification.

Absorption Spectra.—The absorption spectra of these solutions were recorded with a Cary recording spectrophotometer, Model 11, Serial No. 68, using a 2-cm. silica absorption cell. To compensate for the slight turbidity caused by the detergent micelles, the spectra were always measured relative to water containing the same amount of quaternary as was present in the dye solution being studied. The absorbance, A , which was plotted as a function of the wave length, is defined by the familiar relation

$$A = \log_{10} \frac{I_0}{I} = abc$$

where I_0 is the intensity of light emerging from the solvent, I , the intensity of light emerging from the solution, a , the absorptivity, b , the length of the light path through the absorption cell and c , the concentration of the absorber expressed in moles per liter. The temperature at which these measurements were made was $25 \pm 1^\circ$.

Procedure.—The procedure used in the preparation of the dye solution was as follows: to a 100-cc. volumetric flask 10 ml. of a 2.04×10^{-4} molar solution of methyl orange was added. Then an appropriate amount of a concentrated quaternary solution was pipetted in. Finally, an appropriate amount of acid, alkali or phosphate buffer was added to the volumetric flask so that when the entire contents of the flask were diluted to the 100-ml. mark the desired pH and detergent concentration would be obtained. These solutions were then stoppered and allowed to equilibrate to the temperature of the room, which was roughly 25° .

Results and Discussion

The spectra of methyl orange solutions vary markedly with increasing concentration of the quaternary salt at a fixed pH. Figure 1 presents some typical data to illustrate the effects observed when the quaternary concentration is progressively increased in a 2.04×10^{-5} molar dye solution maintained at pH 1.1. In this graph the absorbance of the solution is plotted as a function of the wave length. The various curves are for the concentrations of the quaternary salt listed in the legend. It will be observed that when no quaternary salt is present the methyl orange is completely in its acid form, possessing an absorption peak at $507 \text{ m}\mu$. As the quaternary salt concentration is increased, it will be observed that this peak at $507 \text{ m}\mu$ gradually decreases in height and finally disappears, while in the meantime, a new peak arises at $426 \text{ m}\mu$. Increasing the quaternary salt concentration beyond 1.6×10^{-3} molar does not cause any additional change in the spectrum, although it does lead to an increasing turbidity due to the increasing concentration of micelles.

These data show that the interaction between the dye and the quaternary salt is a relatively simple one consisting of a transition from the acid form to a form in association with the quaternary salt. The data have all the characteristics of a dye system to which variable amounts of alkali have been added causing it to shift over to its basic form. It differs from such a situation because the base form of methyl orange does not peak at $426 \text{ m}\mu$ as is the case here but has a peak at $463 \text{ m}\mu$.

In Fig. 2 data are presented for the methyl orange system when treated with a quaternary salt

in a solution buffered at pH 7.95. In this case it will be observed that as the quaternary salt concentration is increased, the base form is at first precipitated out of solution, but when the quaternary salt concentration reaches a point where micelles are formed, the dye begins to redissolve. Finally, when the concentration of the quaternary salt is 1.44×10^{-3} molar or greater complete solubilization has been effected and no further spectral changes are observed. Spectral curves 2, 3, 4, 5 and 6 were obtained by allowing the mixing flasks to stand until all of the precipitate had settled on the bottom. Then samples were withdrawn for the spectrophotometer, taking care to keep the sediment undisturbed.

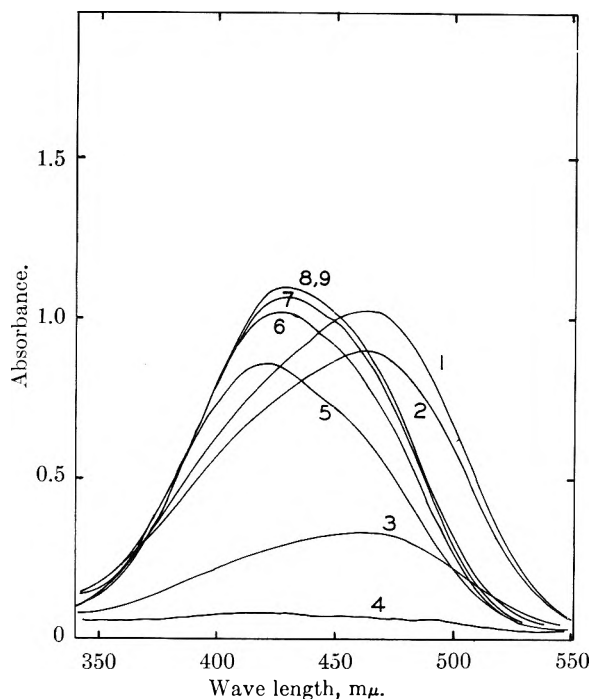
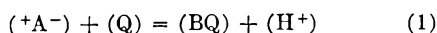


Fig. 2.—Absorption spectra of methyl orange solutions to which various amounts of octadecyltrimethylammonium chloride have been added; concn. of M. O. = 2.04×10^{-5} M, pH 7.95; concn. of quaternary salt $\times 10^5$ M: 1 = 0.0; 2 = 0.72; 3 = 1.44; 4 = 3.60; 5 = 7.20; 6 = 14.4; 7 = 57.6; 8 = 144; 9 = 288.

To facilitate the comparison of the various limiting forms of the spectra of methyl orange, a plot of four spectral curves is given in Fig. 3. Curve A is the spectrum for the acid form of methyl orange, that is, for the dipolar ionic form. Curve B on the other hand is for the basic and anionic form of the dye. Curve C represents the spectrum of the dye in an acid solution which has a large excess of quaternary salt and curve D represents a solution of equal ionic strength at a pH of 12, also containing a large excess of quaternary salt. Here we see that the limiting forms when large excesses of quaternary salt are present have identical spectra. The only meaning which this can have is that forms C and D are the same thing and are the interaction product of the methyl orange and the detergent.

It has been possible to account for these spectral changes in terms of the following equilibrium process



In this expression $(+A^-)$, (Q) and (BQ) represent the concentrations, respectively, of the acid form of the dye, of the quaternary salt and of the interaction product between the dye and the quaternary salt.

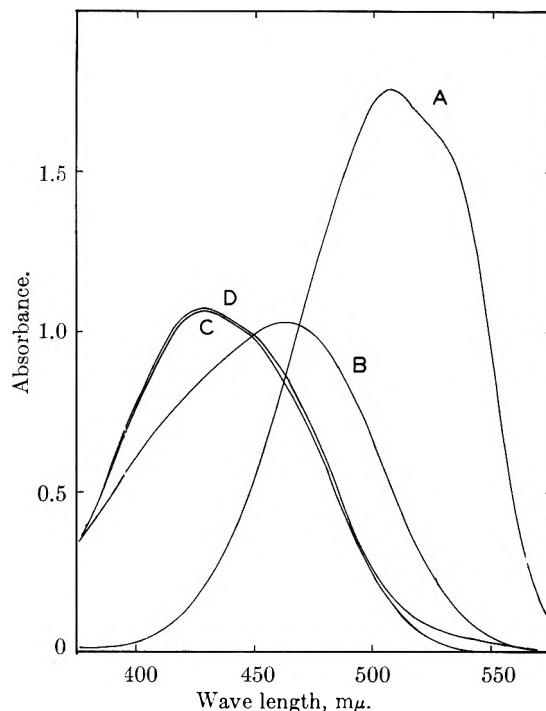


Fig. 3.—Comparison of the limiting spectra of methyl orange solutions; concn. of M. O. = 2.04×10^{-5} M; curve A, pH 1.1, not quaternary; curve B, pH 9.0, no quaternary; curve C, pH 1.0, concn. of quaternary = 0.015 M, HCl concn. = 0.10 M; curve D, pH 12.0, concn. of quaternary = 0.015 M, NaOH concn. = 0.01 M, KCl concn. = 0.09 M.

Because of a preferential affinity for the anionic form of the dye, the quaternary salt binds it, displacing the equilibrium to the base form and forcing the proton off the azo group. Two factors are responsible for the formation of this interaction product. The first of these is a coulombic interaction between the negatively charged sulfonic group on the methyl orange and the positive charge on the quaternary ion. The second factor is a van der Waals-London type of interaction between the hydrocarbon portions of these two molecules. The mass action relation for formulation (1) may be written as in (2)

$$K = \frac{(HQ)(H^+)}{(+A^-)(Q)} \quad (2)$$

This in turn can be rearranged into the following logarithmic form

$$\log(Q) + pH - pK = \log(BQ)/(+A^-) \quad (3)$$

Now, when $(BQ) = (+A^-)$ then the right-hand term of (3) will equal zero and

$$pK = \log(Q) + pH \quad (4)$$

Thus, to evaluate pK it is only necessary to plot $\log(BQ)/(+A^-)$ as a function of $\log(Q)$ and by interpolation find that value of $\log(Q)$ for which $\log(BQ)/(+A^-)$ equals zero.

This has been done in Fig. 4 where a line with a slope equal to unity has been fitted to the calcu-

lated data. The interception of the line at the point where $\log(\text{BQ})/(\text{+A}^-) = 0$ occurs at -3.57 . Since the $pH = 1.1$ in this case, we find that $pK = -2.46$.

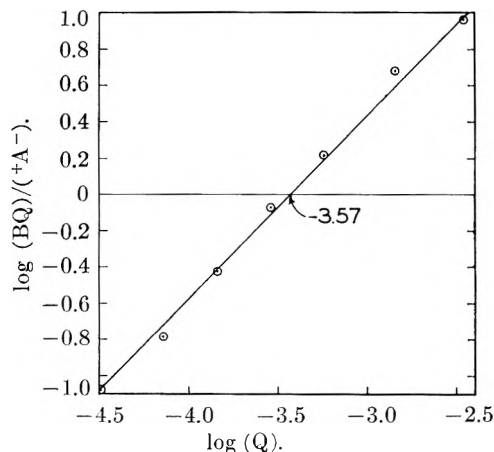


Fig. 4.—Evaluation of pK for the interactions, pH 1.1.

The calculation of the concentrations of (+A^-) and (BQ) was effected by solving the absorbance relationship (5) simultaneously at wave lengths 507 and 426 $m\mu$.

$$A = a_{AC}A + a_{BQC}BQ \quad (5)$$

The important absorptivity values are listed in Table I.

TABLE I

ABSORPTIVITY VALUES OF METHYL ORANGE AT IMPORTANT WAVE LENGTHS

Dye form	Wave length of max. absorptivity and absorptivity value, $m\mu$	Other wave length and absorptivity values, $m\mu$
A	507 42,600	426 4,400
B	463 25,200	...
BQ	426 25,400	507 4,890

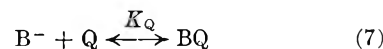
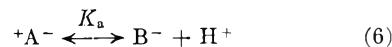
The absorbance values were taken from each spectral curve.

Because the experimental points in Fig. 4 fit a linear curve with a slope of unity this can be taken as an indication of a first power relation for the quaternary concentration in the mass action formulation. The significance of this observation is that the spectrophotometric measurements reveal no stepwise building up of the interaction product such as occurs in complex ion formation. It would seem, therefore, that one quaternary ion per molecule of dye is required to produce the spectral changes which have been observed. This does not mean, however, that the entire chemical process responsible for the color effects observed is restricted to the interaction of a single quaternary ion with a single dye molecule. It is possible to give an alternative explanation of the effects here observed and this will be done below.

Additional confirmation of the validity of the equilibrium given in (1) was effected by a study of the effects of varying the hydrogen ion concentration in a dye solution containing sufficient quaternary salt to produce a 50% conversion of the acid form over to the BQ form. It was found that as the

hydrogen ion concentration increased the BQ form disappeared completely from solution. On the other hand, if the hydrogen ion concentration was lowered then more of the dye was converted to the BQ form. Values of the equilibrium constant calculated according to the method outlined above gave values consistent with that obtained graphically.

The equilibrium, K , is actually the product of two partial constants corresponding to the two partial reactions (6) and (7).



Since the pK_a of methyl orange is about 3.7 it follows from (8) that pK_Q will have a value of -6.2 .

$$pK = pK_a + pK_Q \quad (8)$$

The total effect is as though the pK_a of methyl orange were decreased by approximately 6.2 units. Under these conditions therefore, methyl orange appears to be a very strong acid indeed. This shift in the apparent pK_a of an indicator is the largest ever reported. It corresponds to a free energy change of about 8.5 kcal.

An alternative explanation may be offered for the partial reaction (7). It can be argued that this formulation merely represents the extraction of the basic dye form from aqueous solution to a micellar oil phase. The equilibrium constant, K_Q , then represents nothing more than a partition coefficient for distribution between two immiscible phases with appropriate insertion of a volume term for the quantity of micellar oil phase present. Viewed in this manner the Q term is nothing more than a proportionality term to the volume of micellar oil phase present in the system. As the volume of the oil phase increases it is only reasonable that a greater fraction of the dye should be extracted into it and there possess a different absorption spectrum.

When the equilibrium process is thus considered, the question arises of how many molecules of the quaternary salt need associate with the dye molecule to cause the color change. A method of arriving at this term may be had from an investigation of the solubility of the salt BQ in the detergent solution. Difficulties associated with evaluation of the solubilization from the data in Fig. 2 led us to the preparation of the salt BQ.

This compound was prepared by mixing equimolar amounts of the dye and the quaternary salt allowing precipitation to take place. The precipitate was filtered from solution, followed by extensive washing with distilled water. It was then dried in a vacuum desiccator to constant weight. It was analyzed colorimetrically by dissolving it in 1.2 molar hydrochloric acid and measuring the absorbance at 507 $m\mu$. The ratio of $(\text{B}^-)/(\text{BQ})$ was found to be 0.489, in good agreement with the theoretical 0.493. An excess of this preparation was now suspended in solution along with varying quantities of the quaternary salt and equilibrated for several days. The quantity dissolved was measured spectrophotometrically in 1.2 N hydrochloric acid. The results which were obtained have been plotted in Fig. 5, where it will be seen that not

until the concentration of the quaternary salt has increased to about 3×10^{-4} molar is there any effective solubilization of the BQ salt. At lower quaternary salt concentrations the solubility product principle applies and consequently the solubility of the BQ salt falls for lower values of the quaternary salt. Beyond the critical micelle concentration, which is presumed to occur at 3×10^{-4} molar, the BQ salt increases in solubility in a linear way with respect to the concentration of the quaternary ion. The slope of this solubility relation indicates that 2.3 moles of quaternary ion are required for the solubilization of a mole of BQ. Thus, in the micelle which is being formed there are somewhat more than three quaternary ions surrounding each one of the methyl orange anions. Thus it can be seen that the quaternary ion is indeed a very effective solubilizing agent for this particular dye.

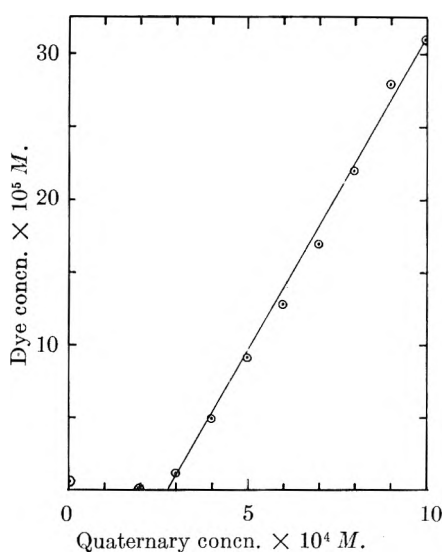


Fig. 5.—Solubility of BQ in quaternary salt solutions; pH 7, temp., 25°.

Discussion

In a great many dye systems studied previously by other workers¹²⁻¹⁵ a lateral shift of the absorption spectrum has been observed with increasing concentration of the colloid substance. Such a situation makes the interpretation of the spectral data somewhat more difficult than is the case here.

On the other hand, with this particular system the spectral shift is abrupt so that the dye either exists in solution in its dipolar acid form or in its anionic basic form in association with the quaternary ion. The existence of any detectable amount of the basic form, B, devoid of association with the quaternary ion could not be demonstrated in these solutions. In view of the large value for K_Q , it would be anticipated that its concentration would be too low to be detectable by our method.

The spectrum of the BQ form is very similar to that of the acid form of the dye with the exception that the absorptivity is generally reduced. In

addition, there is a shift of the absorption peak by about 80 $m\mu$ toward the ultraviolet. The spectrum of the BQ form is practically identical with that published for the base form dissolved in ethanol or in normal amyl alcohol.¹⁶ It seems very probable that similar spectra result because the same factors are operating in these cases.

Klotz has argued that the spectral shift to the 426 $m\mu$ region is a reflection of short range electrostatic forces operating between the sodium and azosulfonate ions. In aqueous solution where ion pair formation is largely prevented by the shielding effect of the high dielectric medium, the freely ionized azosulfonate ion has its absorption peak at 463 $m\mu$.

This explanation of the spectral shift also seems quite applicable in this instance. When the azosulfonate ion interacts with the quaternary ion they coalesce into a charged micelle or submicelle. The charged groups will be found at the periphery of this micelle. In view of the low dielectric constant of the hydrocarbon portions of these ions very little shielding may be expected between their charges, so that the electrostatic interaction will be very great. Even though the charges are on the surface of the micelle and therefore bathed by the aqueous medium, one can only expect a relatively small shielding effect from that cause.

If one examines the data in Fig. 1 carefully, it can be observed that the absorbance at wave length 507 $m\mu$ changes by as much as 0.11 unit for a 3.6×10^{-4} molar increase in concentration of the quaternary ion. If we recall that the instrument is capable of detecting as little as 0.001 absorbance unit, this means that we can detect the effect of as little as 3.3×10^{-6} mole of the quaternary salt by the spectral change induced. It seems very likely indeed that at these exceedingly low concentrations, submicellar units are being formed consisting of at least one dye and one quaternary ion but more probably of one dye and three quaternary ions.

As shown in Fig. 6 the change in absorbance at 507 and at 426 $m\mu$ alters continuously as the quaternary concentration is increased. It has previously been shown that as little as 3×10^{-6} mole of quaternary ion would have altered the absorbance appreciably. This continuous variation in the absorbance makes it difficult to decide at what point

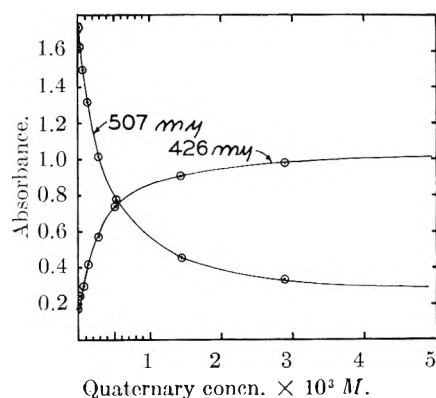


Fig. 6.—Variation of absorbance with quaternary concn.; pH 1.1, dye concn. = 2.04×10^{-5} M.

(12) E. L. Colichman, *J. Am. Chem. Soc.*, **73**, 3385 (1951).

(13) B. Carroll and A. W. Thomas, *J. Chem. Phys.*, **17**, 1336 (1949).

(14) I. M. Klotz, R. K. Burkhard and J. M. Urquhart, *J. Am. Chem. Soc.*, **74**, 202 (1952).

(15) G. Oster, *J. chim. phys.*, **48**, 217 (1951).

(16) I. M. Klotz, R. K. Burkhard and J. M. Urquhart, *This Journal*, **56**, 77 (1952).

the formation of the critical micelle concentration as outlined by Corrin and Harkins begins to occur. It is true that these authors have not recommended the use of such an indicator dye as this for the detection of the critical micelle concentration of the cationic detergent. It seems to us that these experiments serve to show one very important thing about indicators for the detection of the formation of micelles. Such indicators probably must be restricted to those that have a large number of charge points on them so that the interaction is at the surface of the micelle and thus a color change cannot be effected until the normal micelle has a chance to form. Another type of indicator would be one which possesses no charge and which is absorbed into the body of the micelle and there has its spectrum altered.

Acknowledgment.—The authors wish to acknowledge the kind assistance rendered by Mr. F. R. Hedger, Director of the Analytical Laboratories of Chas. Pfizer Co., for making the Cary spectrophotometer available to them for this investigation. In addition they would like to acknowledge the assistance rendered by Dean R. E. Kirk of the Polytechnic Institute of Brooklyn in the final stages of the preparation of the manuscript.

DISCUSSION

F. M. FOWKES.—The authors of this paper have set forth to discredit the most popular method for determination of the critical concentration for micelle formation. This method is widely used because it is rapid, works well in the

presence of salt (unlike conductivity methods) and because it gives correct values, or very close to the correct values as obtained by other methods. The Corrin-Harkins method is based on two phenomena: (1) the formation of an indicator-detergent complex (BQ) which is much more oil-soluble than water-soluble; and (2) the extraction of BQ from aqueous solution by solubilization into micelles (as illustrated in Fig. 5). Many indicator-detergent combinations may be used, but a sharp increase in color is most probable if the type and concentration of indicator are so chosen that only a small amount of the indicator is in the BQ form at the onset of micelle formation. Under these conditions extraction of BQ from solution into the micelles drives the equilibria for formation of BQ far toward completion.

The authors of this paper have not chosen such an indicator; instead they have chosen an indicator which forms such a strong BQ complex that it precipitates out of solution well below the CMC. They have also used a much larger ratio of indicator to detergent than is usually used for this method. I agree with the authors that one cannot obtain accurate measurements of the CMC with this indicator-detergent combination (unless the concentration of indicator were reduced). However, I believe that rather than suggesting that the method itself is incorrect, the authors should have concluded only that incorrect values of the CMC may be obtained with the method by poor choice of kind and concentration of indicator.

M. L. CORRIN.—The findings reported in this paper are not in disagreement with the views adopted by Corrin and Harkins. These authors postulated that the dye in many instances could form a complex with the long-chain ions below the critical concentration and that the dye is extracted from this complex into or onto the micelle when this is formed. The formation of this dye-ion complex is in many instances desirable since it serves to intensify the magnitude of the color change occurring at the critical concentration. It is obvious, however, that the complex should be sufficiently unstable so that the micelle extraction process occurs readily. I feel that any dye would be suitable if its color differs sufficiently in its ionic complex from that displayed on or in a micelle. I feel that this is essentially what Hiskey is saying.

EXPERIMENTS ON THE DEGRADATION OF LIPOPROTEINS FROM SERUM¹BY B. ROGER RAY, EDWIN O. DAVISSON² AND HENRY L. CRESPI³*Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois**Received March 5, 1954*

The degradative changes which β -lipoproteins isolated from rabbit and human sera undergo upon dialysis against water and various salt solutions were studied in terms of patterns obtained in ultracentrifugal analyses. If all traces of cupric ion were removed from the environment, the lipoprotein was found to be stable upon dialysis. Degradation was readily detectable at 0.1 p.p.m. Cu^{++} . Numerous other metal ions were without effect. Several substances were found which would stabilize the lipoprotein under ordinary conditions. These were antioxidants or else complexing agents for copper. The data support the view that the degradative process is oxidative in nature and is catalyzed by copper.

Although lipoproteins and the interactions of lipids and proteins have been studied for over half a century, renewed interest has resulted from the work of Gofman and colleagues,⁴ who have developed ultracentrifugal methods for the isolation and analysis of blood lipoproteins. By these techniques they have shown that correlations exist between the levels of classes of lipoproteins and several pathological conditions which involve lipid metabolism.⁵ Heuper⁶ had previously suggested that such diseases might be due to the instability of colloidal lipids. However, little is known concerning the nature and chemistry of these complex proteins, partly because of the difficulties of isolation and of preservation.

The lability of serum lipoproteins is widely recognized. For example, Pedersen⁷ observed that washing his isolated "x-protein" caused partial denaturation. Differences in the solubilities of α -lipoprotein isolated from fresh blood and from blood stored for 72 hours were demonstrated by Cohn.⁸ The isolation of the β -lipoprotein fraction without extensive degradation has been achieved only by centrifugal methods.^{4,9} The experience of several laboratories studying the significance of lipoproteins in human sera has been that the components remain unaltered (in centrifugal behavior) for a matter of weeks if left in the serum in the cold, but that changes occur when the isolated material is stored.¹⁰

A recent brief communication¹¹ has emphasized the *in vitro* lability of rabbit and human β -lipoproteins. For instance, when a centrifugally isolated fraction is dialyzed against a large volume of buffered saline, a typical degradation occurs which, however, is prevented if the saline contains a small

amount of serum or a dialyzate from serum. We have extended our study of the factors involved and in the present paper evaluate a number of substances, including metallic ions, as to their influence.

Experimental Details

Isolation of Lipoproteins.—Untreated sera from rabbits fed cholesterol at suitable levels and periods of time¹² were used as the main source of lipoprotein. Human sera were utilized in a number of tests. An initial centrifugation at 40,000 *g* for 30 minutes eliminated the coarse material, mostly lipid in nature. The density then was increased by adding an equal volume of saline solution (0.171 g. sodium chloride per 1 ml. "distilled" water) and the lipoprotein fraction isolated by flotation according to the general procedure of Gofman, *et al.*⁴ The runs were made in a Spinco Model L centrifuge with a No. 30.2 rotor using lusteroid tubes with paraffin-coated cap assemblies.

Ultracentrifugal Analyses.—Determinations of flotation patterns were carried out under uniform experimental conditions in so far as possible. The temperature was $24 \pm 2^\circ$. Protein concentrations were approximately uniform. Since the flotation rate is extremely sensitive to the density of the medium, it was desirable to adjust this density in each lipoprotein sample to exactly 1.063 g./ml. with sodium chloride before making the analysis. In experiments involving traces of metal ions Kel-F center pieces were used in the cells.

The purposes of the present contribution are served by comparing the general features and differences of the flotation patterns as run under the same experimental conditions; it is not pertinent to tabulate flotation rates and concentrations. The patterns in Figs. 1–4 are traced from the photographic negatives. All runs were made at 52,640 r.p.m. in a Spinco Model E ultracentrifuge. The acceleration time was 6 minutes. In Figs. 1, 3 and 4 the exposures were recorded at 8-minute intervals following the first exposure of each run (that on the left) which was taken after 12 minutes at speed. The several sets of exposures in each figure are comparable as to elapsed times of centrifugation. Flotation in each pattern is proceeding from right to left.

Dialysis Procedures.—The lipoprotein sample was placed in a small pre-tested Visking cellophane casing that was then securely tied with a minimum of entrapped air. The bag was immersed in the desired solution (pre-cooled) and dialysis carried on at $0-4^\circ$ with rocker or intermittent shaking for 7–10 days, unless otherwise noted. The regular procedure called for 1.0 ml. of lipoprotein solution and 200 ml. of external solution.

In the first experiments to be described the external solution was, in each case, made up by dissolving the substance to be tested in dilute sodium chloride solution, buffering to a pH between 6.8 and 7.8 with 0.01 *M* phosphate, and adjusting the solution density to 1.063 with concentrated sodium chloride solution. In the more quantitative experiments designed to test the effects of traces of metal ions, the particular salt, in each case, was dissolved in metal-free water or else in purified buffered saline. After dialysis and before analysis, purified sodium chloride was added to the lipoprotein solution to bring the medium density to 1.063. The pH of the external solution following dialysis was in every case between 6.8 and 7.2, except for a value of 6.4 for ferrous chloride.

(1) In part from the thesis of Edwin O. Davison submitted to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the Ph.D. degree, 1953.

(2) G. D. Searle and Company Research Fellow in Chemistry, 1951–1952.

(3) Public Health Service Predoctorate Research Fellow, 1953–1954.

(4) J. W. Gofman, F. T. Lindgren, H. A. Elliott, W. Mantz, J. Hewitt, B. Strisower and V. Herring, *Science*, **111**, 166 (1950).

(5) J. W. Gofman, H. B. Jones, F. T. Lindgren, T. Lyon, H. A. Elliott and B. Strisower, *Circulation*, **2**, 161 (1950)

(6) W. C. Heuper, *Arch. Path.*, **38**, 162 (1944).

(7) K. O. Pedersen, "Ultracentrifugal Studies on Serum and Serum Fractions," Uppsala, 1945.

(8) E. J. Cohn, *Discs. Faraday Soc.*, **6**, 92 (1949).

(9) J. L. Oncley, F. R. N. Gurd and M. Melin, *J. Am. Chem. Soc.*, **72**, 458 (1950).

(10) G. V. Mann, "Symposium on Lipoproteins and Ultracentrifugal Technique," Chicago, 1952, Auspices Committee on Lipoproteins and Atherosclerosis, National Advisory Heart Council.

(11) B. R. Ray, E. O. Davison and H. L. Crespi, *J. Am. Chem. Soc.*, **74**, 5807 (1952).

(12) D. M. Cook, B. R. Ray, E. O. Davison, L. Feldstein, L. Calvin and D. Green, *J. Exptl. Med.*, **96**, 27 (1952).

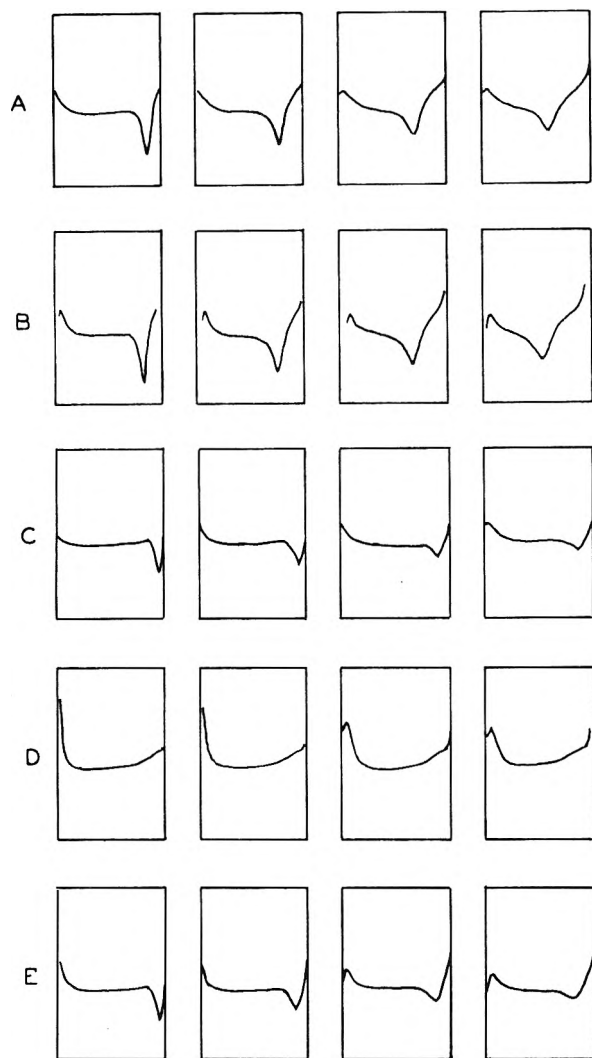


Fig. 1.—Flotation patterns showing general trend of degradation of lipoproteins during dialysis: A, (#1739), original before dialysis; B, (#1755), after 8 days against serum dialyzate; C, (#1746), after 4 days against saline; D, (#1758), after 8 days against saline; E, (#1775), after 4 days against saline followed by 7 days against serum dialyzate.

Determination of Densities.—A Westphal balance was utilized for liter quantities of saline solutions. Densities of dialyzate solutions and of the lipoprotein media were determined and adjusted by use of the falling-drop method of Barbour and Hamilton.¹³ This method, requiring very small volumes, was particularly suited for determinations on lipoprotein solutions where usually 1 ml. was available for both density and analytical analyses. From a comparison of the times of fall of 0.01-ml. drops of unknown and of reference solutions, the density of the unknown could be calculated. Protein was first removed from the lipoprotein solutions by heating in a sealed tube in boiling water, then centrifuging to obtain a clear supernatant, which was considered to be the medium.

Purification of Materials.—In those experiments discussed in the first two sections under Results, reagent grade chemicals were used along with “distilled” water from the laboratory supply line. The experiments concerning the effect of specific metal ions, however, necessitated the removal of traces of heavy metal contaminants. The dithizone method¹⁴ proved satisfactory for purifying reagents and for the estimation of concentrations.

(13) H. Barbour and W. Hamilton, *J. Biol. Chem.*, **69**, 625 (1926).

(14) E. Sandell, “Colorimetric Determination of Traces of Metals,” Interscience Publishers, Inc., New York, N. Y., 1950.

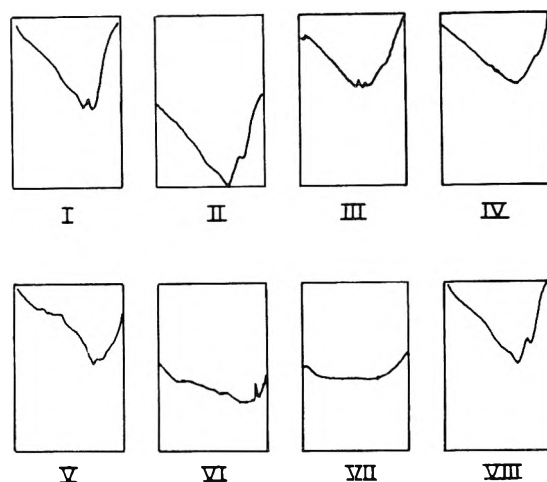


Fig. 2.—Flotation patterns of lipoproteins showing progressive degradation during dialysis against sodium chloride solution. In each case the third exposure of the run is shown, taken at 22 minutes after reaching speed: I, (#1254-W), original before dialysis; II, (#1254-P), after 2 days; III, (#1257-W), after 3 days; IV, (#1263-W), after 4 days; V, (#1270-W), after 7 days; VI, (#1284-P), after 10 days; VII, (#1309-P), after 21 days; VIII, (#1324-W), control—1 day against saline, followed by 26 days against serum dialyzate. (The different vertical displacements are because some runs were made in cells with wedge windows.)

Metal-free water and hydrochloric acid were prepared by distillation from a Pyrex still. Purified dithizone was available. To remove the heavy metals from sodium chloride, a saturated solution in metal-free water was successively extracted at acidic, basic and neutral pH with excess dithizone in CCl_4 , the pH being adjusted with redistilled HCl and reagent Na_2HPO_4 . After a final adjustment to pH 7.2, repeated extractions were made with the dithizone- CCl_4 solution. The last traces of dithizone were removed by extracting the salt solution with CCl_4 which had been previously washed with metal-free water to remove traces of heavy metals. Finally, heating removed the residual CCl_4 .

Results

Changes Accompanying Dialysis.—When a lipoprotein concentrate from human or rabbit serum is dialyzed against a large volume of buffered sodium chloride solution or ordinary water, several related changes, both concomitant and progressive, take place as observed by ultracentrifugal analysis.

(1) The heterogeneity of the lipoprotein material increases, as evidenced by the spreading of the peak.

(2) Low density material of lipid nature appears. This rises rapidly to the meniscus and tends to form a compact layer.

(3) The concentration under the lipoprotein peak diminishes and there may be observed an increasing amount of material which sediments under the experimental conditions.

(4) The rate of flotation of the lipoprotein peak progressively decreases and may finally even become a sedimenting peak (or, better, a region, since it is small and very heterogeneous by this stage).

In addition, there frequently develops a visible turbidity due to the aggregation of lipid-like material mentioned in (2) above.

These changes for a typical example are illustrated in Fig. 1. A S_f 5-9 lipoprotein concentrate was divided into several portions following isola-

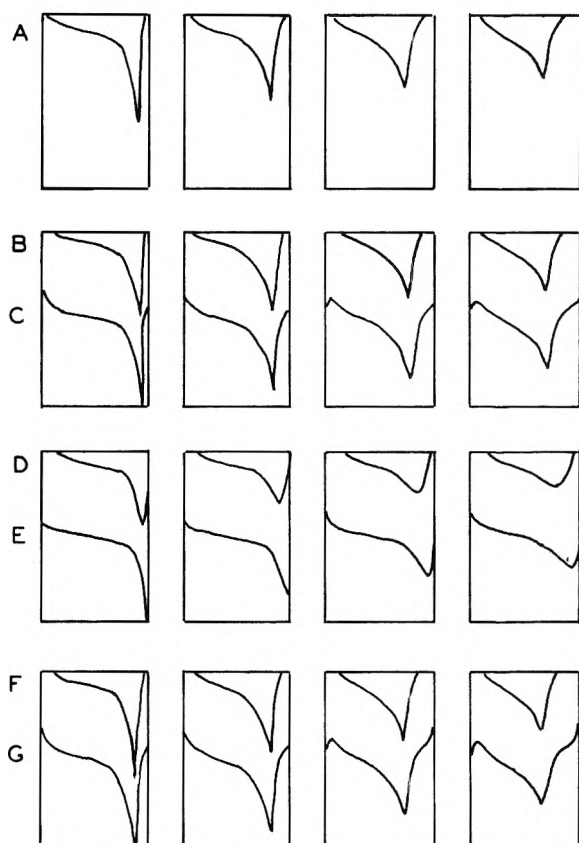


Fig. 3.—Flotation patterns showing the effects of traces of metal ions during dialysis against purified saline. Dialysis time, 5 days in each case: A, (#A-233), original before dialysis; B, (#A-252-W), against serum dialyzate; C, (#A-252-P), against purified saline; D, (#A-254-W), against 1 p.p.m. Cu^{++} and saturated with nitrogen; E, (#A-254-P), against 1 p.p.m. Cu^{++} ; F, (#A-258-W), against 2 p.p.m. Ag^{++} ; G, (#A-258-P), against 1 p.p.m. Zn^{++} .

tion. Run A shows the flotation pattern at this time. Run B demonstrates the stabilizing action of serum dialyzate. Run D shows the characteristic result of extensive degradation while in C can be seen an intermediate stage of this process. Evidence that the degradation can be stopped but that it is not reversible under the conditions is given by comparing runs E and C.

In agreement with others, we find that the lipoprotein is quite stable if it is not concentrated, but simply stored in the whole serum at 1° . This is evidenced by the fact that the flotation patterns after 10 days are indistinguishable from those of the original sample. When an isolated lipoprotein fraction is stored in a sealed vial at 1° decomposition takes place, but at a very much slower rate than if dialyzed. In the dialysis experiments the rate and extent of degradation at a given lipoprotein concentration are, in general, proportional to the volume of external solution. Increasing the lipoprotein volume or decreasing the volume of solution can result in the lipoprotein becoming temporarily stabilized at some intermediate condition.

An idea of the rates with which different classes of lipoproteins decompose can be gained from Fig. 2. Fifty ml. of a freshly prepared lipoprotein solution containing lipoproteins of the S_f 5-30 range were set to dialyze against 400 ml. of buf-

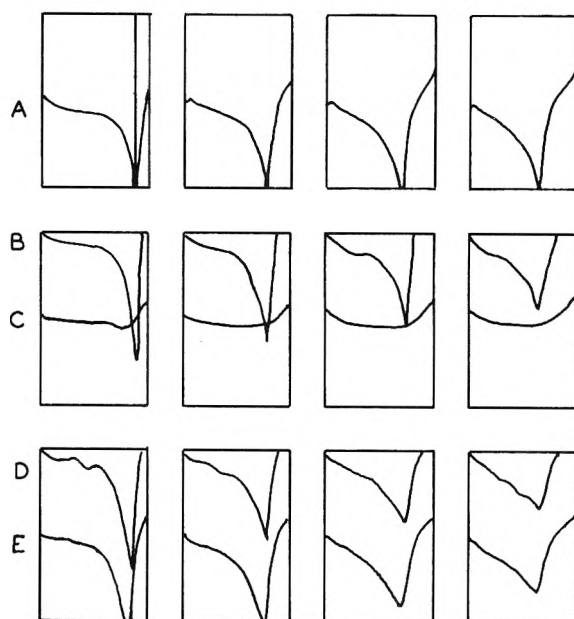


Fig. 4.—Flotation patterns showing the effects of traces of metal ions during dialysis against purified water. Dialysis time, 5 days in each case: A, (#A-8), original before dialysis; B, (#A-16-W), against metal-free water; C, (#A-16-P), against 1 p.p.m. Cu^{++} ; D, (#A-20-W), against 2 p.p.m. Au^{+++} ; E, (#A-20-P), against 3 p.p.m. Pt^{+++} .

fered saline. Samples were withdrawn at intervals for centrifugal analysis and the external salt solution was replaced daily. To conserve space only one exposure from each analytical run is reproduced. The exposures are comparable as to times and other conditions. The control sample dialyzed against saline solution for 24 hours before being placed in the serum-saline solution. Comparison with the original pattern shows that the saline initiated some degradation, but the serum-saline dialyzate stopped the process. It appears that the so-called normal lipoprotein, the S_f 5-9 class, shows effects of dialysis more quickly than does the S_f 10-30 class. The S_f 10-30 class releases much more lipid, as is manifested by the high turbidity which develops during the saline dialysis as well as by the large amount of lipid material which rises to the meniscus in the centrifuge cell.

It has been observed that the physical character of the layer that accumulates at the meniscus in an analytical determination is quite a sensitive test of stability. If the lipoprotein is not degraded, the floated material is easily dispersed upon shaking, and a repeated centrifuge run will duplicate the original run. When degradation has occurred, the lipid-like material is difficult to break up and flakes can be seen in the solution. Often this effect can be observed before a detectable change in S_f value has been produced.

Stabilization of Lipoprotein.—Human, dog, rat and bovine serum dialyzates were all found to protect rabbit lipoproteins. Working with bovine serum it was found that the stabilizing action was independent of pH in the range investigated, 5.5-9.0, whereas buffered saline solutions caused typical decomposition. Treatment of the dialyzate with Dowex-2 resin in the formate phase removed part of the stabilizing activity, which could then be

eluted with 2% sodium chloride solution. All the activity was held on an IR-120 resin column in the acid phase when the dialyzate was 0.1 *N* with respect to HCl. Again, activity could be eluted with salt solution.

The procedure developed for the extraction of a stabilizing fraction from the lyophilized bovine serum has been given.¹¹ At a level of 0.05% in water or saline this fraction would stabilize a lipoprotein sample in a dialysis. Heating the preparation to the carbonization point completely destroyed the activity. However, it was not destroyed by boiling in aqueous solution at pH 1.0 or 10. Extractions of solutions with chloroform and ether at pH's of 7.0 and 3.0 failed to remove any active material. Extraction of the dry powder in a Soxhlet

apparatus with methanol, ethanol or chloroform partially removed the activity in the form of a precipitate in the cold organic solvent.

Several complex mixtures were tested for stabilizing activity. Egg yolk, lemon juice, crude corn lecithin, saliva and serum albumin hydrolyzate proved active. Numerous known compounds were likewise tested, but in a quantitative manner. The results are summarized in Tables I and II. The second column in each table gives the initial concentration of the substance. The regular dialysis procedure was followed with concentrates of S₁ 5-9 lipoprotein. The centrifugal pattern after dialysis was compared to the original pattern and to the control pattern given by a portion dialyzed against saline solution. Substances listed in Table I did not show stabilizing activity save for the last three, which showed slight activity; substances in Table II stabilized, at various concentrations, to the degrees indicated in the last column.

Effects of Traces of Metal Ions.—Application of the dithizone method of analysis showed that the laboratory "distilled" water contained an average of 0.1 p.p.m. of heavy metals (total at neutral pH and based upon a copper standard solution). Approximately half of this total was copper. This water was used to prepare the solutions of reagent grade sodium chloride. At the usual salt concentration used (density of 1.063) these solutions were found to carry approximately 0.1 p.p.m. Cu⁺⁺. Therefore, in order to proceed it became necessary first to remove the metal contaminants by the steps described under Materials. In addition, especial care was taken to prevent contamination of the lipoprotein samples.

The results of the dialysis studies carried out with the purified materials were striking: freeing the external solution of metal ions susceptible to dithizone extraction rendered the lipoprotein stable in the absence of stabilizing substances. Figure 3 illustrates this. Here runs A, B and C refer, respectively, to an original concentrate of lipoprotein, a portion which had dialyzed 5 days against dilute serum, and a third portion which had dialyzed the same length of time against metal-free saline solution. The three sets of patterns are seen to be nearly identical. When cupric ion was added to purified saline at a level of 1.0 p.p.m. (1.5×10^{-5} *M*), extensive degradation occurred in 5 days as shown by the patterns of run E. This degradative effect of cupric ion at 1.0 p.p.m. was decreased by saturating the saline solution with nitrogen gas before dialysis as illustrated by run D. The ions Ag⁺, Al⁺⁺⁺, Fe⁺⁺, Fe⁺⁺⁺, Hg⁺⁺, Pb⁺⁺, Pt⁺⁺, Sn⁺⁺ and Zn⁺⁺, each tested at a concentration of 1.5×10^{-5} *M* in purified saline, were found to be inert, *i.e.*, to have no degradative effect. Runs F and G, for Ag⁺ and Zn⁺⁺, illustrate the uniform behavior.

When a lipoprotein fraction was dialyzed against metal-free water for 5 days and then analyzed, after adjusting the density to 1.063 with purified sodium chloride, the resulting patterns, run B of Fig. 4, were essentially the same as those of the original material, run A of Fig. 4. When Cu⁺⁺ at 1 p.p.m. was present in the pure water practically complete

TABLE I
SUBSTANCES WHICH FAILED TO STABILIZE ISOLATED
LIPOPROTEIN FRACTIONS

Compound	Concn., g./100 ml. saline
Choline	0.1
Inositol	.1
Glucuronic acid	.1
Glucose	.1
Fructose	.1
Sucrose	.1
Stachyose	.05
Sorbitol	.1
Dextran	.1
Potassium thiocyanate	.1
Sodium heparin	.3
Sodium alkyl sulfate	.1
Renex L-170	.1
Triton X-100	.1
Atlas G-7596 S	.1
Aerosol OT	.1
Desoxycholate	Saturated
Sphingomyelin mixture	0.1
Acetylglucosamine	.1
Protamine	.2
Glucosamine	.1
Glycine	.1

TABLE II
SUBSTANCES WHICH STABILIZED ISOLATED LIPOPROTEIN
FRACTIONS

Compound	Concn., g./100 ml. saline	Degree of stabilizing activity
Glucosaminic acid	0.02	Complete
	.005	Partial
Ascorbic acid	.02	Complete
	.005	Complete
	.001	Slight
Hesperidin	.002	Complete
	.0005	Partial
Rutin	.002	Complete
	.0005	Negligible
Amino acid mixture	.005	Complete
	.001	Slight
Serine	.05	Complete
Bovine serum albumin	.5	Complete
Versene	.1	Complete
<i>p</i> -Aminobenzoic acid	.1	Partial
Glucoscorbic acid	.01	Complete

degradation resulted in 5 days, as shown by C of Fig. 4. The ions Au^{+++} , Pt^{++} , Co^{++} , Cd^{++} and Ni^{++} were likewise tested in pure water at a concentration of $1.5 \times 10^{-6} M$. They were without effect as runs D and E, referring to Au^{+++} and Pt^{++} , illustrate.

The results of additional dialysis experiments pertaining to Cu^{++} are summarized in Table III, where the degradative effects at different concentrations in purified saline and in purified water are compared. The lengths of the dialysis periods are given and the relative degrees of degradation are estimated.

TABLE III
EFFECT OF THE CONCENTRATION OF CUPRIC ION ON
DEGRADATION OF LIPOPROTEIN

Concn., moles/l.	Water as dialyzate		Saline as dialyzate	
	Time, days	Degree	Time, days	Degree
1.5×10^{-5}	5	Complete	5	Nearly complete
1.5×10^{-6}	5	Partial	10	Partial
1.5×10^{-7}	5	Doubtful	10	Slight

Discussion

The decrease in the S_f values of lipoproteins upon dialysis is probably due to an increase in particle density and to a decrease in particle mass, both through loss from the complex of low-density material. This belief is supported by the appearance of a sedimentation peak, the decrease in area beneath the flotation peak, and by the lipid material which rapidly rises to the surface of a degraded lipoprotein solution. Oncley and Gurd⁵ have observed several changes, including a decreased S_f , in their β -lipoprotein preparations upon storage.

Cohn and co-workers⁸ suggested that the instability of β -lipoprotein might be due to the oxidation of the lipids of the complex by the peroxides formed in serum during the fractionation steps. Oncley and co-workers^{15,16} have found the changes in the lipoprotein on aging to be similar to the changes which occur in unsaturated fatty acids during lipoperoxide formation. He mentions¹⁵ that "attempts to prevent these changes by storing at 0° in the absence of light and oxygen and/or with various antioxidants present were not very successful, possibly due to the formation of peroxides during the preparation."

The stabilizing activity of ascorbic acid supports an oxidative mechanism since ascorbic acid is a good antioxidant and would be preferentially oxidized before the lipids.¹⁷ Pure ascorbic acid did not stabilize in our dialysis experiments above pH 8.0, therefore other antioxidants would be required in serum dialyzate or serum extract.

Of the numerous metal ions tested, at $1.5 \times 10^{-6} M$, cupric ion was unique in producing degradation. The behavior of human and rabbit β -lipoproteins were analogous in sensitivity to copper. At a level of $1.5 \times 10^{-6} M$, or 1.0 p.p.m.,

degradation was rapid and was practically complete in 5 days. At 0.1 p.p.m. the effect was clearly evident within 5 days. At 0.01 p.p.m., a 5-day dialysis was insufficient to give an unequivocal result. Also, in this lowest range our experiments were less reproducible probably due to traces of copper contamination and to the variability of different lipoprotein samples.

Oncley⁸ has pointed out that trace metals might serve to catalyze the oxidation of purified lipoproteins. Traces of copper ion are known to powerfully catalyze the oxidation of labile substances such as ascorbic acid¹⁸ and it well may play a similar role in the decomposition of the lipoproteins, perhaps involving the formation of lipoperoxides. We produced changes in lipoprotein concentrates similar to the changes resulting from dialysis by the addition of 1% hydrogen peroxide and a trace of Cu^{++} . When copper was not present or when it was complexed with Versene the peroxide did not seem to affect the lipoprotein. The observations were made after 2 hours at room temperature.

The findings suggest that compounds which are antioxidants or else form complexes with Cu^{++} should protect the lipoproteins against degradation. All of the substances listed in Table II, *i.e.*, active stabilizing agents, do possess one or the other of these properties.^{18,19} Since the properties of the active fraction extracted from serum were similar to those of several of the amino acids, it is believed that the fraction contained some of them. Dialysis experiments showed that this fraction would stabilize the lipoprotein in the presence of a large concentration of copper ion ($10^{-2} M$). The greater catalytic effect (Table III) of Cu^{++} at 1 p.p.m. in pure water than in purified sodium chloride solution may be due to the Cl^- in the latter which probably reduces the effective concentration of Cu^{++} by complex formation.²⁰ In comparing effects, the length of the dialysis step must be taken into account.

Trace metals in protein systems are recognized as being of great significance. As discussed by Cartwright,²¹ and others, copper plays an important role in human metabolism. Serum copper is bound to a high degree, partly as the copper protein, ceruloplasmin, an oxidase. However, little is known as to the nature of the bonds nor the mechanisms by which copper functions. Recently Lahey, *et al.*,²² showed that a good correlation existed between the levels of serum copper and β -globulins. Glavind and colleagues²³ have demonstrated the presence of lipoperoxides in atherosclerotic aortas of humans, but could not detect such material in normal aortas. One may be permitted to speculate that Cu^{++} has a role in the formation of atherosclerotic

(18) K. Giri and P. Rao, *Proc. Indian Acad. Sci.*, **24B**, 264 (1946).

(19) W. G. Clark and T. A. Geissman, *Trans. Third Conf. Biol. Antioxidants* (Macy Foundation), 92 (1948).

(20) S. Nakamura and K. Hemmi, *J. Agr. Chem. Soc. Japan*, **19**, 603 (1943).

(21) G. E. Cartwright, "Symposium on Copper Metabolism," Johns Hopkins Press, Baltimore, Md., 1950, pp. 274-315.

(15) J. L. Oncley and F. R. N. Gurd, "Blood Cells and Plasma Proteins," Section VII, Chapter 1, Academic Press, Inc., New York, N. Y., 1953.

(16) J. L. Oncley, "Rutgers Annual Conference on Protein Metabolism," Rutgers University, New Brunswick, N. J., Jan. 30, 1953.

(17) V. Calkins and H. Mattill, *J. Am. Chem. Soc.*, **66**, 239 (1944).

(22) M. E. Lahey, C. J. Gubler, D. M. Brown, E. I. Smith, B. V. Jager, G. E. Cartwright and M. M. Wintrobe, *J. Lab. Clin. Med.*, **41**, 829 (1953).

(23) J. Glavind and S. Hartmann, *Experientia*, **7**, 464 (1951).

lesions in the arteries at points where the blood has its maximum supply of oxygen. The role of copper could be essential either in the decomposition or in the peroxidation of the deposited lipid.

Acknowledgment.—It is a pleasure to express our appreciation to Dr. D. M. Cook of G. D. Searle and Company for supplying large amounts of lipemic rabbit serum.

DISCUSSION

HERBERT L. DAVIS.—Would your findings be compatible with a picture of continuing hydrolysis of the lipoproteins, a precipitation of metallic soaps resulting from the fatty acids produced, and the consequent increase in density as the lighter triglycerides are removed from the emulsion particles? The work with cupric ions is strongly reminiscent

of the tremendous effects these have on milk and cream, where an oxidation of the fats is induced, and huge losses result from a few cupric ions. Would not the dynamic interchange of the chylomicron tide tend to minimize in vivo such effects as you studied?

EDWIN O. DAVISSON.—If continuing hydrolysis of the lipoprotein is occurring during the degradation, it must be linked with the catalytic action of the cupric ion. Concomitantly, oxidation of the liquid presumably occurs since peroxidized products have been identified by Oncley by ultraviolet absorption. There are not enough metallic ions present to account for all the insoluble material released from the lipoprotein as insoluble soaps. Also, there is not a sufficient amount of triglyceride present in the normal β -lipoprotein to account for all the material lost from the lipoprotein.

If the lipid protein complex actually becomes lodged in the arterial wall, it would be very difficult to predict what effects these findings might have.

MONOLAYERS OF BOVINE PLASMA PROTEINS

BY J. L. SHERESHEFSKY AND MAURICE E. KING¹*Contribution from the Chemistry Department, Howard University, Washington, D. C.**Received March 5, 1954*

Surface pressure-area measurements were made on monolayers of bovine plasma protein fractions of albumin, β - and γ -globulins and fibrinogen. These measurements were made at different values of pH and salt concentration of substrates. Molecular weights calculated from an analog of Amagat's gas equation are lower than those obtained from osmotic pressure or sedimentation measurements, and vary with pH and salt concentration. The data on albumin were also fitted to an equation which includes a force constant, and the value of the constant is at a minimum at the isoelectric point and decreases with increasing cation concentration of the substrate. The molecular weights are higher than those obtained from the Amagat equation and are approximately a multiple of a Svedberg unit.

Introduction

In 1945 Bull² reported the results of his studies of monolayers of egg albumin and β -lactoglobulin on concentrated salt solutions using the Wilhelmy type film balance. By applying an analog of the Amagat gas equation in two dimensions to the low pressure regions of the force-area curves, values were obtained for the molecular weights which agreed with those found from osmotic pressure and sedimentation data. It was considered desirable to apply this method of molecular weight determination to crystalline bovine albumin which has become available and to study the effect of pH and salt concentration on molecular weights obtained in this manner.

Experimental

The film balance used in this study was of the type used in the Colloid Science Laboratory and as previously described.³

The bovine plasma protein fractions, albumin, β -globulin, γ -globulin and fibrinogen were obtained from the Armour Packing Company in the solid form. The albumin fraction was the crystalline material prepared by this company and used as a standard in osmotic pressure measurements.⁴

Stock solutions containing 1 mg./ml. of the fractions were prepared by dissolving albumin in water, the β -globulin and the γ -globulin in 2 M sodium chloride and the fibrinogen in 0.05 M sodium citrate. Spreading solutions⁵ were prepared by mixing two ml. of stock solution with propyl alcohol and distilled water to produce a total volume of ten ml. One ml. of 1.7 M sodium acetate was added to the globulin solutions to prevent coagulation.

The buffered substrates were prepared according to Green.⁶ The acetic acid-sodium acetate system was used for solutions of pH 4.4 and 4.8 and the monopotassium phosphate-dipotassium phosphate system for the higher values of pH.

For the study of the effect of salt concentration on the protein films, a stock solution was prepared containing 54.560 g. of sodium chloride, 7.760 g. of disodium phosphate and 1.162 g. of monopotassium phosphate per liter. This solution was one molar with respect to uni-univalent ion concentration and contained the phosphate buffers to maintain a pH of 7.3. Hypotonic, isotonic and hypertonic solutions were made by diluting, respectively, 100, 160 and 200 ml. of the stock solution to a volume of one liter.

The trough of the film balance was filled with the appropriate substrate until the liquid was one mm. above the edges. Surface contamination was removed by sweeping on both sides of the mica float until the zero position remained constant. The spreading solution was deposited on the sur-

face of the substrate with an Agla micrometer syringe and three to five minutes allowed for the film to spread. The area of the film was then slowly compressed and the corresponding surface pressure measured. At the end of each

TABLE I

SUMMARY OF CONSTANTS FOR ALBUMIN FROM COMPOSITE

Substrate	pH	FORCE-AREA CURVES		nRT , ergs	Mol. wt.
		Limiting area (ex- trap.), sq. m. per mg.	(slope of curve), sq. m. per mg.		
0.2 M	4.4	0.94	0.70	2.2×10^3	11,320
Acetate	4.8	1.00	.73	3.4×10^3	7,340
0.2 M	5.9	0.94	.75	2.2×10^3	11,320
Phos-	6.8	1.04	.60	3.6×10^3	6,920
phate	7.2	1.07	1.00	3.2×10^3	7,780
0.1 m NaCl	7.3	0.96	0.79	2.0×10^3	12,450
0.16 m NaCl	7.3	1.04	.36	3.4×10^3	7,340
0.2 m NaCl	7.3	1.00	.75	2.3×10^3	10,800

TABLE II

SUMMARY OF CONSTANTS FOR γ -GLOBULIN FROM COMPOSITE

Substrate	pH	FORCE-AREA CURVES		nRT , ergs	Mol. wt.
		Limiting area (ex- trap.), sq. m. per mg.	(slope of curve), sq. m. per mg.		
1.0 M Acetate	4.8	1.00	0.69	1.0×10^3	24,900
0.2 M	5.5	1.06	.63	1.6×10^3	15,600
Phos-	6.8	0.78	.57	2.4×10^3	10,380
phate	7.2	1.01	.89	4.0×10^3	6,240
0.1 m NaCl	7.3	0.60	.50	1.6×10^3	15,600
0.16 m NaCl	7.3	0.95	.70	2.0×10^3	12,450
0.2 m NaCl	7.3	0.61	.47	1.3×10^3	19,150

TABLE III

SUMMARY OF CONSTANTS FOR β -GLOBULIN FROM COMPOSITE

Substrate	pH	FORCE-AREA CURVES		nRT , ergs	Mol. wt.
		Limiting area (ex- trap.), sq. m. per mg.	(slope of curve), sq. m. per mg.		
1.0 M Acetate	4.8	0.55	0.40	0.8×10^3	31,150
0.2 M	5.5	0.76	.54	1.8×10^3	13,650
Phos-	6.8	1.17	.77	4.0×10^3	6,240
phate	7.2	1.07	.73	4.0×10^3	6,240
0.1 m NaCl	7.3	0.62	.46	1.4×10^3	17,800
0.16 m NaCl	7.3	0.62	.46	1.7×10^3	14,630
0.2 m NaCl	7.3	0.66	.56	1.3×10^3	19,150

TABLE IV

SUMMARY OF CONSTANTS FOR FIBRINOGEN FROM COMPOSITE

Substrate	pH	FORCE-AREA CURVES		nRT , ergs	Mol. wt.
		Limiting area (ex- trap.), sq. m. per mg.	(slope of curve), sq. m. per mg.		
1.0 M Acetate	4.8	0.95	0.77	1.2×10^3	20,750
0.2 M	5.5	0.95	.68	2.2×10^3	11,320
Phos-	6.8	1.18	.80	2.4×10^3	10,380
phate	7.2	1.08	.90	2.4×10^3	10,380
0.1 m NaCl	7.3	0.76	.56	2.6×10^3	9,600
0.16 m NaCl	7.3	0.93	.76	1.8×10^3	13,850
0.2 m NaCl	7.3	0.90	.57	1.9×10^3	13,100

(1) Based on a thesis submitted by Maurice E. King in partial fulfillment of the requirements for the Master's degree.

(2) H. B. Bull, *J. Am. Chem. Soc.*, **67**, 4 (1945).

(3) J. L. Shereshefsky and A. A. Wall, *ibid.*, **66**, 1072 (1944).

(4) G. Scatchard, A. Batchelder, A. Brown and M. Zosa, *ibid.*, **68**, 2610 (1946).

(5) S. Stalberg and T. Teorell, *Trans. Faraday Soc.*, **35**, 1413 (1939).

(6) A. A. Green, *J. Am. Chem. Soc.*, **55**, 2331 (1933).

run, the film was swept to the end of the trough and removed with a suction pipet. In each case at least three runs were made and composite surface pressure-area curves drawn from the data.

Results and Discussion

The type of force-area curves obtained for the four different protein fractions is shown in Fig. 1, and a typical $FA-F$ curve is shown in Fig. 2.

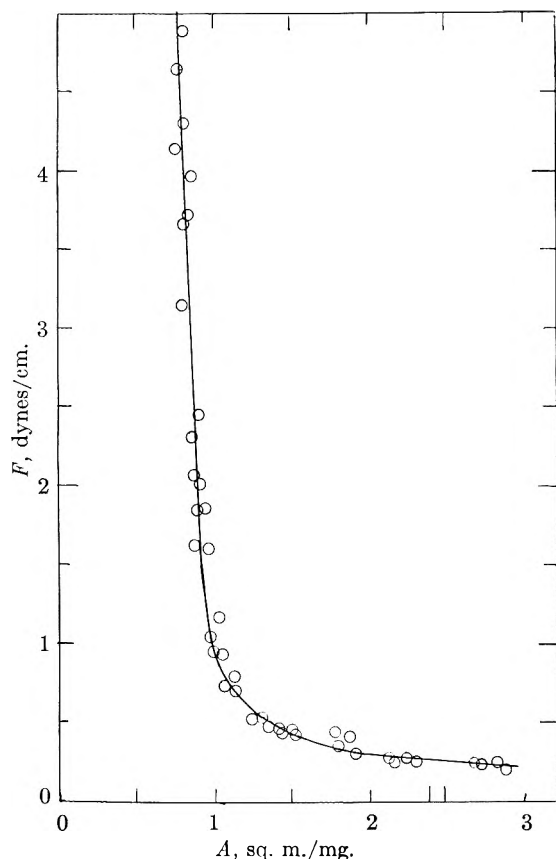


Fig. 1.—Typical curve of surface pressure vs. area for plasma proteins.

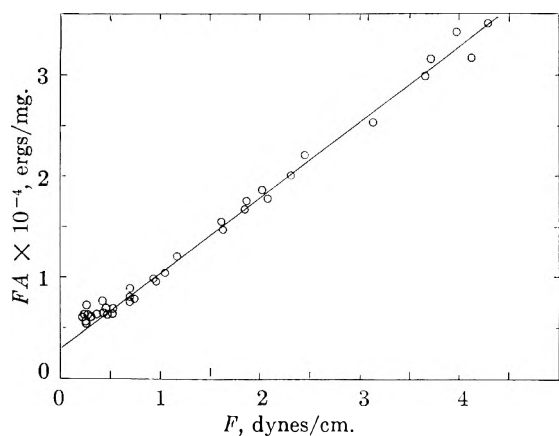


Fig. 2.—Typical curve of FA vs. F for plasma proteins.

In Tables I-IV are given the characteristic values for the various protein films on the several substrates of different pH and salt concentrations. In Tables V-VIII are given at several constant areas, the surface pressures at different pH .

The "limiting area" given in the third column of

TABLE V

SURFACE PRESSURES OF BOVINE ALBUMIN MONOLAYERS

Area, sq. m. per mg.	Surface pressure (dynes per cm.)					pH constant (7.3)		
	pH Variable					Concn.		
	4.4	4.8	5.9	6.8	7.2	0.10 m	0.16 m	0.20 m
1.0	0.76	0.94	0.85	1.44	1.40	0.77	1.22	0.70
1.2	.52	.61	.58	0.82	0.73	.57	0.77	.48
1.5	.35	.38	.38	.46	.50	.35	.52	.34
2.0	.24	.28	.28	.36	.40	.24	.42	.24

TABLE VI

SURFACE PRESSURES OF BOVINE γ -GLOBULIN MONOLAYERS

Area, sq. m. per mg.	Surface pressure (dynes per cm.)				pH constant (7.3)		
	pH Variable				Concn.		
	4.8	5.5	6.8	7.2	0.10 m	0.16 m	0.20 m
0.80	0.68	0.86	0.88	3.20	0.64	2.20	0.56
0.90	.46	.64	.65	1.50	.57	0.92	.49
1.00	.37	.53	.56	1.03	.55	.67	.25
1.20	.31	.44	.45	0.56	.52	.45	.22
1.50	.28	.37	.36	.51	.50	.32	.21
2.00	.25	.32	.33	.38	.50	.26	.20

TABLE VII

SURFACE PRESSURES OF BOVINE γ -GLOBULIN MONOLAYERS

Area, sq. m. per mg.	Surface pressure (dynes per cm.)				pH constant (7.3)		
	pH Variable				Concn.		
	4.8	5.5	6.8	7.2	0.10 m	0.16 m	0.20 m
0.80	0.42	0.79	5.00		3.00	0.49	0.47
1.00	.38	.55	1.60	1.70	0.58	.40	.34
1.50	.34	.37	0.56	0.60	.25	.24	.23
2.00	.31	.35	0.40	0.44	.22	.24	.20

TABLE VIII

SURFACE PRESSURES OF BOVINE FIBRINOGEN MONOLAYERS

Area, sq. m. per mg.	Surface pressure (dynes per cm.)				pH constant (7.3)		
	pH Variable				Concn.		
	4.8	5.5	6.8	7.2	0.10 m	0.16 m	0.20 m
0.90	1.00	1.05	3.60		0.75	0.76	0.54
1.00	0.50	0.77	2.35	4.00	.63	.60	.48
1.50	.34	.48	0.64	0.50	.52	.35	.33
2.00	.30	.40	0.42	0.32	.32	.26	.29

Tables I-IV was obtained by extrapolating the F - A curve to zero surface pressure, F .

The "area constant" given in the fourth column was obtained from the slope of FA - F curve, and in the fifth column are given the intercepts of this plot when extrapolated to zero pressure, F . The molecular weights given in the sixth column were calculated from the intercept by equating it to nRT , where n is the number of moles in 1 mg., R the gas constant and T the absolute temperature.

Bovine plasma albumin and fibrinogen show complete or nearly complete spreading under the various conditions of pH and salt concentration with the exception that fibrinogen is incompletely spread on 0.1 m sodium chloride with a pH of 7.3. The average limiting area for albumin is 1.0 ± 0.04 sq. m. per mg. and for fibrinogen, 0.96 ± 0.09 sq. m. per mg.

γ -Globulin and β -globulin do not spread as readily as albumin or fibrinogen. Their limiting area when spread completely is about 1 sq. m. per mg.

Tables V-VIII show that the surface pressure of the protein films is greatly affected by the hydrogen ion and cation concentration. The surface pressure increases with the pH of the substrate, but is

affected irregularly by the salt concentration. Thus albumin and γ -globulin show maximum surface pressures on an isotonic substrate, while for β -globulin and fibrinogen, the surface pressure decreases with salt concentration. Similarly, but to a lesser extent, the specific area of the protein fractions at constant surface pressure seem to increase with the pH of the substrate.

The calculation of the molecular weights was based on the two-dimensional analog of Amagat's gas equation

$$FA = nRT + B_0F$$

where B_0 is the difference in area per n moles of the real and ideal monolayer. The value of B_0 which is also taken as the area of the molecules in the monolayer is less than the "limiting area" obtained by extrapolation of the F - A curve.

This equation accounts for the osmotic factor and the area, but fails to account for the attractive forces. The values of the molecular weights obtained from this equation are low, and vary with the pH or salt concentration.

The low values of the molecular weights and their variation with pH and salt concentration, and the variation of the area with these factors at constant surface pressure, strongly support the presence of denaturation.⁷

The variation of the surface pressure with pH and salt concentration of the substrate is indicative of strong interaction forces between the protein molecules in their different ionized states. It was, therefore, of interest to try to apply to at least part of the present data an equation of state that includes a force constant. The equation

(7) E. Mishuck and F. Eirich, 12th International Congress of Pure and Applied Chemistry, September 10-13, 1951, Paper #31, "Surface Films of Synthetic Polypeptides."

$$(F - F^0)(A - A^0) = nRT$$

was thus applied to the data for albumin at several pH 's and salt concentrations and the constants F^0 , A^0 and the molecular weights evaluated. The A^0 values are higher than the B_0 values obtained from Amagat's equation, and approach closely the values of "the limiting areas." The F^0 values are positive and vary with pH ; at pH 4.8, the isoelectric point for bovine albumin, it is a minimum. At constant pH these values decrease with salt concentration. The molecular weights are higher than those obtained from the analog of Amagat's equation. At pH 4.8 the value is approximately 67,000, and at higher pH it varies from 20,000 to 23,000.

DISCUSSION

HERBERT L. DAVIS.—Are your results compatible with the suggestion that in these proteins charge and hydration play roles comparable to those known to apply in dispersion? Thus, for albumin, increasing pH results in increasing pressure and this might reflect increasing hydrate volume. Likewise, salt increases charge through a maximum as it is known to do in sol stability. If these be justified, it will be necessary to distinguish how solvation here gives increased volumes, and in the sedimentation findings of Dr. Ross gives decreased volumes.

F. M. FOWKES.—It appears that the authors have used the "Amagat" equation incorrectly for the determination of molecular weight. As discussed by N. K. Adam ("Physics and Chemistry of Surfaces"), the "Amagat" plot of FA vs. F for monolayers goes through a minimum when the film is in the liquid expanded state; a gaseous monolayer is obtained only at much lower film pressures and at larger values of FA . The intercept at $F = 0$ of FA for gaseous films may be several times the intercept obtained by extrapolation of FA from the high pressure portion of the plot as was done in this paper. The use of the Langmuir equation (*J. Chem. Phys.*, 1, 1 (1933)) for liquid expanded films ($(F - F^0)(A - A^0) = nRT$) appears novel for determination of molecular weight and may prove very useful.

MONOLAYERS OF SOME SYNTHETIC POLYMERS

BY JOSEPH PARKER¹ AND J. L. SHERESHEFSKY*Contribution from the Chemistry Department, Howard University, Washington, D. C.**Received March 5, 1964*

Monolayers of fractions of polystyrene, cellulose acetate and polymethyl methacrylate were studied by means of film balance measurements. Average molecular weight values were calculated from a two-dimensional equation of state and the measurements of surface pressure and area. The molecular weights obtained in this manner were found to be in good agreement with known values of molecular weight of the samples of polystyrene and polymethyl methacrylate, the monolayers of which were in an expanded state. Evidence is presented to show that the molecular weights of the rather condensed and incompletely spread monolayers of cellulose acetate can be determined by the monolayer methods if the molecular weight is sufficiently high to permit high energy molecular chain vibrations and if the film is sufficiently compressed to permit chain vibrations to contribute to the total surface pressure.

Introduction

The use of monolayer studies for the elucidation of the structure of complex molecules has received considerable attention in recent years.^{2,3} Only a limited amount of this work, however, has been applied to synthetic high polymers. Although the general composition and structure of these polymers have been determined by other methods, monolayer studies may provide a useful supplementary means of obtaining basic properties of a polymer sample such as molecular size, relative cohesive forces and average molecular weight.

The equation of state for ideal gaseous films which has been derived⁴ from essentially the same kinetic theory considerations governing the derivation of the three-dimensional ideal gas law is

$$FA = nRT$$

where F is surface pressure in dynes per centimeter, A is the film area in square centimeters, n is the number of moles of film spread, R is the gas constant in ergs per mole per °K. and T is the absolute temperature in °K. Although the molecular weight obtained from this equation is a number average molecular weight, these values may be directly compared with other average molecular weights when measurements are made on fractionated samples. In analogy to the molecular volume correction applied in modified three-dimension equations of state, a corrected two-dimensional equation may be written⁵

$$F(A - b) = nRT$$

where b is a correction for the area occupied by the molecules and is the slope of a plot of FA versus F . The intercept (at $F = 0$) of this plot is the value of nRT from which the value of average molecular weight may be calculated.

Extrapolation of the straight-line portion of a plot of surface pressure versus area to zero pressure gives an area value which may be interpreted as a measure of the area occupied by the monolayer, and is referred to as the "limiting area."

In addition, cohesive forces can be estimated in relative terms from the shape of this plot. A pres-

sure-area curve which approaches the area axis asymptotically indicates an expanded film while an abrupt increase in the pressure as the area is decreased indicates a condensed film.

The present work was directed toward an evaluation of average molecular sizes and weights and of relative cohesive forces by measurements made on monolayers of fractions of polystyrene, cellulose acetate and polymethyl methacrylate.

Experimental

Materials.—The polystyrene fraction was obtained from the Dow Chemical Company. The stated average molecular weight of the sample was 206,000 and it was designated as fraction 5, sample #56380M. The spreading solution was made up with redistilled C.p. benzene.

All three of the cellulose acetate fractions, 3, 4 and 6 were obtained from the Eastman Kodak Company. Spreading solutions were made up in redistilled C.p. acetone.

The samples of polymethyl methacrylate were obtained by solvent fractionation⁶ of a sample of du Pont "fine crystal" Lucite. Toluene and *n*-hexane were used as the fractionating solvent and non-solvent, respectively. Spreading solutions of the three selected fractions, MH 1.3, MH 0.2 and ML 0.6 were made with redistilled C.p. benzene. The average molecular weights of these fractions were determined by a solution viscosity method.⁷

Apparatus.—Calibrated Ostwald-type viscometers were used in a water-bath kept at $30.6 \pm 0.05^\circ$ for the solution viscosity measurements. The constants for the viscosity-molecular weight relation were taken from a paper by J. H. Baxendale, *et al.*,⁸ who compared values of intrinsic viscosity with molecular weights determined by osmotic pressure measurements for solutions of polymethyl methacrylate fractions.

The film balance used is similar to the balance system used by Wilhelmy⁹ and Harkins and Anderson.¹⁰ An ordinary Ainsworth analytical balance, capable of measurement to 0.1 mg. with a rider, was positioned on a box serving as an air thermostat tray enclosure, so that a rod suspended from the left balance arm and passing through holes in the balance floor and the enclosure top was centered over the tray. The tray enclosure box rested on three adjustable screw feet and its front consisted of a removable glass panel. A Pyrex dish with its top edges ground flat and coated with paraffin served as the tray. The barriers for sweeping the substrate surface and compressing the films were also of Pyrex and paraffin-coated. The barrier-moving device consisted of a tray-supporting framework which also held a calibrated screw thread upon which rode the barrier-carrying fingers. The area-measuring system consisted of a scale placed along the side of the tray, a revolution counter geared to the screw shaft, and a pointer and protractor scale permitting the measurement of fractions of a revolution. A small mirror attached to the end of the central

(1) Based on the thesis of Joseph Parker presented to the Graduate School of Howard University in partial fulfillment of the requirements for the M.S. degree.

(2) N. K. Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, London, 1941, pp. 79-92.

(3) (a) S. Stallberg and E. Stenhagen, *J. Biol. Chem.*, **143**, 171 (1942); (b) H. B. Bull, *ibid.*, **185**, 27 (1950).

(4) J. S. Mitchell, *Trans. Faraday Soc.*, **31**, 980 (1935).

(5) Reference 2, p. 120.

(6) L. H. Cragg and H. Hammerschlag, *Chem. Revs.*, **39**, 79 (1946).

(7) A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

(8) J. H. Baxendale, S. Bywaters and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).

(9) L. Wilhelmy, *Ann. Physik*, **5**, 48 (1899).

(10) W. D. Harkins and R. J. Meyers, *J. Chem. Phys.*, **4**, 716 (1936).

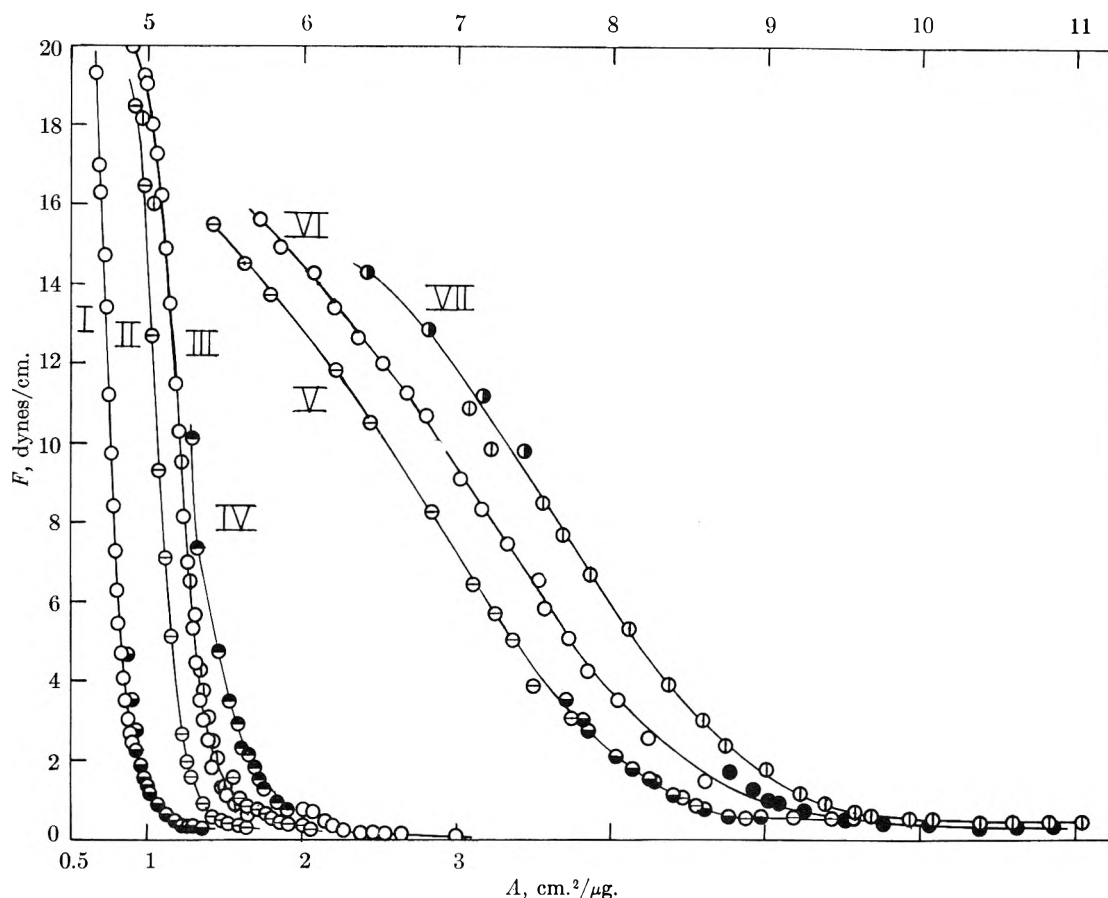


Fig. 1.—Surface pressure *versus* area plots: I, cellulose acetate fraction 6; II, cellulose acetate fraction 3; III, cellulose acetate fraction 4; IV, polystyrene fraction 5; V, polymethyl methacrylate MH 0.2; VI, polymethyl methacrylate MH 1.3; and VII, polymethyl methacrylate ML 0.6. The lower scale refers to plots I, II, III and IV and the upper scale refers to plots V, VI and VII

balance knife edge was used in conjunction with a lamp and scale arrangement to amplify movements of the balance arm. Rectangular microscope cover glasses were used as the pressure-measuring slides. A slide holding arrangement was constructed of vinyl strips and iron wire clips. On top of the holder was a short vertical length of aluminum tubing containing a set-screw permitting easy attachment to or removal from the rod suspended from the balance arm. An "Agl" calibrated micrometer syringe, obtained from Burroughs Wellcome, Inc., was used to spread the film on the substrate. The substrate was a 0.01 *N* HCl solution.

Procedure.—The balance system was brought to zero deflection with the suspended slides partly immersed in the clean surface of freshly made substrate by adjusting the weights on the right hand balance pan and the rider. The sum of the rider and pan weights was recorded as R_w . The film solution was then spread on the substrate surface enclosed by the sides of the tray and a fixed and a movable barrier. The weight of the film spread was computed from the micrometer syringe reading. The balance system was reset to zero deflection and the pan weight recorded as R_f . The film was then compressed by the movable barrier and values of R_f and film dimensions were recorded at appropriate intervals. The surface pressure, F , was calculated from a relation derived from a balance of forces acting on the slides. This relation is

$$F = \frac{g(R_w - R_f)}{L \cos \theta}$$

in which g is the gravitational constant in cm. per sec.², θ is surface to slide contact angle, and L is the length, in centimeters, of the intersection line of the perpendicular planes of the monolayer and the slides. The area, A , in square cm. was calculated from the film dimensions and plots of FA *versus* F and F *versus* A were made.

Results and Discussion

Polystyrene.—The pressure *versus* area curves (Fig. 1) indicate a film in an expanded state. The limiting area, found by extrapolating this plot to zero pressure, was about 6000 square Å. per molecule, based on the given molecular weight. This is a rather small value for molecules containing an average of 2000 styrene units each. A stretched out molecule would occupy about 36,000 square Å., according to molecular model measurements. It has been shown that polystyrene and other synthetic macromolecules in solution may take on various shapes depending upon the nature of the solvent and the molecular weight.¹¹ High molecular weights and poor solvents favor the coiled form. The plane projection of a sphere 80 Å. in diameter is inscribed by a square 6000 square Å. in area. The thickness of the film at the limiting area calculated from the bulk density of 1.06 g. per cc. and the weight of the film, is 88 Å. Thus, if a spherical or nearly spherical molecule is assumed, the film is one molecule thick. A randomly coiled, flexible molecule could also satisfy the observed area restrictions if the molecules are randomly matted to form a collapse-resistant film several molecules thick. This type of film might produce the

(11) C. E. H. Bawn, "The Chemistry of High Polymers," Interscience Publishers Inc., New York, N. Y., 1948, pp. 140-178.

observed molecular weight values through the chain vibrations of the meshed molecules.

At the lower pressures the polystyrene film appeared to be collapsing under compression since the pressure deflections drift back to zero in as little as three minutes. At higher pressures the deflections were more stable. It was observed that the spreading of the polystyrene films required as long as 20 seconds as compared with about 10 seconds for cellulose acetate films and less than 0.5 second for films of polymethyl methacrylate.

Plots of FA versus F were linear and gave values of nRT (at $F = 0$) of 16 and 21 ergs for runs A and B, respectively. The corresponding molecular weights are 238,000 for run A and 246,000 for run B. The unstable low pressure regions of the plot were not used in the extrapolation to zero pressure. The agreement between the experimental and the known value (206,000) for average molecular weight makes the assumption of spherical and unmeshed molecules seem more plausible than the random mesh possibility since the former is in greater harmony with the assumptions upon which the equations of state are based.

Cellulose Acetate.—The form of the pressure-area curves (Fig. 1) indicates that the cellulose acetate films are in a relatively condensed state. The results given below represent an average of the results of duplicate experimental runs. The areas, in square Å. per molecule, for fractions 3, 4 and 6 are 1300, 990 and 430, respectively, based on the given molecular weight values of 57,000, 45,000 and 29,000 for these three fractions. The corresponding film thicknesses at the limiting area, calculated from the bulk density of 1.3 g. per cc., are 53, 58 and 83 Å. The limiting area values are from $1/7$ to $1/10$ of the area required by molecular models for a completely spread film. It seems likely that the low molecular weights and the presence of polar groups along the chain of the cellulose acetate molecules would favor crystallite formation in monolayers of this material. One form of polymer crystallite consists of a bundle of molecular chains, well aligned near the center of the bundle, but since the center of the bundle is not necessarily the center of a constituent chain, there may be long chain parts, free, in some degree, to vibrate at the ends of the bundle.

Extrapolation of FA versus F plots in the pressure region up to 2 dynes/cm. gives average molecular weight values of 162,000, 142,000 and 179,000 for fractions 3, 4 and 6, respectively. Similar extrapolation in the pressure region from 2 to 6 dynes/cm. gives molecular weights of 56,300, 56,900 and 86,800. Except for the results for fraction 6 these molecular weights are in fair agreement with the given values. Although fractions 3 and 4 are probably incompletely spread, the thinner films and disproportionately larger areas per molecule show that more spreading has taken place in these fractions than in fraction 6.

Some justification for disregarding the low pressure regions in these molecular weight determinations may be found in the fact that if, at the larger areas, the film consists of isolated crystallites moving freely on the substrate surface the low pressure

region will give rise to erroneously high molecular weights because the vibrations of the individual molecules cannot contribute to the total surface pressure. But, as these groups are brought in contact by compression the effect of individual molecules can be measured by their vibrational contributions to the total pressure.

Adam and Harding¹² investigated films of cellulose acetate and found definite indications of incomplete spreading which is in agreement with our observations. At the same time, however, the pressure versus area curve approached the area axis asymptotically, which implied an expanded state and a uniformly spread film. To reconcile this apparent contradiction, Adam, following a suggestion by Haller¹³ that the vibratory motions of long chain molecules should be taken into account in the osmotic pressure theory, proposed the possibility that the vibrating molecules in the isolated groups could contribute to the pressure at large areas. Zoicher and Stiebel,¹⁴ discounting minor discontinuities as being due to impurities, reported that their cellulose acetate films appeared fully spread under dark ground illumination.

These diverse results can be accounted for by considering first, that the film "islands" or condensed groups are numerous and quite small, consisting of perhaps only 100 or so molecules, second, that the translatory motions of these molecular groups could account for the small pressures and large molecular weights measured at the large areas, and third, that at intermediate areas the transition from the isolated group condition to the closely packed condition is smoothed out, in the pressure-area curves, by the contributory effects of molecular chain vibrations. It is in this transition region that the pressure measurement counts individual molecules rather than molecular groups. This possibly explains the improvement of the agreement between the experimental and the given values when the intermediate, rather than the low pressure, region is used in the extrapolation of the FA versus F curve to zero pressure. It is conceivable that the vibrational energy of long chain molecules in some two-dimensional films could correspond to the translational energy of gaseous films of monomeric molecules.

The fact that the molecular weight of fraction 6 is high even when determined from measurements made in the intermediate pressure region may be explained by the reasonable assumption that the number of vibrational modes of a molecule in a crystallite decreases with decreasing molecular chain length.

Polymethyl Methacrylate.—The wide sweep and gradual approach to the area axis of the pressure-area curves of polymethyl methacrylate indicated that these films were in a considerably expanded state. The results given below represent an average of the results of duplicate runs.

The limiting areas in square Å. per monomer unit, calculated from the extrapolated area of the pressure-area curve and the viscosity average

(12) J. B. Harding and N. K. Adam, *Trans. Faraday Soc.*, **29**, 837 (1933).

(13) Von W. Haller, *Kolloid Z.*, **49**, 74 (1929).

(14) H. Zoicher and F. Stiebel, *Z. physik. Chem.*, **147A**, 401 (1930).

molecular weights (Table I), are 27.4, 23.6 and 27.3 for fractions MH 1.3, MH 0.2 and ML 0.6, respectively. These values are in agreement with molecular model measurements. The limiting area and the bulk density of 1.18 g. per cc. were used to calculate film thicknesses. The thickness values for all three fractions are between 9 and 10 Å. This range of values could account for the thickness of one molecule. The magnitudes and the close agreement between different fractions, of the area of a monomer unit and of the film thickness lead to the conclusion that the polymethyl methacrylate film was probably completely spread to a layer one molecule thick with the non-polar portions of the poly-

mer chain partly lifted from the surface at the limiting area.

Molecular weights obtained from *FA versus F* curves are 72,500 for MH 1.3, 32,000 for MH 0.2 and 33,200 for ML 0.6. These values agree very well with average molecular weights determined by the solution viscosity method which were 76,000 for MH 1.3, 32,600 for MH 0.2 and 30,500 for ML 0.6.

A summary of the molecular weight results for the samples of polystyrene, cellulose acetate and polymethyl methacrylate is shown in Table I.

Acknowledgments.—The authors wish to express their appreciation to the U. S. Naval Ordnance Laboratory for permitting the use of its facilities for this investigation.

TABLE I

SUMMARY OF MOLECULAR WEIGHT RESULTS

Material	Fraction no.	Mol. wt. from <i>FA vs. F</i> plots		Mol. wt. given or obtained by sol. viscosity
		Low pressure regions	Intermediate pressure region	
Polystyrene	5	242,000	...	206,000
Cellulose acetate	3	162,000	56,300	57,000
	4	142,000	53,900	45,000
	6	179,000	86,800	29,000
Polymethyl methacrylate	MH 1.3	72,500	...	76,900
	MH 0.2	35,700	...	32,600
	ML 0.6	33,200	...	30,500

DISCUSSION

F. M. FOWKES.—The authors do not mention the principal studies in this subject, by D. J. Crisp at Cambridge (*J. Colloid Sci.*, 1947-1948). In Crisp's studies several high polymers were spread as monolayers 5-10 Å. in thickness, rather than the 80 Å. reported here. Dr. M. J. Schick of the Shell Development Laboratories in Emeryville also has spread many polymers to form true monolayers 5-10 Å. thick, and where his studies overlapped Crisp's the agreement was excellent. Therefore it appears that in the above work, only 10-30% of the polymer was spread on the water as a monolayer. Other spreading solvents should have been used.

SIZE DISTRIBUTION ANALYSIS IN PLASMA EXTENDER SYSTEMS. II. DEXTRAN¹

BY J. W. WILLIAMS AND WINIFRED M. SAUNDERS

Laboratory of Physical Chemistry, University of Wisconsin, Madison, Wisconsin

Received March 2, 1954

The sedimentation methods are particularly useful in the study of replacement fluids because they provide the only satisfactory means by which a direct and unambiguous analysis can be made of the macromolecular solute size distributions. The two sedimentation methods, those in which sedimentation rates are involved and those in which the sedimentation equilibrium condition is studied, can be combined to give a satisfactory analysis. In this report a new approach to this combination is given and size distribution data are presented for a representative dextran. Size distribution information is here of value because one can learn from it about the retention times of the smaller molecules and about the need for additional observations aimed at giving data about the final clearance of the larger molecules from the system.

Part I. Introduction

It is often suggested that the utility of any plasma extender depends among other things upon its molecular weight and form. At least in the case of the more common "substitutes" these solutions are characterized by polydispersity of solute so that the use of the term "molecular weight" in connection with them is highly ambiguous. Since there appears to be a close relationship between molecular "size" and retention time in the system we have given much attention to sedimentation analyses, methods which are unique in giving information about the actual size distributions. In the extension of the sedimentation methods to the study of the plasma extenders, there were several problems to be solved. The solution of some of these problems and the use of the analyses to give size distribution data for a representative dextran system form the subject of this article.

The principal complication by way of molecular weight determination lies in the fact that different methods of observation lead to different types of average molecular weight, thus preventing a direct comparison of measurements on the same sample by different methods. We have sought to solve the problem whereby the actual *distribution* of molecular weights may be found by experiment. With success in this effort it follows that any of the average values could be then computed from the distribution curves.

When a solution of macromolecules is subjected to centrifugal fields of intermediate strength an equilibrium distribution of the solute may be achieved to give a considerable amount of detail concerning the molecular weight distribution. There has taken place in effect a physical (as contrasted with chemical) fractionation of the material, and the optical system of the low-power ultracentrifuge makes it possible to "count" or "weigh" the amount of the material in the several size classes. Actually, it is a difficult and time-consuming experiment but it will be shown that it is a useful one in that it can be used for the calibration of sedimentation constant distributions to give quite reliable information about both molecular size distribution and molecular form in the plasma extender solution.

In the high-velocity ultracentrifuge sedimenta-

tion velocities are deduced from the motion of the "sedimentation boundaries" which are recorded photographically in the experiment. One can go further than this and remark that the shape of the boundary and its variation with time and distance in the cell gives information about the distribution of sedimentation coefficients. Since the sedimentation velocity experiment is the much more common and practical one, it is perhaps not out of place here to give some descriptive statements about two approaches to the problem of finding a distribution function for these coefficients. (The word "coefficient" rather than "constant" is used because the "observed" sedimentation rate is dependent on concentration; the sedimentation constant is obtained by an extrapolation to zero concentration.) The basic notion is that sedimentation rate increases as a single-valued, increasing function of the molecular weight. Thus, if the sedimentation diagrams which are observed at some finite concentrations can be extrapolated to infinite dilution it will give a true distribution of sedimentation constants and reflect to a considerable degree the distribution of molecular weights within the sample. This method is at an appreciable advantage in resolving power as compared to the sedimentation equilibrium method.

Method 1. (Jullander, Gralén, Kinell, Rånby).—In this analysis²⁻⁴ the width of the usual sedimentation curve, defined as the ratio of area to height, is used to measure the heterogeneity. If this width is plotted as a function of the position of the peak of the sedimentation curve it is found to vary in a linear fashion with this distance. Since the slope of this curve varies regularly with total concentration, the value of the slope at infinite dilution can be found, and it turns out to be a useful relative measure of the heterogeneity. The limiting values of this slope, when obtained for polymer fractions of known molecular weight, provide a means for the calibration of the distributions of sedimentation constant in terms of molecular weight.

Method 2. (Baldwin-Williams).—The study of boundary spreading in the velocity ultracentrifuge was begun by Signer and Gross⁵ but their analysis of the problem was valid only for systems in which diffusion is negligible and in which no variation of

(1) This investigation has been carried out under contract between the Office of the Surgeon General, Department of the Army, and the University of Wisconsin (DA-49-007-MD-114). Released for publication on October 15, 1953.

(2) I. Jullander, *Arkiv Kemi Mineral Geol.*, **21A**, No. 8, 1 (1945).

(3) N. Gralén, Dissertation, Uppsala, 1944.

(4) P. O. Kinell and B. G. Rånby, *Adv. Colloid Sci.*, **III**, 161 (1950).

(5) R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 726 (1934).

sedimentation rate with concentration is present. With these two limitations it became a simple problem to transform the observed boundary curve into a sedimentation constant distribution. Baldwin and Williams⁶ presented an analysis of the situation for the case when diffusion must be considered, but also when concentration dependence of sedimentation coefficient is small and negligible. More recently and independently of one another they have broadened the treatment to include situations in which there is an appreciable concentration dependence of sedimentation coefficient. The analytical solution of the problem by Baldwin⁷ is described in a recent article; our own graphical method is illustrated in this report. The two methods should and do give the same result.

Having provided improved methods of evaluation of sedimentation equilibrium and sedimentation velocity experiments some more exact statements about them are given in the following two sections. In a fourth and final section we have set for ourselves the task of showing how the results from the two basically different experiments may be construed to give useful molecular weight distribution data. For a given macromolecular system, in this instance the plasma extender dextran, the calibration curve, sedimentation constant in terms of molecular weight, may be used in connection with the relatively rapid sedimentation velocity experiments to give the distribution. As a by-product of the actual relationship the general molecular form of the dextran molecules is indicated—this in spite of the fact that there is known to exist a certain degree of chain-branching.

Part II. Sedimentation Equilibrium

Many derivations are available for the basic equations which are used in the evaluation of sedimentation equilibrium experiments.⁸⁻¹⁰ For a homogeneous system the expression for the molecular weight of the solute is

$$M = \frac{RT}{(1 - \bar{V}\rho)\omega^2} \frac{(dc_x/dx)}{x \cdot c_x} = \frac{1}{2A} \times \frac{(dc_x/dx)}{c_x}$$

or in exponential form, $c = c_0 \exp(\omega^2 x^2 M_e / 2RT)$. In these equations, the symbol c_x means the concentration at the point x in the cell, M_e (the effective molecular weight) is $M(1 - \bar{V}\rho)$, $\frac{1}{2A} = \frac{RT}{(1 - \bar{V}\rho)\omega^2}$, ρ is the density of the solution; and \bar{V} is the partial specific volume of the solute.

The data required for the computation of the molecular weight are the variation of concentration with distance in the cell, or if, as in the usual form of the Svedberg apparatus, the Lamm scale method is used, the variation of scale line displacement with distance along the static column. It is a characteristic of the scale method that it is necessary to perform an integration to convert the line displacement

(Z) vs. distance (x) curve over to a concentration vs. distance curve if the formulas we have presented are to be used directly. However, the molecular weight result may be obtained by using another common form

$$\bar{M} = \frac{2RT \ln Z_2 x_1 / Z_1 x_2}{(1 - \bar{V}\rho)\omega^2(x_2^2 - x_1^2)}$$

If the system contains a macromolecular solute which is heterogeneous with respect to molecular weight, it can be assumed that each molecular species sets up its own equilibrium, independently of the others. In this event we may write the following equations

$$c = \sum_i c_{0,i} \exp(\omega^2 x^2 M_{e,i} / 2RT)$$

$$\sum_i c_i M_i = \frac{RT}{\omega^2 x (1 - \bar{V}\rho)} \sum_i dc_i / dx$$

$$\text{and } M_{wx} = \frac{\sum c_{ix} M_{ix}}{\sum c_{ix}} = \frac{RT \, dc_x / dx}{c_x \omega^2 x (1 - \bar{V}\rho)} = \frac{dc_x}{dx} \times \frac{1}{2Ax c_x}$$

In order to obtain the weight average value of the molecular weight, M_w , for all the material in the cell, the summation must be carried out over the entire cell depth, a to b . In a sector-shaped cell the expression for M_w becomes

$$M_w = \frac{\int_a^b M_{wx} c_x dx}{\int_a^b c_x dx}$$

By using other equations, the number average and "Z"-average molecular weights may be obtained from the same sedimentation equilibrium experiment.

To this point it has been assumed that the macromolecular solutions are "ideal" in behavior. Actually this is perhaps never the situation, and equations descriptive of the modified sedimentation equilibrium are used in the evaluation of the experiment. Such equations have been developed by Schulz¹¹ and by Wales, *et al.*¹² In brief, the argument may be put in a simple but antiquated form. In concentration dependent systems, the osmotic pressure is given by an expression of the form

$$\pi = \frac{RT}{M} c + bc^2$$

Now, if the back diffusion in sedimentation equilibrium is a result of osmotic pressure differences along the column, the steady state is described by the equation

$$\omega^2 x (1 - \bar{V}\rho) c_x dx = \frac{\partial \pi}{\partial x} dx$$

These expressions can be combined to give the result

$$M_{wx} = \frac{dc_x / dx}{c_x (2Ax - B dc) / dx}$$

where

$$B = 2b / RT$$

Such an approach is open to the criticism that the value of the non-ideality coefficient B , deter-

(6) R. L. Baldwin and J. W. Williams, *J. Am. Chem. Soc.*, **72**, 4325 (1950); **74**, 1542 (1952).

(7) R. L. Baldwin, *ibid.*, **76**, 402 (1954).

(8) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Clarendon Press, Oxford, 1940.

(9) R. J. Goldberg, *THIS JOURNAL*, **57**, 194 (1953).

(10) J. W. Williams, *J. Polymer Sci.*, **12**, 351 (1954).

(11) G. V. Schulz, *Z. physik. Chem.*, **A193**, 168 (1944).

(12) M. Wales, M. M. Bender, J. W. Williams and R. H. Ewart, *J. Chem. Phys.*, **14**, 353 (1946); M. Wales, *THIS JOURNAL*, **52**, 235 (1948).

mined in this way, might not be quite proper when used with the sedimentation equilibrium experiment. It can be shown theoretically that

$$\left(\frac{dM_w^{\text{ideal}}}{dc_0}\right)_0 = -BM_w^2$$

In this case, then, we may expect the following relationship to hold

$$\frac{1}{M_{wx}^{\text{ideal}}} = \frac{1}{M_{wx}} + Bc_x$$

or, to a good approximation

$$\frac{1}{M_w^{\text{ideal}}} = \frac{1}{M_w} - Bc_0$$

By M_w^{ideal} is meant the weight average molecular weight obtained at some finite experimental condition, which would have been obtained if the ideal limiting expression for M_w had been used in the calculation. Hence on plotting $1/M_w^{\text{ideal}}$ as a function of concentration one obtains a straight line with slope B , and an intercept which has the value of the reciprocal of the true weight-average molecular weight. Actually, the values of the non-ideality factor B as obtained independently of the ultracentrifuge and in self-contained ultracentrifuge experiments agree very well, as they should.

Having corrected for the non-ideality in a given system the question remains as to what can be done by way of an actual description of the heterogeneity. The simplest means of detection of heterogeneity is found in a comparison of the several average molecular weights M_n , M_w , M_z , etc. If the system were homogeneous, all of the averages would have the same value, and as a qualitative statement, the greater the spread of the average molecular weights, the greater the heterogeneity.

A method which has been quite generally employed is to fit an assumed parametric function to the observed average molecular weights. Several functions have been useful: (a) the Lansing and Kraemer function¹³; (b) the Schulz function¹⁴; (c) the Wales, *et al.*, series of Laguerre polynomi-

als.¹⁵ The necessary computations are more tedious than difficult because there are reasonably simple rules by which the numerical integrations required for the calculations can be carried out. Simpson's rule reduces to quite simple form provided equal spacing along the column is used. At the meniscus there will usually be an odd interval which leads to some difficulty. Otherwise the procedures are quite satisfactory and lead to useful results.

As another alternative, one could solve an integral equation involving the concentration of solute as a function of the distance from the center of rotation. This procedure has been described by Rinde.¹⁶

For practical application to dextran samples we have elected to use the Lansing-Kraemer logarithmic number distribution function. Here

$$f(M)dM = dW = \frac{W}{M_n\beta\sqrt{\pi}} \exp\left(-\frac{1}{\beta} \ln \frac{M}{M_0}\right)^2 dM$$

where

- dW = wt. of material having mol. wt. between M and $M + dM$
- W = total wt. of material, usually normalized to one
- M_0 = mol. wt. at the maximum value of dW/dM
- M_n = no. av. mol. wt.
- β = non-uniformity coefficient

A number of sedimentation equilibrium experiments with dextrans have been carried out. For example, we have studied in this Laboratory the size distributions for representative dextrans from England, Sweden and the United States. For purposes of illustration of the method we present here data for the Commercial Solvents Dextran #84688A. For this particular sample the following characteristic constants are found from the experiments: $M_0 = 33,600$, $M_n = 42,000$, $M_w = 65,000$, $\beta = 0.94$. It is of course a fractionated material.

The actual molecular weight differential distribution curve for this particular sample of dextran appears as Fig. 1, where

$$f(M) = \frac{dW}{dM} = \frac{1}{42,000 \times 0.94 \times 1.77} \exp\left(-\frac{1}{0.94} \ln \frac{M}{33,600}\right)^2$$

Some actual data from which both differential and integral distribution curves were prepared have been collected to form Table I.

Part III. Sedimentation Velocity

In sedimentation experiments where centrifugal fields of high intensity are employed, the process of sedimentation is very rapid compared to that of diffusion, and we observe a rate of fall in the force field. The macromolecules, starting from rest, are accelerated until a steady state of velocity is attained. The centrifugal force is then balanced by the frictional resistance of the medium and the velocity is

$$\frac{dx}{dt} = \frac{\omega^2 x M (1 - \bar{V}\rho)}{f} = \frac{\omega^2 x M (1 - \bar{V}\rho) D}{RT}$$

In this equation x represents the position of the boundary in the cell as a function of time, t , ω is the

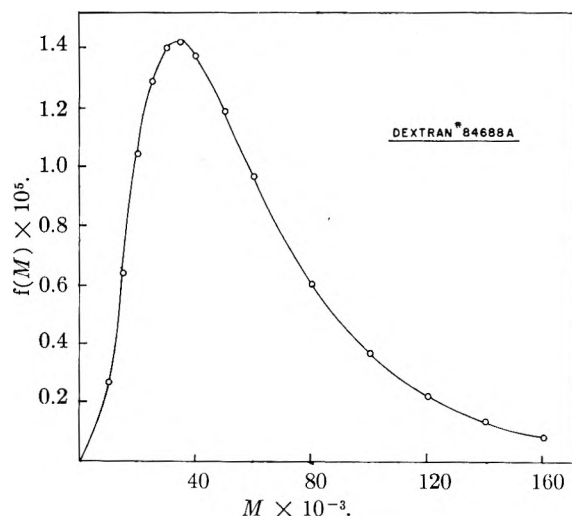


Fig. 1.—Differential molecular weight distribution curve for Dextran No. 84688A.

(13) W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **57**, 1369 (1935).

(14) G. V. Schulz, *Z. physik. Chem.*, **B43**, 25 (1939).

(15) M. Wales, F. T. Adler and K. E. van Holde, *THIS JOURNAL*, **55**, 145 (1951).

(16) H. Rinde, Dissertation, Uppsala, 1928.

TABLE I
COMPUTATION OF SIZE DISTRIBUTION FOR DEXTRAN NO. 84688A
 $M_w/M_p = e^{1.24\beta^2}$, $M_0/M_p = e^{0.5\beta^2}$, $M_p = 21,700$, $M_0 = 33,600$

M	M/M_0	$\frac{\ln M/M_0}{\beta}$	y^2	e^{-y^2}	$\frac{W}{M_0\beta\sqrt{\pi}} e^{-y^2} \times 10^5$	$F(M')$
10,000	0.298	-1.2882	1.659	0.190	0.272	0.0136
20,000	.595	-0.5521	0.305	.737	1.054	.0714
30,000	.893	-.1202	.014	.986	1.410	.2102
40,000	1.190	+.1851	.034	.967	1.383	.3406
50,000	1.488	.4228	.179	.836	1.195	.4814
60,000	1.786	.6170	.381	.683	0.977	.5786
80,000	2.381	.9229	.852	.427	.611	.7347
100,000	2.976	1.1602	1.346	.260	.372	.8312
120,000	3.571	1.3544	1.834	.160	.229	.8904
140,000	4.167	1.5183	2.305	.0998	.143	.9265
160,000	4.762	1.6603	2.757	.0635	.0908	.9490

angular velocity of the ultracentrifuge, and D is the diffusion coefficient. The sedimentation coefficient is defined as

$$s = \frac{dx/dt}{\omega^2 x}$$

in other words, a sedimentation rate at unit field strength. It often appears in other forms, thus

$$s = \frac{\ln x/x_0}{\omega^2 t} \cong \frac{2(x_2 - x_1)}{\omega^2(x_2 + x_1)(t_2 - t_1)}, \text{ etc.}$$

The distances x , x_1 and x_2 represent positions in the cell at times t , t_1 and t_2 , respectively. The position x_0 is that of the meniscus in the cell, and is related to the distance x by the equation $x = x_0 \exp(\omega^2 t)$. The combination of sedimentation and diffusion constants for the determination of the molecular weights of the globular proteins has been highly successful. Such constants are obtained by the extrapolation of sedimentation and diffusion coefficients to zero concentration to give the corresponding constants. For the linear high polymers the situation is much more complicated. For the polymer type molecules the sedimentation coefficient is a very complicated function of size and shape of the molecules; in addition, it is highly dependent upon the concentration of the solution in which it is observed. Thus, even if diffusion constant data could be readily made available any calculation of molecular weight from sedimentation velocity data would have to be made under the assumption that concentration dependence of sedimentation velocity can be eliminated by extrapolation.

In the sedimentation analysis of the polydisperse macromolecular systems additional difficulties arise. Invariably, the observed distribution of sedimentation coefficient is concentration dependent. Thus, for the dextrans, any such distribution obtained at a single finite concentration will be an apparent one, designated by the function $g(s)$ in the sections to follow. Since the distribution of molecular weights can be calculated only from a distribution of sedimentation velocities which corresponds to infinite dilution, an extrapolation procedure was developed to obtain the limiting or true distribution, $g(s)$, from several apparent distributions, observed at several finite concentrations.

There are several methods by which sedimentation velocity distributions may be obtained. As

suggested in the introduction Jullander and others²⁻⁴ have made studies with an exponential distribution function, the three parameters of which are determined from experimental distributions of sedimentation velocity at a series of concentration levels, with each parameter being extrapolated separately to infinite dilution.

Another method, the one which we shall adopt, is based upon our own analysis of the problem.⁶⁻⁸ The distribution function, $g(s)$, which gives the relative amount of the molecular species with sedimentation constant s is given by

$$g(s) = \frac{dn}{dx} \times \frac{\omega^2 x t}{n_1 - n_0}$$

when diffusion is negligible. When diffusion is not negligible, an "apparent distribution" defined in this manner may be extrapolated to infinite time to give the actual distribution of sedimentation constants since the spreading of the boundary due to difference in s is proportional to $\bar{x}t$, while the spreading due to diffusion is proportional to $t^{1/2}$.

The apparent distribution of sedimentation coefficients at any concentration is calculated by using the formula

$$g^*(s_e) = x' \frac{dn}{dx} \times \frac{\omega^2 t}{(A)_{t \rightarrow 0}} \times \exp(2s_e \omega^2 t)$$

where

- s_e = experimentally detd. sedimentation coefficient
- t = time in sec. after attainment of steady state speed
- x' = position in cell from reference bar for material of s_e at time t
- dn/dx = height at x'
- A = area = limiting area obtained by plotting the area of various pictures vs. time and extrapolating to zero time

Viscosity corrections have not been indicated in the interest of simplicity.

By plotting $g^*(s_e)$ vs. $1/\bar{x}t$ and extrapolating to infinite time, the actual distribution, $(g(s))$, of the sedimentation constants is obtained.

To obtain the true distribution of sedimentation constants with concentration effects eliminated, we can perform a reliable extrapolation to infinite dilution of several sedimentation velocity distribution diagrams obtained at finite concentration. This true distribution curve, $g_0(s)$ vs. s , is still a function of the molecular parameters of size and shape, but we can assume that the value of the effective

axial ratio is parallel to the molecular weight in the distributions.

In Fig. 2 we present the $g(s)$ vs. s curves for the Commercial Solvents Dextran No. 84688A at four finite concentrations and, after extrapolation of these curves, the true distribution of sedimentation constant curve, $g_0(s)$ vs. s , *i.e.*, the distribution at $c = 0$. The actual extrapolation is somewhat laborious. In the process values of the function $g(s)$ for given s values are plotted as a function of concentration c , the limiting value, $g_0(s)$, being obtained by extrapolation to infinite dilution.

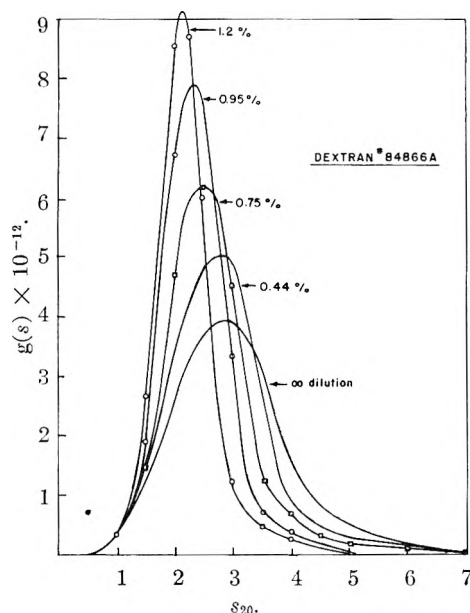


Fig. 2.— $g(s)$ vs. s curves at several concentrations and at infinite dilution for Dextran #84688A.

Part IV. Combination of Sedimentation Velocity and Sedimentation Equilibrium Experiments to Give Molecular Weight Distributions

It has been observed that sedimentation equilibrium studies provide absolute values of the molecular weight of a solute and much information about the distribution of molecular weights. However, when one requires size distribution analyses in non-ideal systems the situation becomes quite complicated. It is practically necessary to assume a general form of the distribution function so that any minor details of the distribution will fail to make their appearance. This is not true with the velocity diagrams and their evaluation, because any arbitrary distribution of sedimentation velocities can be handled. By a combination, the latter distribution can be converted to a distribution of molecular weights.

Such an analysis presupposes a knowledge of the relation between sedimentation constant and molecular weight. There are theoretical relationships, but for the present an empirical approach is of utility. We assume that $g(s)$, the distribution of sedimentation constants, and $f(M)$, the distribution of molecular weights, are known for some polydisperse sample. Now if to each species there corresponds one and only one sedimentation constant and a given molecular weight, we may write

$$w_{is} = w_{im}$$

where w_{is} = weight fraction with sedimentation constant s and w_{im} = weight fraction with molecular weight M .

If we consider continuous distribution functions, this equation becomes

$$g(s)ds = f(M)dM$$

where $g(s)ds$ = weight fraction with sedimentation constant between s and $s + ds$, and $f(M)dM$ = weight fraction with molecular weight between M and $M + dM$. Furthermore

$$\int_0^{s'} g(s)ds = \int_0^{M'} f(M)dM$$

or

$$G(s') = F(M')$$

where $G(s')$ = weight fraction with $s \leq s'$, $F(M')$ = weight fraction with $M \leq M'$, and s' corresponds to M' . It should be noted that so far it has been assumed that s is a single valued, increasing function of M .

Now if $g(s)$ and $f(M)$ are known, $G(s)$ and $F(M)$ can be obtained by a numerical integration. If we then construct a double plot, $G(s')$ vs. s and $F(M')$ vs. M and from this plot take values of the two abscissas at equal ordinates, we may determine the s' corresponding to a given M' so that the entire curve of s vs. M can be constructed. Such a double plot is shown in Fig. 3, in which sedimentation equilibrium and sedimentation velocity data for the representative dextran have been combined. Both curves show *integral* distribution, one of molecular weight and the other of limiting or true sedimentation constant.

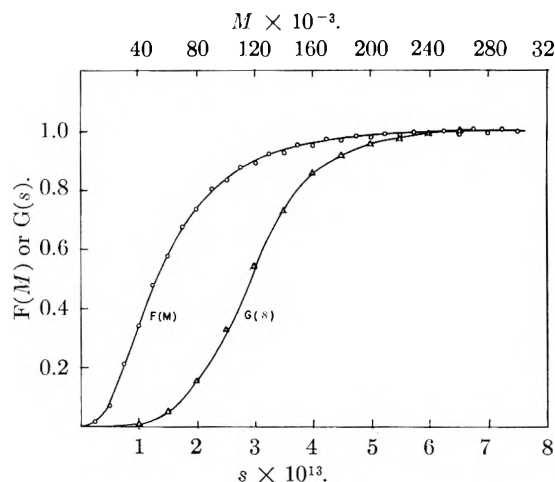


Fig. 3.—Double plot of integral distribution curves of molecular weight, $F(M)$, and sedimentation constant, $G(s)$, for the representative Dextran #84688A.

It may be of value to give a more precise description of the use of two curves such as those of Fig. 3 to give the calibration of sedimentation constant in terms of molecular weight. If it is desired to find the molecular weight M which corresponds to sedimentation constant $s = 2.5S$, a line is drawn from the sedimentation constant scale at $s = 2.5S$ perpendicular to the $G(s)$ vs. s curve. At the point of intersection, a horizontal line is now drawn from the $G(s)$ vs. s curve to the $F(M)$ vs. M curve and the desired molecular weight can be read from the

M scale at the top of the diagram. In this way it can be seen that every s value measures a particular M , *i.e.*, for $s = 2.5S$, $M = 40,000$; for $s = 3.5S$, $M = 80,000$, etc. The charts can be used with accuracy from sedimentation constant $s = 1.1S$ to $6.0S$ corresponding to molecular weights of dextran samples from $M = 10,000$ to $200,000$.

Further, there have been plotted as ordinates values of $F(M')$ or $G(s')$ in such a way that the proportion of the total dextran below any given molecular weight may be read directly from the scale. Thus, it would be possible to prepare tables to give the percentage of the total dextran in any given molecular weight class. It should be mentioned as well that *both* the curves of Fig. 3 have been obtained by integration of distribution curves corresponding to infinite dilution of solution; in other words, the necessary corrections for non-ideal behavior have been applied.

Having obtained the relationship between sedimentation constant s and molecular weight M of a representative dextran it was of interest to prepare a plot of sedimentation constant against square root of the molecular weight, Fig. 4. It is seen at a glance that close proportionality exists between these two quantities, much too close to be accounted for by accident. Thus, we may write $s = KM^{1/2}$. An exponent of value 0.50 to 0.55 is known to be characteristic of flexible, long chain molecules which form "random coils" with much

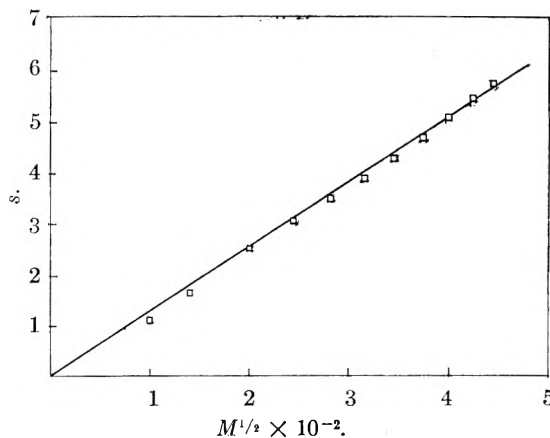


Fig. 4.—Sedimentation constant and square root of molecular weight for Dextran #84866.

immobilized solvent. It may be expected to vary somewhat according to the structure of the several dextrans (branching of the chains) and their molecular weights.

Acknowledgment.—The authors wish to make recognition of the fact that they have received substantial assistance from others during the progress of this research. Particular mention is made of Armin Fuhlbrigge, Arthur Haltner, Jr., Kensal van Holde and Janet Williams, whose cooperation is greatly appreciated.

FILM DRAINAGE TRANSITION TEMPERATURES AND PHASE RELATIONS IN THE SYSTEM SODIUM LAURYL SULFATE LAURYL ALCOHOL AND WATER

BY M. B. EPSTEIN, A. WILSON, C. W. JAKOB, L. E. CONROY AND J. ROSS

Colgate Palmolive Co., Jersey City, N. J.

Received March 5, 1954

A detailed examination has been made of drainage transition temperatures of films formed from solutions of varying concentration of sodium lauryl sulfate or sodium myristyl sulfate containing lauryl alcohol or myristyl alcohol. Some observations of the phases occurring in these solutions are described. Crystalline adducts of sodium alcohol sulfate and long chain alcohol have been isolated and analyzed. The relationship of film drainage transition temperatures to the composition of the solution is discussed.

Earlier work has shown that the drainage rate of certain detergent foams and single films may be lowered greatly by the presence of small amounts of organic polar compounds.^{1,2} When heated sufficiently, such slow draining foams or single films become fast draining, the transition occurring reversibly over a narrow range of temperatures which is the same for foams as for single films.³

Many combinations of detergents and organic polar compounds which can show such transitions have been reported, along with a tentative outline of the required structural characteristics.² For the long chain alcohol sulfates and alcohols, some preliminary indications of the effect of concentration and of alcohol chain length upon the transition temperature were given. In the present paper a more detailed examination of the film drainage transition temperatures and the phase relations are reported for the system sodium lauryl sulfate, lauryl alcohol and water. Some observations of transition temperatures are also given for combinations with sodium myristyl sulfate and myristyl alcohol.

Experimental

Materials and Preparation of Solutions.—The sodium lauryl sulfate used in the transition temperature and solubility measurements was prepared and purified according to the method of Dreger, *et al.*,⁴ and was free of higher homologs and unsulfated alcohol as shown by the absence of a minimum in the surface tension-concentration curve.

A second sample of sodium lauryl sulfate was used in the preparation of adducts. This sample was estimated from the film drainage transition temperature of a 0.2% solution to contain 0.1% lauryl alcohol on a sodium lauryl sulfate basis. From the data presented below it is evident that film drainage transition temperatures can provide a sensitive method for the estimation of lauryl alcohol in sodium lauryl sulfate.

The sodium myristyl sulfate was prepared and purified according to the method of Dreger, *et al.*⁴ Film drainage transition temperatures indicated a negligible amount of myristyl alcohol.

The lauryl alcohol was refractionated commercial material, b.p. 133° at 3.5 mm., n_D 1.4410 at 25°. The myristyl alcohol was also refractionated commercial material, b.p. 143° at 3 mm., n_D 1.4350 at 50°.

Film Drainage Transition Temperatures.—To conserve solutions, film drainage tubes² requiring only one ml. of solution were used. The measurements were made in a

well stirred bath which could be adjusted over a wide range of temperatures (8 to 60°) and controlled to 0.05° or less. The solutions were aged in the bath below the transition temperature and the bath temperature then slowly raised until the film changed from slow to fast draining. With solutions below the critical micelle concentration and on the steeply rising parts of the curves (Fig. 1) transitions sometimes were observed which were below the finally accepted transition temperatures. In these cases, films which had become fast draining at a given temperature reverted to slow draining ones when reformed at the same temperature after further aging and, thus, the upper limit could be determined.

Determination of Phase Boundaries.—Phase studies were carried out with solutions aged at low temperatures to produce crystals or a birefringence. Volumetric flasks were clamped in holders driven by a rotary reciprocating drive mounted above the bath which had been used in the film drainage observations. The solution level in the flasks was well below the water level of the bath. The flasks were oscillated through 180° one to two times per second while the temperature was raised slowly at intervals. Both a crystalline phase and a birefringent phase of undefined structure have been observed, and their solubility temperatures, as well as the transition temperature of one to the other, were determined. The length of time taken to make a measurement has varied, but some measurements have taken three days or more. At times the presence of crystals could be verified only by their twinkling reflection of a strong, narrow light beam.

A microscopic method was used for several measurements. It employed an optical cell 20 mm. long \times 25 mm. diameter mounted in a small bath which consisted of a horizontal brass cylinder, 150 mm. long \times 100 mm. diameter, having an opening at the top and flat glass windows at each end. The bath temperature was controlled by circulation of water from a much larger, well regulated bath. A small Polaroid disc was fastened directly to the rear window of the cell. The barrel of a polarizing microscope was mounted in front of the bath and the analyzer was set as closely as possible to total extinction. The microscope could be focused on the contents of the cell.

The solution was placed in the cell and allowed to age at low temperatures until crystals or birefringence appeared. The bath temperature was slowly raised and the solution stirred at intervals by means of a brush of nichrome wires which could be rotated slowly. When a first-order red plate was inserted in the microscope, crystals appeared either yellow or blue according to their orientation. The birefringent phase appeared as waves of yellow or blue when the solution was stirred. The lowest temperature was noted at which complete disappearance of crystals or birefringence could be observed.

Analysis of Adducts.—Sixty mg. of adduct was weighed to 0.1 mg. into a 2-ml. medium fritted glass filter funnel containing a short stirring rod. The adduct was extracted with small increments of Skellysolve A, using gentle suction while warming under a heat lamp, until 20 ml. of filtrate had been collected. After drying for a few minutes in a vacuum desiccator, the loss in weight was determined. This process was repeated until the weight was constant.

Results and Discussion

Film Drainage Transition Temperatures.—In Fig. 1 (Table I), film drainage transition tem-

(1) G. D. Miles, L. Shedlovsky and J. Ross, *THIS JOURNAL*, **49**, 93 (1945).

(2) G. D. Miles, J. Ross and L. Shedlovsky, *J. Am. Oil Chemists Soc.*, **27**, 268 (1950).

(3) M. B. Epstein, J. Ross and C. W. Jakob, *J. Colloid Sci.*, **9**, 50 (1954).

(4) E. E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky and J. Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).

peratures are plotted against concentration of lauryl alcohol at a series of fixed concentrations of sodium lauryl sulfate. An alternative plot can be prepared in which the transition temperatures are given as a function of sodium lauryl sulfate concentration at a series of fixed lauryl alcohol concentrations. A number of the points in Fig. 1 are metastable, being values for clear solutions which subsequently may precipitate sodium lauryl sulfate or some other phase. The phases which have been observed are described later.

TABLE I
FILM DRAINAGE TRANSITION TEMPERATURES AND SOLUBILITY TEMPERATURES FOR SODIUM LAURYL SULFATE-LAURYL ALCOHOL-WATER

Sodium lauryl sulfate, g./100 g. soln.	Lauryl alcohol $\times 10^2$, g./100 g. soln.	Transition temp. of film, °C.	Solubility temp., °C.	
			Crystals	Birefringence
0.100	0.0125	17.9		
	.025	27.7		
	.05	37.0		
	.1	39.2		
	.2	40.2		
	.3	40.1		
	.5	40.3		
	.813	40.7		
	1.016	40.8		
	0.150	0.038	36.1-36.8	
0.200	0.025	22.6		
	.05	27.4		
	.10	31.7		
	.20	33.7		
	.40	34.8		
	.60	35.0		
	1.0	35.1		
	1.626	35.7		
	2.032	35.6		
	0.250	0.0635	17.0	
.127		21.9	18-19	None
.254		26.6		
.508		31.2	28.0-28.5	None
.762		33.2	28.5-29	None
1.016		34.1	28.5-29	31.5-32 ^a
1.270		34.3	28-29	32-34 ^a
2.032		34.1	28-29	33-35 ^a
2.540		34.3	29.3	
0.400		0.05	<8	
	.203	10.6		
	.4	16.1		
	.8	20.9		
	1.2	24.9		
	2.0	28.9	28-29	None
	3.251	32.0	29.9	None
	4.064	33.3		
	7.24	33.6	29.9	33.6-34.2 ^a
	18.8	34.4		
0.600	0.3048	7.6		
	0.6096	12.5		
	1.20	18.2		
	1.80	21.3		
	3.0	25.9		
	6.096	31.3	30.3	
	20.0	33.2		
31.0	33.5			
0.667	0.333	8.0-9.0		

0.800	0.8	11.0	16.5-17	None
	1.6	16.6	19-20	None
	2.40	19.9	21-22	None
	4.0	24.6	24.5-25.0	None
	8.128	30.1	27.4	None
	12.90	32.7		30.6-30.8 ^a
	14.23	32.9		32.2-32.6 ^a
	17.77	33.0	30.2	32.8-33.6 ^b
	37.5	33.2		
	1.00	1.0	9.3	
2.0		15.4		
3.0		18.8		
4.0		21.4		
1.50	1.0	<6		
	2.0	11.2		
	3.0	14.6		
	4.0	17.4		
2.00	1.0	<6		
	2.0	9.4		
	3.0	11.9		
	4.0	14.5		
	19.4	27.4		

^a Turbidity above this temperature. ^b Turbidity appeared below 32.8° in the birefringence region.

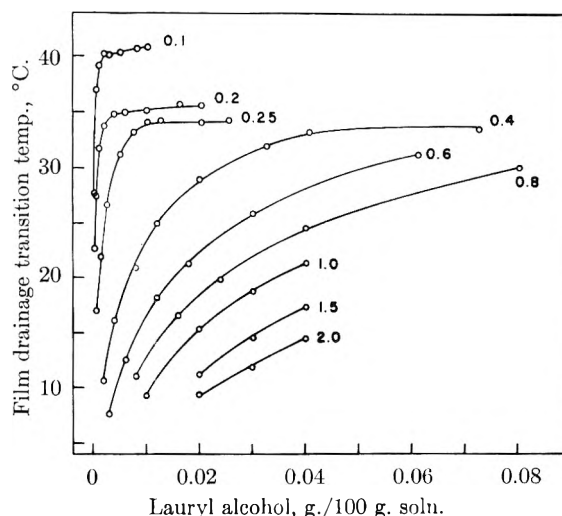


Fig. 1.—Film drainage transition temperatures. Numbers adjacent to curves give concentration of sodium lauryl sulfate in g./100 g. soln.

For any given sodium alcohol sulfate concentration, the transition temperature rises with increasing concentration of lauryl alcohol, at first rapidly, but then slowly if at all. Conversely, for any given alcohol concentration, the transition temperature falls with increasing concentration of sodium alcohol sulfate.

The isotherms which may be constructed from the data are shown in Fig. 2. Their distinguishing features are the sharp break which occurs near the critical micelle concentration (CMC) for pure sodium lauryl sulfate (0.23%) and the almost linear relation between alcohol sulfate and alcohol concentration which exists above the break. There is a striking resemblance to the isotherms for certain other properties of similar systems in which the CMC plays an important role, such as would be expected with the corresponding solubility iso-

(5) This Laboratory, unpublished data

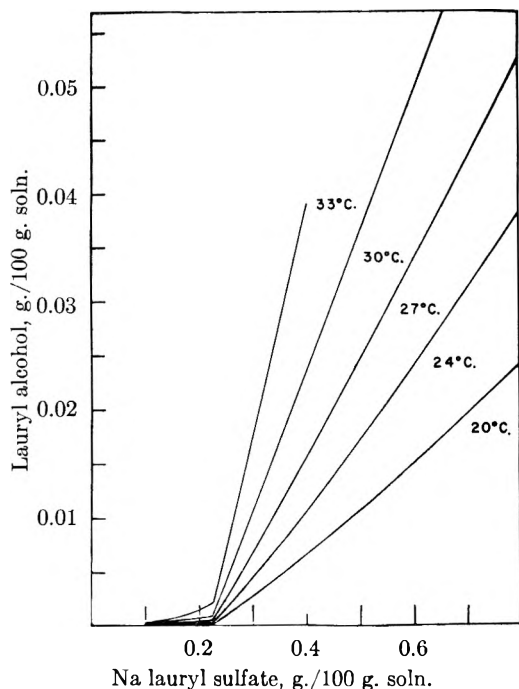


Fig. 2.—Isotherms of film drainage transition temperature.

therms. It may be inferred that the relations between film drainage transition temperature and concentration undergo a radical change when the solution passes from non-micellar to micellar concentrations.

In the region below the CMC on an expanded plot of the logarithm of the lauryl alcohol concentration *versus* the sodium lauryl sulfate concentration, the isotherms extrapolate to 0.012×10^{-2} g. alcohol/100 g. soln. at zero sodium lauryl sulfate concentration.

For concentrations above the CMC, a quantity, termed here the "apparent micellar mole fraction of alcohol," Z , may be defined as the mole fraction of alcohol computed from the moles of alcohol sulfate diminished by the CMC, and the moles of alcohol in the system. The value of the CMC used in the calculation, 0.226%, has been taken from Fig. 2 to maintain the internal consistency of the data. In Fig. 3, for each experimental point the transition temperatures are plotted against $\log Z$ with the result that the various curves of Fig. 1 have been reduced by the transformation to essentially a single curve. A similar curve may be obtained by plotting transition temperatures against the logarithm of an "apparent micellar mole ratio."

The basis for the calculation is empirical and lies in the isotherms shown in Fig. 2. Consequently it is preferable to denote the calculated ratios as "apparent." A simple interpretation would be that they are indeed an expression of the true micellar composition. It is implied that the partition of the alcohol between the micellar and non-micellar portions of the solution is almost entirely in favor of the micelles and that the non-micellar alcohol sulfate is given by the CMC. With these assumptions, above the CMC the transition temperature is a function of the composition of the micelles and is independent of their number.

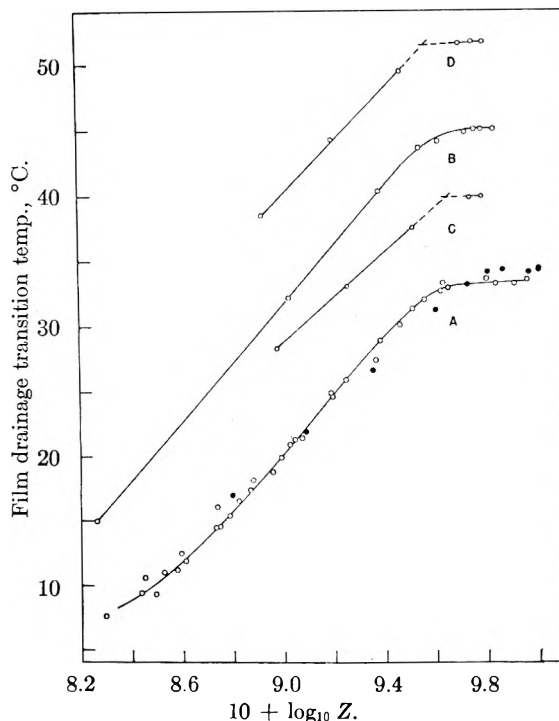


Fig. 3.—Film drainage transition temperature *vs.* $\log Z$: A, sodium lauryl sulfate + lauryl alcohol (solid circles, 0.25% sodium lauryl sulfate; open circles, higher concn.). B, 0.6% sodium lauryl sulfate + myristyl alcohol. C, 0.2% sodium myristyl sulfate + lauryl alcohol. D, 0.2% sodium myristyl sulfate + myristyl alcohol.

Over a wide range of concentrations and temperatures the curve of Fig. 3 is nearly linear. The slight curvature noted on the isothermal plot appears on Fig. 3 as a deviation which is most evident near the CMC. At the lower end the curve must be bounded by the Krafft temperature, the temperature at which the micelles cease to exist for lack of solubility. Near 34° further addition of lauryl alcohol results in no significant increase in the transition temperature; this effect suggests that the maximum concentration of alcohol in the micelles has been reached. Higher transition temperatures than this maximum are found in the region below the CMC.

The data for three other closely related systems are shown on Fig. 3 and are summarized in Table II. In the calculations the CMC for sodium lauryl sulfate has been taken as 0.226% as before, and for sodium myristyl sulfate as 0.0645%.⁵

TABLE II

Sodium alcohol sulfate, g./100 g. soln.	Alcohol	Slope	Flat, °C.	Break, g. alcohol/100 g. soln.	ρ , (Figs. 4 and 5) g. alcohol/100 g. soln.
0.25 C ₁₂	C ₁₂	19.0	34.1	0.009	0.009
.80 C ₁₂	C ₁₂	22.0	33.2	.124	.123
.60 C ₁₂	C ₁₄	22.8	45.0	.089	
.20 C ₁₄	C ₁₂	17.2	39.9	.031	
.20 C ₁₄	C ₁₄	20.0	51.6	.028	

Phase Boundaries.—Figures 4 and 5 describe the observed phase boundaries as a function of lauryl alcohol concentration for 0.25 and 0.80% sodium lauryl sulfate. For each, the curve of film drainage transition temperature is also given.

A solution having the composition a, Fig. 4, on aging at the indicated temperature will eventually separate a second phase of crystals whose size depends upon the conditions of formation and growth. Often considerable supercooling is necessary to induce crystallization within a reasonable time. If the temperature is raised along the line aa' the crystals will dissolve completely to an isotropic solution when the crystal solubility curve, B, is reached.

A second solution having a composition b when aged at 22° will ultimately separate crystals from solution. If the temperature is raised along bb', the following observations can be made.

1. At 28.5 to 29°, the crystals dissolve and the solution develops a birefringent appearance.

2. Between 32 and 33° the birefringence disappears and the solution is now turbid.

3. The turbidity does not vanish as the temperature is raised further and for a detergent concentration of 0.25% seems to increase with temperature. For this reason the hypothetical turbidity boundary, D, has been drawn with a negative slope in Fig. 4.

Along the path bb', isotropic solution completely free of birefringence or turbidity has not been observed, and therefore at no time is the composition of the solution phase identical with that of the overall system.

Figure 5, which describes the phase boundaries for 0.80% sodium lauryl sulfate, is quite similar to Fig. 4. It differs mainly in that the crystal solubility curve crosses the film drainage transition temperature curve at a much higher temperature. Below the intersection the film drainage transition temperatures are for metastable compositions.

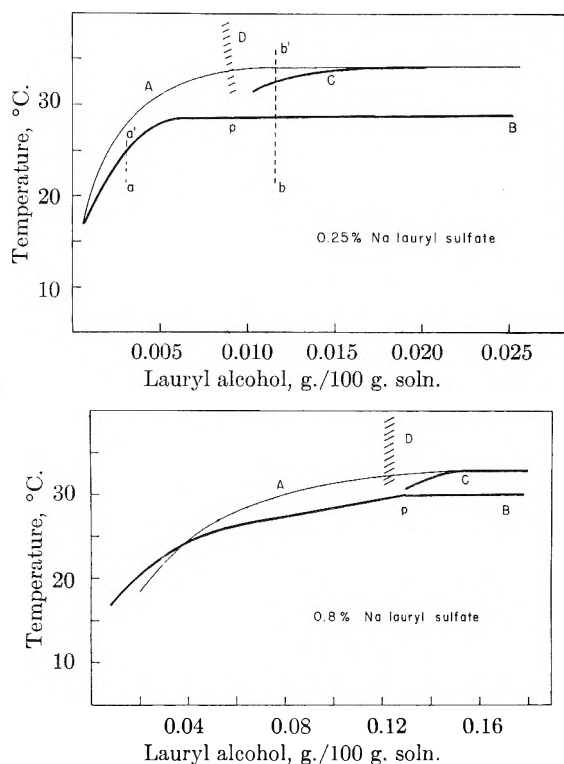
In Table II, the point p, in the region in which the birefringence and turbidity first appear, is compared with the break in the plot of $\log Z$.

On each of Figs. 4 and 5 the four regions seem to have a point p in common. However, according to the phase rule, for this system four phases cannot coexist at equilibrium except at an invariant point. Point p, appearing at two arbitrarily selected sodium lauryl sulfate concentrations clearly is not an invariant point, suggesting further study of the nature of the phases.

If systems rich in alcohol are allowed to stand at room temperature for long periods of time, several days or weeks, or are centrifuged, a white, opaque, gelatinous mass gathers at the top of the solution. Under a polarizing microscope the gel shows anisotropy.

The crystals mentioned earlier grow as plates, often 1 × 2 mm., but always extremely thin. Recovery is facilitated by decantation of clear liquid. The crystals may be dried over CaCl₂ but holding at low pressures leads to a continuous loss of weight. When observed under a microscope they undergo decomposition at 50 to 60° with deposition of liquid droplets near the crystals.

It has also been found possible to recover crystalline adducts from systems containing sodium myristyl sulfate and either lauryl or myristyl alcohol. Thus far, an adduct of sodium lauryl sulfate and myristyl alcohol not obviously contaminated with



Figs. 4 and 5.—Phase relations: A, film drainage transition; B, crystal solubility; C, birefringence disappearance; D, turbidity boundary.

myristyl alcohol has not been obtained. These adducts have been analyzed by extraction with Skellysolve A, as described earlier, and also by determination of the film drainage transition temperature of a solution of the corresponding alcohol sulfate to which known amounts of the adduct were added. The results of the analyses were as follows.

TABLE III
ANALYSES OF ADDUCT

	Loss of wt. on extraction	% alcohol by F.D.T.T.	Theoretical ^a
Lauryl alcohol, sodium lauryl sulfate	23.6, 25.7	26.8, 25.8	24.5
Lauryl alcohol, sodium myristyl sulfate	23.1		22.7
Myristyl alcohol, sodium myristyl sulfate	25.1	25.6	25.3

^a For a ratio of 2 moles of alcohol sulfate to one mole of alcohol.

Examination of the residue of the Skellysolve A extraction by film drainage procedures demonstrated the absence of alcohol. Analysis of the first compound listed by means of the Karl Fischer reagent gave 0.4% H₂O, indicating the absence of water of crystallization.

The X-ray diffraction pattern for these crystals is unlike the pattern for the sodium alcohol sulfate recrystallized either from ethanol or water. The pattern obtained with the residue of the analytical extraction also differs from the pattern for pure sodium alcohol sulfate and retains unchanged the principal lines of the original adduct. This result suggests a simple leaching out of the long chain alcohol without disrupting the lattice.

The analysis and properties of the crystalline material indicate that it is an intermolecular compound in which sodium alcohol sulfate and long chain alcohol are combined in a ratio close to two to one.

It is believed that the phenomenon of slow drainage is probably due to an ordered surface structure of considerable rigidity. It is known from the work of Brown, Thuman and McBain⁶ that the surface viscosity of such systems is extraordinarily high. It is often noticed that supercooling below the film drainage transition temperature is necessary to obtain slow draining films, a phenomenon which points strongly to the occurrence of some phase change, probably at the surface of the film. That the necessary forces are available for the formation of such surfaces is shown by the existence of compounds between long chain alcohols and sodium alcohol sulfates which have a definite solubility or decomposition temperature in a given solution. The significance of complexes in the bulk with respect to surface behavior has been discussed by Schulman and Rideal.⁷

It is this requirement that the molecules in the surface be capable of extensive interaction and association in order to produce slow draining films that imposes severe steric limitations upon the combinations which can produce such films.² Interaction of the polar groups, possibly through hydrogen bonding, and van der Waals interaction of the hydrocarbon chains can combine to provide considerable energy. Long chains which readily adlineate favor this process, apart from ensuring the necessary surface adsorption. Widely divergent chain lengths, branching and the presence of non-terminal functional groups in general are unfavorable.

It cannot be asserted that the composition of the surface is the same as that of the recovered crystalline adduct. Indeed, the composition of the birefringent material is not at present known. From film balance measurements using their monolayer penetration technique, Goddard and Schulman⁸ have concluded that in surfaces containing long chain alcohols and sodium cetyl sulfate, strong interaction occurs, although complexes were not observed.

It appears probable that slow draining films may be obtained with systems from which it is not possible to recover adducts of the kind described. However, one may regard the transition from slow to fast draining films as occurring at the temperature at which the molecules in the surface have sufficient

thermal energy to overcome the bonding energies with a consequent decrease in the rigidity or surface viscosity.

J. G. Baldinus made the examination by X-ray diffraction. We wish also to acknowledge the helpful criticism of G. D. Miles and L. Shedlovsky throughout the course of this work.

DISCUSSION

C. R. SPORCK.—In an article appearing in the "Journal of the Oil Chemists Society" in early 1953 we offered an explanation for slow and fast draining films which we recount here briefly. In a gravitational field a film must have a vertical tension gradient. If the surface is a gaseous film the required tension gradient can be obtained only by a great vertical surface concentration gradient. This will necessitate much stretching of the film surface. Hence the walls of the film will descend with the intersurface liquid. This film will be fast draining. If the surface has a condensed film little stretching will be required to fulfill the conditions. The walls will remain substantially firm and only intersurface liquid can descend. This film will be slow draining. For solutions in which micelles are present can the curves of Fig. 1, p. 861 be shown to attain asymptotically the same temperature? This possibility is suggested by the proximity of the levels of the curves for 0.2, 0.25, 0.4% sodium lauryl sulfate. Perhaps these curves cannot be carried to higher concentrations than here indicated because of precipitation.

AUTHORS.—The curves are not asymptotic to the same value of temperature, but are bounded by an envelope which over the micellar region does not vary much with temperature. The behavior over the micellar region is most easily seen on Fig. 3, where the concentration scale in effect is compressed.

C. R. SPORCK.—If the conditions described in our previous question hold (1) can the composition of the surface be determined, (2) can the composition of the micelles be determined? If these determinations have been made, are these concentration ratios of the two components the same and equal to that in the adduct?

AUTHORS.—Slow draining films are observed below the CMC, and the theory presented (Fig. 3) therefore is not a complete theory, since it relates the film drainage transition temperature to the micellar composition. Equilibria exist between the surface layer, micellar, and non-micellar parts of the solution and the composition of the surface cannot be identified with the composition of the micelles.

In the calculation of the micellar composition, allowance should be made for the non-micellar alcohol as well as the non-micellar detergent. A possible approach, suggested by U. P. Strauss, is through the use of a distribution ratio calculated from the measured solubility at the concentration in question. The necessary data are being gathered.

C. R. SPORCK.—On page 862, column 2, paragraph 1, it is stated with reference to Fig. 3 that at the flat of the curve the micelles have acquired this maximum of lauryl alcohol. Isn't it more likely that the surface has reached a stationary state with respect to composition and that changes which do not affect the surface are taking place in the micelles? Otherwise where would the further alcohol which is being added go in order to be retained in solution. Certainly it cannot be in the aqueous medium outside the micelle.

AUTHORS.—More than one phase lies to the right of point "p," Figs. 4 and 5, as we have shown, and this is true of any composition occurring to the right of the break in curve A, Fig. 3. The final column of Table II correlates the available information.

(6) A. G. Brown, W. G. Thuman and J. W. McBain, *J. Colloid Sci.*, **8**, 491 (1953).

(7) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc. (London)*, **B122**, 29 (1937).

(8) E. D. Goddard and J. H. Schulman, *J. Colloid Sci.*, **8**, 329 (1953).

NON-SOAP THICKENERS OF LUBRICATING OILS.

I. SEDIMENTATION VOLUMES¹

BY SYDNEY ROSS AND HAROLD F. SCHAEFFER

*Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.**Received March 5, 1954*

The sedimentation volumes of solid thickeners of lubricating oils were observed in two liquids of low dielectric constant, dioxane and cyclohexane, in one of which water is miscible and in the other immiscible. The effect of added water is not the same for both. In dioxane-water solutions either a polar or a non-polar portion of the total solid surface determines the value of the sedimentation volume, and its variation with the amount of water added. Reductions of sedimentation volume on addition of water to dioxane are caused by a polar solid surface, and increases are caused by a non-polar surface. Significant characteristics of the solid surface can therefore be obtained from the sedimentation volumes in a series of water-dioxane solutions ranging from pure water to pure dioxane. In cyclohexane-water mixtures only polar portions of the total surface are operative. If such portions are present, preferential adsorption of water leads to a large increase in the sedimentation volume. The difference in behavior caused by the presence of miscible or of immiscible water is described in terms of the surface energies of the interfaces present.

Introduction

The thickening action of certain finely divided solids when dispersed in lubricating oils is the basis of the formation of lubricating greases. Solids able to withstand temperatures that would decompose soaps are of present practical use and great future promise as thickening agents for greases required to withstand extreme conditions or for special purposes. As a problem in colloid science, the thickening action can be studied by means of the phenomenon of sedimentation volumes, about which a background of scientific information is already known, and which, because of the relative simplicity of the systems in which it can be produced, is capable of better experimental control of variables than are greases made of lubricating oils. The present paper reports studies of sedimentation volumes of solids, some of them of familiar surface properties, such as silica and graphite, and others such as copper phthalocyanine and Attapulgitic clay, which, though less well known, are important as thickeners for hydrocarbon oils. The sedimentation volumes of these solids were observed in a variety of two-component liquid media. The observed behavior is interpreted by a consideration of the surface energies of the various interfaces present.

Methods and Materials

In preparing samples for the determination of sedimentation volumes, each solid in a shallow vessel was kept in an evacuated desiccator containing phosphorus pentoxide for at least 24 hours. To a weighed amount of solid is added a small quantity of the liquid in which the dispersion is to be made. This paste is thoroughly mixed, using a Hayman micro-spatula, and more liquid is gradually added with constant stirring, until 25 ml. had been added.² The stoppered tube is finally given 40 shakes, and set aside for observation in a constant temperature room or air thermostat. The tubes used were Hart casein tubes (Fisher, Catalog No. 5-630) or, for larger volumes, gas burets. All corks were pretreated with an appropriate organic solvent to prevent contamination during the test. Readings were taken after 20 days, unless otherwise indicated. Duplicate samples were used for each experiment, and when agreement of the duplicates was poor, the experiment was repeated.

The graphites were kindly furnished by the Acheson Colloids Company. The powder designated "No. 39 Graphite" is supplied by National Carbon Company and has a BET area of 15 m.²/g. The samples designated "EC-753-15A," "EC-753-72A" and "EC-753-144A" have BET surface areas of 91, 319 and 466 m.²/g., respectively.

The silica is designated Santocel-ARD and is supplied by Monsanto Chemical Company. The copper phthalocyanine, labeled PL-168, is a specially purified grade suitable for the preparation of lubricating greases, and was supplied by du Pont de Nemours and Co., Inc. Attapulgitic clay was provided by the Attapulgitic Minerals and Chemicals Corporation. It has a surface area of about 120 m.²/g.

Experimental Results

The variation of the sedimentation volumes of a series of Acheson graphites in different liquids is shown in Fig. 1 as a function of their specific surface.

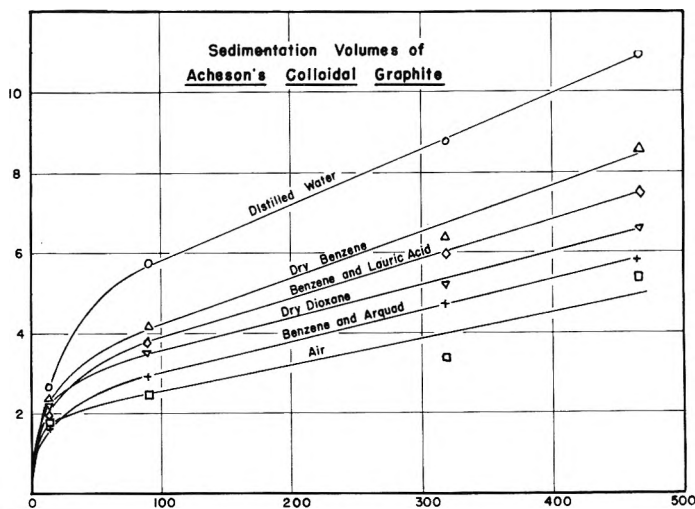


Fig. 1.—Sedimentation volumes in cc./g. of graphites of various surface areas suspended in different fluids.

The regular variation shown is a characteristic of this solid, and is not necessarily to be expected from similar experiments on other solids. Table I reports the sedimentation volumes of a series of zinc oxide pigments, compared with the specific surface of the solid, as measured by nitrogen gas adsorption.³

(3) J. C. Arnell, *Can. J. Research*, **27A**, 207 (1949). The zinc oxide samples were provided by courtesy of the New Jersey Zinc Company.

(1) This paper is based on work done under Contract No. DA-30-115-ORD-249 between the Office of Ordnance Research, U. S. Army, and Rensselaer Polytechnic Institute.

(2) An attempt was made to improve reproducibility of duplicates by resorting to spatulation, using a curved spatula and a round-bottom dish. This was discontinued because the deviation between duplicates became much greater for some of the samples, notably copper phthalocyanine.

TABLE I
SEDIMENTATION VOLUMES OF ZINC OXIDE PIGMENTS

Sample label	Surface area, m. ² /g.	Sedimentation vol., ml./g.	
		In water	In dry benzene
F-1601	9.5	3.45	2.40
K-1602	8.8	2.70	2.20
G-1603	3.9	3.00	2.63
KH-1604	0.66	1.50	0.65

The results of Fig. 1 show a variation of sedimentation volume with the liquid medium, and this theme is developed in experiments where the sedimentation volumes of solids are observed in water-dioxane solutions, in which the dielectric constant of the solution decreases regularly with the percentage decrease of water content. Figure 2 reports the results obtained from observations of Attapulgit,

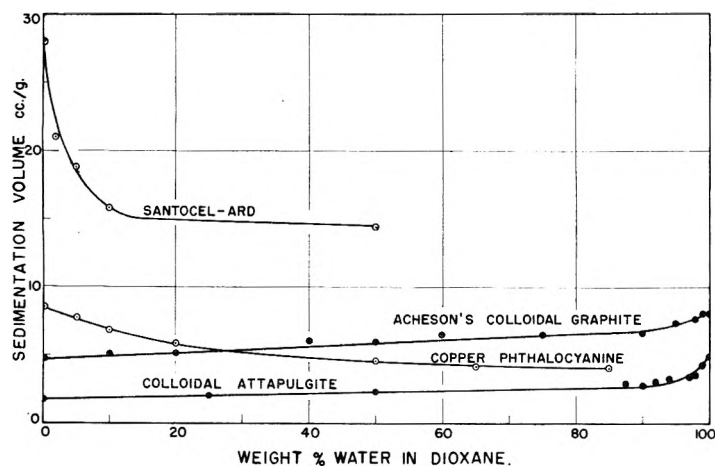


Fig. 2.—Sedimentation volumes in cc./g. of solids suspended in water-dioxane solutions. The dielectric constants of these solutions vary from 2.2 to 80, proportional to the weight per cent. of water present.

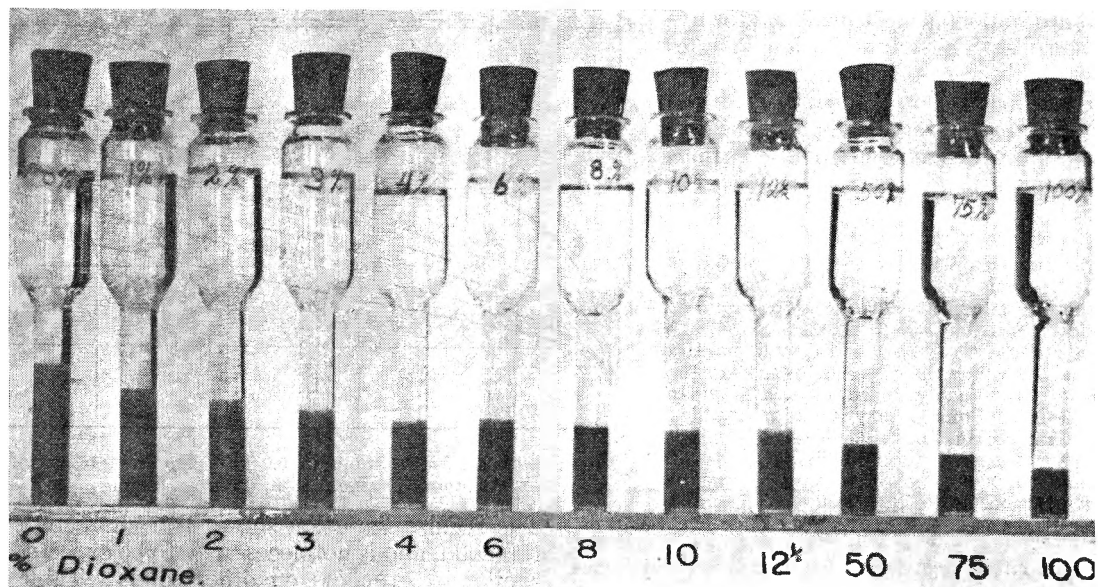


Fig. 3.—Sedimentation tubes containing Attapulgit in dioxane-water solutions, after standing for 20 days.

graphite (319 m.²/g.), copper phthalocyanine and Santocel-ARD. The appearance of the sedimentation tubes and the equilibrium sediments of Attapulgit is represented in the accompanying photograph, Fig. 3.

The effects of added water are also of interest in systems where it is immiscible. Figure 4 represents the sedimentation volumes of graphite (319 m.²/g.) in cyclohexane, to which small percentages of water have been added, and also includes a similar series of observations of copper phthalocyanine.

Discussion of Results

1. **Effect of Surface Area of Interface on Sedimentation Volumes.**—Figure 1 reports the effects of several variables on the sedimentation volumes. The increase of surface area causes a regular increase in the sedimentation volumes, independent of the medium in which the solid is dispersed. It seems, however, that this conclusion must be qualified for solids that have less crystallographic surface uniformity than graphite. The pronounced cleavage of graphite in thin layers produces a preponderance of the same surface plane, and the increase of specific surface shown as a parameter in Fig. 1 could also be read as an increase in the amount of 0001 surface planes per gram of solid. Solids that do not have a single homotactic⁴ surface, do not show the kind of regularity of Fig. 1, as is demonstrated by the results in Table I, for zinc oxide. Several surface variables here contribute simultaneously to obscure the regularity of behavior of each homotactic portion of the surface.

2. **The Influence of the Dispersing Medium.**—The influence of the dispersing medium on sedimentation volumes of a dispersed solid have been known for some time. An historical account has been written by Fischer.⁵ Many properties of liquids, such as heat of vaporization, di-

electric constant and spreading coefficient, are interrelated, and sedimentation volumes frequently

(4) C. Sanford and S. Ross, *THIS JOURNAL*, **58**, 288 (1954).

(5) E. K. Fischer, "Colloidal Dispersions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 109-113.

have been found to be related to one or the other of those properties.

The experiments cited by Fischer that have to do with polar particles, *i.e.*, solids of hydrophilic surface, have now sufficiently established the generalization that the more perfectly the surface of a polar solid is wetted by the dispersion medium, the greater the deflocculation of the particles and the smaller the resulting sedimentation volume. No such generalization has yet been suggested for non-polar solids, such as graphite. McBain asserts that changing the liquid does not affect the sedimentation volume of non-polar graphite.⁶ Figure 1 shows that for graphites of low specific surface, the variation of the sedimentation volume in different liquids is indeed slight, but that the variation increases with the subdivision of the solid and, for very fine graphites, can be pronounced. Figure 2, in addition, also shows the variation of the sedimentation volume of graphite in water-dioxane solutions of different compositions. Since graphite is known to have a surface predominantly hydrophobic, these results are in accord with the generalization that better surface wetting, in this case by non-polar liquids, results in deflocculation and lower sedimentation volumes.

The application of this generalization, applied to solids of hydrophobic surface, is somewhat diminished by the fact, often overlooked, that relatively small amounts of a hydrophilic surface constituent may greatly affect the behavior of solids predominantly hydrophobic. The lubricating properties of graphite, for example, have been shown by Savage⁷ to depend on the presence of traces of water vapor, presumably held at the surface by traces of a hydrophilic surface constituent.⁸ The same cause is held responsible for the lowering of the sedimentation volumes of graphite in benzene solutions by the addition of 0.01% Arquad HT (Armour and Company) or by 0.01% lauric acid. By adsorption on the small hydrophilic surfaces of the graphite, effected by means of the polar portion of the surface-active molecule, the non-polar portion of the molecule then somewhat blankets that part of the surface; the whole particle is therefore better wetted by the benzene and the sedimentation volume is decreased. Arquad HT is apparently more effective than lauric acid for this purpose, since it causes a greater reduction of the sedimentation volume of each graphite (Fig. 1).

3. Influence of Miscible Water.—Bloomquist and Shutt⁹ have found, for glass spheres, that the sedimentation volumes in organic liquids miscible with water were the same as for water. It is probable that too little difference in dielectric constant existed between the various liquids used. In Figs. 2 and 3 results are reported for water-dioxane mixtures, where the dielectric constant varies from 2 to 80, and a regular variation of the sedimentation volumes can be observed. It is found that there is always a greater reduction of the

sedimentation volumes of polar solids on addition of the initial percentages of water to dioxane than there is on further dilution of the solution, and for non-polar solids a similar effect is observed on addition of the initial percentage of dioxane to water. This initial larger relative decrease of sedimentation volume is ascribed to adsorption of water by polar solids in the one case, and to adsorption of dioxane by non-polar solids in the other. The adsorption is particularly marked for silica (Santocel ARD). On further dilution the adsorption becomes less marked, and after 10–15% concentration of solute has been reached there follows a linear proportionality between the decreasing sedimentation volume and the increasing solute concentration. The slope of the curve here is small and could easily lead to the conclusion of Bloomquist and Shutt⁹ that it is zero for glass spheres, or of McBain⁹ that it is zero for graphite.

The slopes of the curves of Fig. 2 are positive for graphite and Attapulgit and negative for silica and copper phthalocyanine. The slope measures the variation of sedimentation volume with dielectric constant, and it is well known that polar solids are deflocculated in liquids of high dielectric constant,¹⁰ and that flocculation occurs in liquids of low dielectric constant.¹¹ These results also support, as do those of Fig. 1, the validity of the converse of this theorem for non-polar solids, taking graphite as the exemplar. Sedimentation volumes of finely divided solids in water-dioxane mixtures can therefore be used to determine whether the surface operative in thickening action is polar or non-polar. Positive slopes to curves plotted as are those of Fig. 2 indicate the operation of a non-polar surface in thickening, and negative slopes are evidence of the action of a polar surface.¹²

When it was attempted to verify the effect of varying the dielectric constant of the dispersing medium by using different single liquids the results failed to show the regular variation of sedimentation volume that had been obtained with water-dioxane solutions. A similar trend indeed could be detected, but it was subject to much exception. It is believed that specific interactions may obscure a relationship that is demonstrated unequivocally by means of a series of solutions differing from each other only in composition.

4. Influence of Immiscible Water.—The effect of immiscible water on sedimentation volumes of polar solids is dramatically opposite to its effect when miscible with the medium. It is well known that immiscible water *increases* the sedimentation volumes of polar solids,⁵ and the present investigation has demonstrated that both by adsorption of water and by the change of dielectric constant, miscible water *decreases* the sedimentation volumes of polar solids. In Fig. 4 the behavior of graphite and copper phthalocyanine is the same as that re-

(10) W. D. Harkins and D. M. Gads, *THIS JOURNAL*, **36**, 86 (1932).

(11) B. Kopelman and C. C. Gregg, *ibid.*, **55**, 557 (1951).

(12) The designation of the copper phthalocyanine surface as polar is contrary to its obvious macroscopic properties, which, as shown by its inability to be wetted by water, are extremely non-polar. The adsorption of water vapor by copper phthalocyanine is the subject of a succeeding paper of this series, and shows the importance of small polar percentages of the total area.

(6) J. W. McBain, "Colloid Science," D. C. Heath and Co., Boston, Mass., 1950, p. 291.

(7) R. H. Savage, *J. Appl. Phys.*, **19**, 1 (1948).

(8) E. V. Ballou and S. Ross, *THIS JOURNAL*, **57**, 653 (1953).

(9) C. R. Bloomquist and R. S. Shutt, *Ind. Eng. Chem.*, **32**, 827 (1940).

ported for solids known to have polar surfaces, and it is therefore deduced that small polar portions of the surface are responsible for the observed effects.

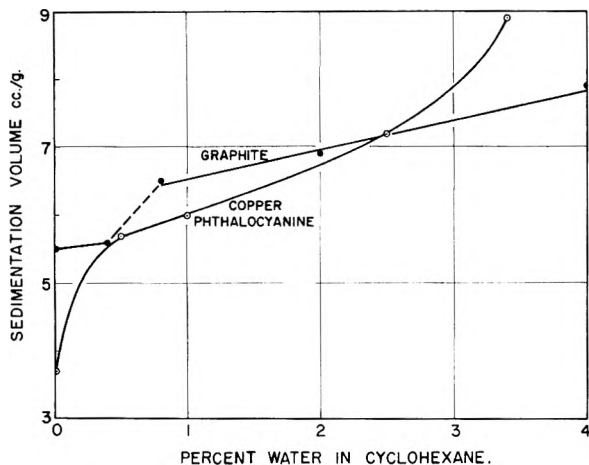


Fig. 4.—Sedimentation volumes of graphite and of copper phthalocyanine in cyclohexane plus immiscible water.

The theory of the behavior of immiscible water is given by Fischer.⁵ "The manner in which flocculation is brought about can be visualized in the following way. The particles initially are distributed uniformly throughout a medium such as mineral oil. It may be assumed that no material is adsorbed at the solid-liquid interface and that the oil has spread over the particle surface. If water, or certain other liquids (as will be shown later), is now added to the suspension, it concentrates at the interface and, if the solid is preferentially wetted by the water, the oil is displaced and a film of water forms on the solid, separating the solid from direct contact with the liquid. The interface is now completely changed and, if sufficient water is present it will act as a cementing medium between the dispersed particles, causing flocculation."

The visual picture of flocculation given above by Fischer supplements the consideration of the surface energies of the system. Two immiscible liquids, such as cyclohexane and water, have large interfacial energies and accordingly tend spontaneously to reduce the area of interface between them. Oil drops in water, or water drops in oil, will therefore, in the absence of a stabilizing agent, which acts by reducing the high interfacial energy, tend to cohere. Polar surfaces of a solid in a non-polar fluid, such as a lubricating oil, have a large interfacial tension and will tend toward flocculation of the particles. When those particles are coated with *immiscible* water, the interfacial tension, now effectively that between oil and water, is made still greater and the tendency to coalesce and flocculate is thereby increased.

When dioxane or other water-miscible organic solvent is substituted for the hydrocarbon oil, the first step of the process, *viz.*, the preferential adsorption of water, will still take place. But since dioxane and water are miscible in all proportions, there is now no interfacial tension between the adsorbed water layer and the surrounding medium. The only surface energy that is present is that between the solid surface and the adsorbed water layer. But this solid/liquid interfacial energy, originally large between the polar solid and the non-polar dioxane, has been reduced by the adsorption of water, which effectively replaces it by an interface of low surface energy between polar solid and adsorbed (polar) water. Since the net effect is a reduction of the original surface energies, there is now less tendency to flocculate and hence there results a decreased sedimentation volume.

It could similarly be expected that a powder with a lipophilic surface when dispersed in water would be deflocculated by a miscible non-polar additive, such as dioxane. The reasoning is an analog of that given above, and observations are in accord with it. Figure 2 shows that both graphite and Attapulgit when dispersed in water are deflocculated by the addition of dioxane. In these cases, it is preferential adsorption of dioxane by a lipophilic surface that is the cause of the phenomenon.

DISCUSSION

HERBERT L. DAVIS.—This is a most interesting and stimulating paper. One might be inclined to expect that the orientation of bound solvent layers might increase sedimentation volumes—the greater the solvation, the greater the volume. But your figures indicate the reverse to be the case—that solids settle more compactly in liquids which wet them best. Increasing solvation is often a mechanism of colloidal stability, and yet in sedimentation the opposite effect holds. Is this a function of the degree of approach of particles to each other with layers of liquid between? Do you conclude that the effects of lauric acid and Arquad show that they are adsorbed on the hydrophilic areas of the graphite so as to render the solid more hydrophobic? Do these techniques appear applicable to arranging many solids and liquids in terms of relative HLB (hydrophilic-lipophil balance) values? This seems a very desirable next step, to replace the uncertainty now prevailing. Are such values likely to be comparable to those measured by Dr. Bartell over the years?

SYDNEY ROSS.—(1) The presence of solvated layers on a well-wetted solid surface affects the sedimentation volume less than does the irregular aggregation induced by poor wetting of the solid. (2) The question of colloidal stability is not germane to these sediments, none of which is stable: nevertheless, slow settling (greater "stability") accompanies solvation and a resulting smaller sedimentation volume. (3) It is indeed concluded that the effects of lauric acid and Arquad show them to be adsorbed on the hydrophilic areas of the graphite, so as to render the solid particles more hydrophobic. (4) At present it would be too much to claim that these techniques can be used to obtain HLB values,¹³ though it is certainly a suggestive idea.

(13) W. C. Griffin, *J. Soc. Cosmetic Chemists*, 1, 311 (1949).

THE CHARACTERIZATION OF PHYSICAL ADSORPTION SYSTEMS. II. THE EFFECTS OF ATTRACTIVE INTERACTION BETWEEN ADSORBED MOLECULES

BY DONALD GRAHAM

Contribution No. 155 from Jackson Laboratory, E. I. du Pont de Nemours and Co., Wilmington, Delaware

Received March 5, 1954

Factors determining the role of attractive interaction in adsorption are outlined. A method for calculating its contribution to the differential free energy of adsorption on uniform surfaces is described and illustrated by application to adsorption data from typical systems.

Introduction

Interaction between adsorbed molecules has been one of the most misunderstood aspects of the adsorption process. This factor has been treated in many different ways by different investigators; sometimes by addition of a parameter to an adsorption isotherm, sometimes by use of an attraction constant in a two-dimensional equation of state. These methods fail in general application to the first monolayer through neglect of the effects of localization or of the entropy change in coalescence. It is, therefore, useful to define some of the factors which determine the character of adsorbate interaction and to measure the contribution of this interaction to the adsorption bond in real systems.

Discussion

Interaction between two or more molecules adsorbed on adjacent sites may cause these molecules to either repel or attract one another. Repulsion may occur when molecules are adsorbed on sites so closely spaced that some interpenetration of atomic radii is required. Also, in the adsorption of similarly charged ions, electrostatic repulsion may overcome the van der Waals attraction, leaving the over-all effect one of repulsion. However, in most cases observed experimentally, the dominant interaction is one of attraction resulting from van der Waals forces, dipole-dipole interaction, or hydrogen-bonding. This paper is, therefore, primarily concerned with the effects of attractive interaction between adsorbed molecules.

Adsorbed molecules which attract one another are bound to the adsorbent surface more strongly than if alone. The energy required to remove one of them must be sufficient to overcome both its bond to the adsorbent and its attraction for its neighbors.

Polar substitution of the adsorbate molecules can either weaken or strengthen this interaction. If the polar groups form relatively strong bonds (for example, hydrogen bonds) with specific atoms or groups in the adsorbent surface, the resulting localization may prevent any appreciable interaction between the adsorbed molecules.

On the other hand, if the adsorption bond involves only van der Waals energy, localization is less important and any polar substituents of the adsorbate are free to interact with each other. In the absence of hydrogen-bonds to the adsorbent, orientation, or polarization, the inherent tendency for adsorbed molecules to attract one another is related to their latent heat of vaporization.

Opposing the tendency for adsorbed molecules to

interact, is their tendency to assume the most random distribution or to increase the entropy of the system. Coalescence of adsorbed molecules is accompanied by a reduction in entropy, other factors remaining constant. If the adsorbed, partially filled monolayer could be considered an ideal two-dimensional gas (both before and after coalescence), the reduction in entropy with coalescence would be $-\Delta S = R \ln 1/\theta$, a quantity very large at low coverage and approaching zero logarithmically at completion of the monolayer. At low coverage, there will be a strong tendency for the adsorbed molecules to keep as far apart as possible. As the average distance between them is reduced, with increasing coverage, the tendency for interaction will increase. The coverage at which interaction becomes important may be expected to vary inversely with the inherent strength of the interaction as measured by the latent heat of the adsorbate.

Application of these relations to real adsorption processes requires a measurement, from adsorption data, of the contribution of interaction between the adsorbed molecules to the strength of the adsorption bond.

A qualitative approach to the problem is found in a previous paper.¹ A simple equilibrium function² is developed which, for ideal monolayer adsorption, yields the equilibrium constant. Ideal conditions are approached in adsorption on uniform surfaces at values of θ below that at which the effects of attractive interaction between adsorbed molecules become appreciable. The resulting constant value of the equilibrium function, from data at low coverage, E.F.₀, thus represents the system in its ideal (non-interacting) state. In systems which permit the adsorbed molecules to interact, the effects of this interaction appear at a value of θ below 0.5 as an increase in E.F. with increasing θ . This increase may be considered due only to this interaction up to the point at which multilayer adsorption becomes important, usually above $\theta = 0.7$ but varying with the strength of adsorption of the first monolayer.

The above concept is now given more quantitative character by the calculation of free energy changes. The strength of adsorption may be measured as the differential free energy of adsorption ($-\Delta F$), defined as the change in free energy accompanying the transfer of one mole of adsorbate from the saturated gas to the adsorbed film at any

(1) D. Graham, *THIS JOURNAL*, **57**, 665 (1953).

(2) E.F. = $\theta/(1 - \theta)(P/P_0)$, where θ = fraction of surface covered, P_0 = vapor pressure of liquid adsorbate, P = equilibrium pressure.

specified coverage (θ) and absolute temperature (T). This quantity is calculated from adsorption data in the usual way

$$-\Delta F = RT \ln P_0/P$$

The corresponding free energy change for an ideal system (without interaction) is obtained from the low coverage equilibrium function

$$(-\Delta F_{\text{ideal}}) = RT \ln \frac{(1-\theta)(E.F._0)}{\theta}$$

The values of $(-\Delta F)$ and $(-\Delta F_{\text{ideal}})$ are the same in the ideal region, but $(-\Delta F)$ becomes the larger as the contribution of lateral interaction becomes important. From this point, up to that at which the effects of other factors (such as multilayer adsorption) appear, the difference between these two values represents the contribution of lateral interaction between the adsorbed molecules

$$(-\Delta F_{\text{interaction}}) = (-\Delta F) - (-\Delta F_{\text{ideal}})$$

Application to Adsorption Data

A. Hydrogen-bonded, Non-interacting Adsorption.—Prevention of lateral interaction by strong localization in hydrogen-bonded adsorption is illustrated by the adsorption of water on asbestos as represented in Fig. 1.³

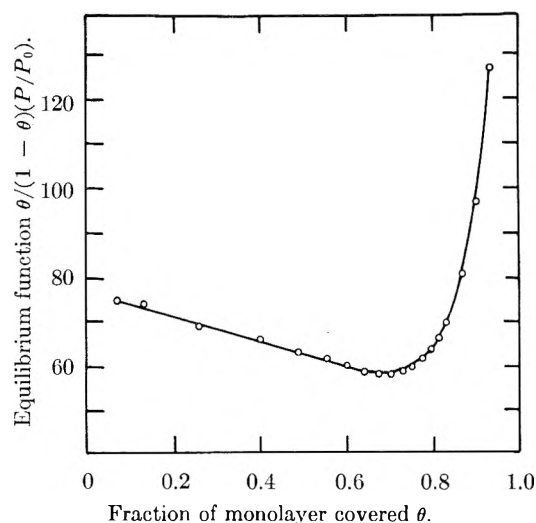


Fig. 1.—Localized adsorption of water on asbestos at 23° (from data of Zettlemoyer, *et al.*).

The decreasing value of E.F. with increasing coverage shows some degree of surface non-uniformity (asbestos is both silicate and aluminate), but the extent is not sufficient to obscure any appreciable effect of interaction between the adsorbed molecules. In localized adsorption, some of the molecules must occupy adjacent sites at any value of θ above 0.5. The first upward inflection of E.F. occurs at $\theta \approx 0.7$, a coverage at which second layer deposition becomes appreciable.

B. Attractive Interaction in van der Waals Adsorption.—If the chemical natures of the adsorbent surface and the adsorbate molecules do

(3) From work reported in part by A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *THIS JOURNAL*, **57**, 649 (1953). The data summarized in Fig. 1 were received in a private communication from Professor Zettlemoyer.

not provide specific atoms or groups capable of direct interaction (either electrostatic or dipole-dipole), the adsorption bond is limited to van der Waals energies. Localization, in this case, is less important than in hydrogen-bonded adsorption, and the adsorbed molecules tend to interact in a manner and to a degree determined by the character of the system as illustrated below.

1. The Effect of Adsorption Strength.—The effect of adsorption strength upon lateral interaction is illustrated in Fig. 2 by data from the adsorption of nitrogen (A), on the 110 face of crystalline copper at 78.1°K.^{4a} and (B), on Graphon at 78.4°K.^{4b}

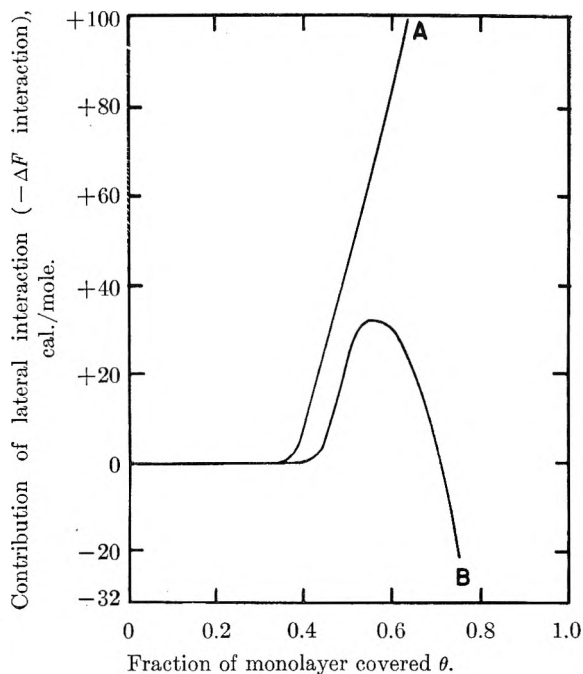


Fig. 2.—Effects of adsorption strength: A, nitrogen on 110 face of copper at 78.1°K. (from data of Rhodin); B, nitrogen on Graphon at 78.4°K. (from data of Joyner and Emmett).

In the case of nitrogen on copper, with adsorption of only moderate strength ($E.F._0 = 61.5$), the lateral interaction contribution appears at $\theta \approx 0.35$, rising almost linearly to a value exceeding 100 cal./mole at $\theta = 0.65$.

In the very much stronger adsorption on Graphon ($E.F._0 = 2600$), this contribution appears at only slightly higher coverage ($\theta \approx 0.40$). Also, the slope of the curve immediately above this point is approximately the same.

A wide variation in adsorption strength thus produces very little effect on either the coverage at which appreciable interaction appears or the strength of the interaction. This is consistent with the thought that these factors are determined by the inherent strength of the interaction and by an entropy which varies with θ but not by adsorption strength.

An important difference between these two sys-

(4) (a) T. N. Rhodin, *J. Am. Chem. Soc.*, **72**, 5691 (1950); (b) L. G. Joyner and P. H. Emmett, *ibid.*, **70**, 2353 (1948). Original data, runs 3 and 5 smoothed, Document 2530, American Documentation Institute, 1719 N St. N.W., Washington, D. C.

tems is indicated by the fall off in the nitrogen-Graphon curve above $\theta \approx 0.6$. This suggests a delayed equilibration involving the necessity for some shifting of adsorbed molecules to permit occupancy of the last portion of the adsorbent surface. This "crowding" may be a result of strong adsorption which tends to magnify the localizing effects of slight variations in energy of adsorption which occur over even the most uniform surfaces.

2. The Effect of Latent Heat of Vaporization of the Adsorbate.—Three different adsorbates representing a wide range of latent heats of vaporization, all adsorbed on Graphon, illustrate the effects of differences in latent heat. The first is nitrogen (the data cited in the preceding paragraph); the second, ethyl chloride,⁵ and the third, methanol.⁶

Pertinent data are summarized in Table I and Fig. 3.

TABLE I
ADSORPTION ON GRAPHON OF SUBSTANCES OF DIFFERENT LATENT HEATS

Adsorbate	Nitrogen	Ethyl chloride	Methanol
Temp. of adsorption, °K.	78.4	273	273
Latent heat of adsorbate (cal./mole)	1300	6000	9100
Ideal equilibrium function $E.F._0$	2600	10.8	0.28
Obsd. differential free energy of adsorption ($-\Delta F$) at $\theta = 0.5$ (cal./mole)	+1257	+1820	+696
Ideal differential free energy of adsorption ($-\Delta F_{ideal}$) at $\theta = 0.5$ (cal./mole)	+1232	+1300	-684
Contribution of lateral interaction to ($-\Delta F$) (cal./mole)	25	520	1380
Coverage (θ) at which strong interaction appears	0.4	0.07	$\rightarrow 0$

For these particular adsorbates, an increase in the latent heat is accompanied not only by a rise in the contribution of adsorbate interaction to the strength of adsorption but also by a marked drop in the strength of non-interacting adsorption. No explanation is offered at this time for the latter effect but the extremely weak adsorption of methanol at low coverage is consistent with the recognized hydrophobic character of pure carbon surfaces.

3. Two Dimensional Condensation.—Adsorption at temperatures below the two-dimensional critical point,^{7,8} if not strongly localized, may involve two-dimensional condensation. When this occurs, the onset of appreciable interaction is accompanied by formation of a condensed phase which tends to maintain equilibrium with the ex-

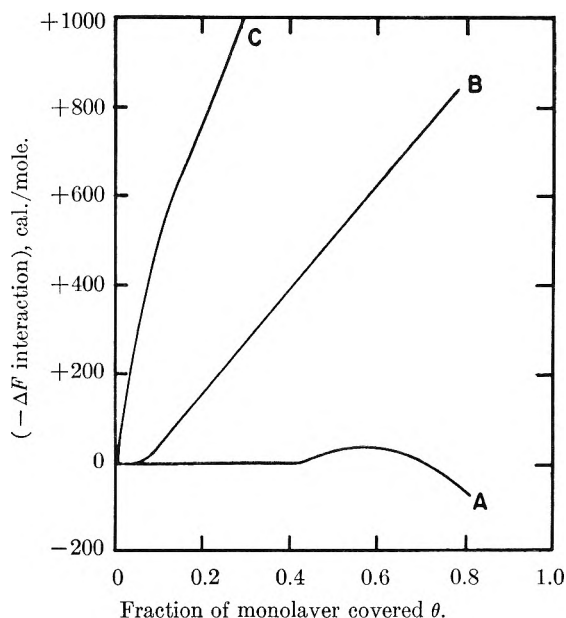


Fig. 3.—Effects of latent heat of adsorbate: A, nitrogen on Graphon at 78.4°K. (from data of Joyner and Emmett); B, ethyl chloride on Graphon at 0° (from data of Mooi, Pierce and Smith); C, methanol on Graphon at 0° (from data of Pierce and Smith).

panded phase during further addition to the monolayer. Adsorption, therefore, proceeds from the beginning of condensation to essential completion of the monolayer without change in the equilibrium pressure. This means that throughout the condensation the value of ($-\Delta F$) is no longer a function of θ but is a constant. Two-dimensional condensation of a monolayer on an adsorbent surface is thus analogous to the more familiar three-dimensional condensation of a vapor pumped into a vessel of fixed volume.

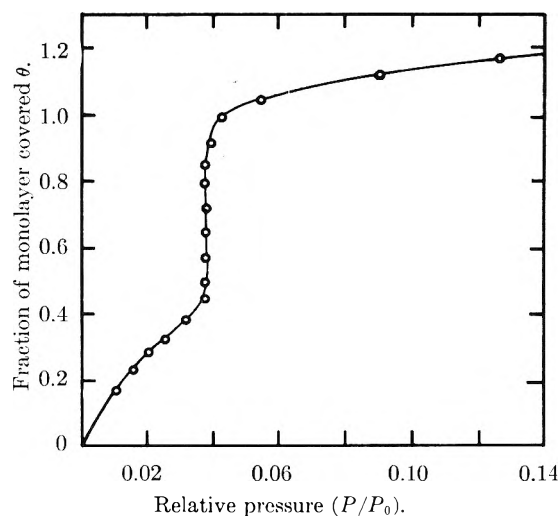


Fig. 4.—The two-dimensional condensation of ethane on cube NaCl at 90°K. (from data of Ross and Winkler).

A clean cut example of two-dimensional condensation is found in the adsorption of ethane on cube NaCl at 90°K.⁹ The isotherm is shown in Fig. 4 employing the following parameters

(9) S. Ross and W. Winkler, *ibid.*, **76**, 2637 (1954).

(5) J. Mooi, C. Pierce and R. N. Smith, *THIS JOURNAL*, **57**, 657 (1953).

(6) C. Pierce and R. N. Smith, *ibid.*, **54**, 354 (1950).

(7) J. H. de Beer, "The Dynamical Character of Adsorption," The Oxford University Press, London, 1953.

(8) H. Clark and S. Ross, *J. Am. Chem. Soc.*, **75**, 6081 (1953).

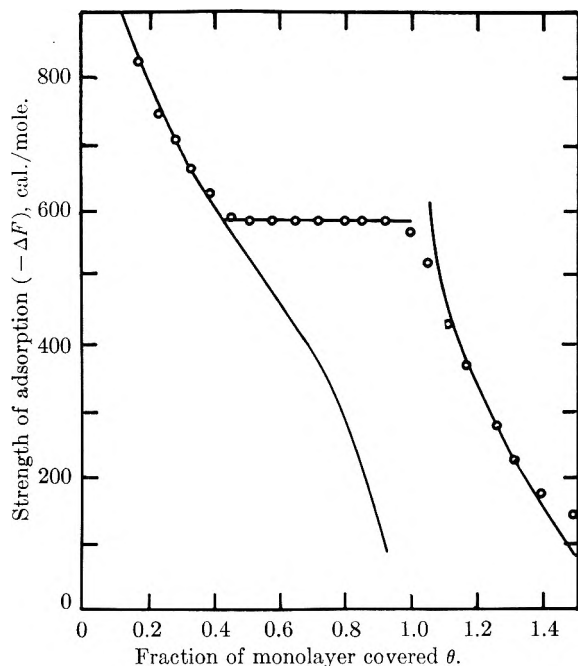


Fig. 5.—Two-dimensional condensation of ethane on cube NaCl at 90°K. (from data of Ross and Winkler).

$V_m = 353$ cc. mm./g. = 0.465 cc. S.T.P./g. (detd. from a $1/P$ vs. $1/V$ plot of the lower portion of the isotherm)

$P_0 = 0.007$ mm.¹⁰

Since $(-\Delta F)$ is not a function of θ during the condensation process, a plot of $(-\Delta F_{\text{interaction}})$ vs. θ would have little meaning. Figure 5 shows the change in $(-\Delta F)$ for the three parts of the process. Up to a coverage of $\theta \approx 0.42$, the ideal curve (E.F.₀ = 19.5) is followed quite closely. At this point, condensation begins and continues at $(-\Delta F) = 587$ cal./mole until essential completion of the monolayer. Theoretically, with perfect equilibration, the adsorption should follow the isobar to the point of intersection with the curve for E.F.₀ (second layer), at a value $\theta \approx 1.05$. The experimental points, although not showing a sharp transition at completion of the monolayer, do join and follow the theoretical curve (E.F.₀ = 1.55) for the second layer up to $\theta \approx 1.3$ where multilayer adsorption becomes important.

Acknowledgment.—The author wishes to thank Professor Sydney Ross and Professor A. C. Zettlemoyer for access to unpublished data, and Dr. A. Di Giacomo and Dr. R. Pariser for helpful discussion of the entropy change in coalescence.

(10) A. W. Tickner and F. P. Lossing, *THIS JOURNAL*, **55**, 733 (1951).

DISCUSSION

W. B. INNES —This approach appears to be a simple and quantitative one for studying interaction on uniform surfaces. Do you think a similar procedure would be useful in studying non-uniformity of surfaces? Do you consider your equilibrium function " EF " as the practical equivalent of the BET " C " value and the actual equivalent for the case where adsorption is limited to a single layer?

DONALD GRAHAM.—The quantitative method outlined here is limited to systems in which the adsorbent is uniform with respect to the adsorbate. Qualitative treatment of interaction on heterogeneous adsorbents was covered in reference (1). Heats of adsorption derived from the BET " C " value are rough approximations at best. The relation of the EF to the standard free energy of adsorption is presented in reference (1).

M. L. CORRIN —Two pertinent points may be mentioned here in connection with this paper. (1) It is possible to adopt one of two extreme points of view in considering the thermodynamics of the adsorption process. (a) One may assume that the effect of the adsorbent is exclusively one of perturbing the adsorbate. Perturbation of the adsorbent by the adsorbate is considered negligible. This point of view seems intuitively to be in error at low surface coverages. It is not true in systems containing liquid surfaces. With solids one might expect that the lattice spacings and potential functions in the surface regions would be altered when adsorption occurs. The free energy function described by the author is derived on the basis of this view (a) and any terms involving surface effects other than in the perturbation of the gas is neglected. (b) The surface region may be considered as an entity and only over-all effects in this region considered. This approach is the one successfully employed with liquid systems. The thermodynamics of this system are similar to those employed, for example, when gravitational effects are significant. With surfaces, surface energy terms are employed. Thus if the chemical potential of the adsorbate in the surface region is defined as equal to that in the gas, the free energy expression will contain not only a term relating the chemical potential of the gas to its standard state but a term relating to the change in free surface energy occurring on adsorption.

(2) We have observed the following with respect to the two dimensional phase changes discussed by the author. For the adsorption of krypton on a calcium halophosphate at liquid nitrogen temperature, an apparent first order phase transition is observed if thirty-minute points are taken; the sample was contained in the usual cylindrical adsorption bulb. A similar effect was observed if the solid was placed in a tray system. If, however, the first increment of gas was allowed to remain in contact with the solid until equilibrium was attained (a matter of several days), no such transition was observed and the smooth isotherm obtained was found to join the previous discontinuous isotherms just above the region of apparent transition. We do not know at this time whether the effect noted above is a general one.

DONALD GRAHAM.—Perturbation of the lattice of a solid adsorbent unquestionably contributes to the free energy of the system. However, if this factor is not appreciably altered by interaction between the adsorbed molecules, it essentially disappears when the effect of interaction is evaluated as the difference between the differential free energies of the real and ideal systems.

THE HEATS OF SORPTION OF BROMINE ON SILICA GEL

By L. H. REYERSON AND ROBERT A. BRAND¹*School of Chemistry, University of Minnesota, Minneapolis, Minnesota*

Received March 5, 1954

An isotherm for the system bromine-silica gel was determined at 28.9° by a gravimetric method. At this temperature the isotherm was a Type II rather than a Type III which was reported at higher temperatures. Differential heats of adsorption were measured calorimetrically for the bromine-silica gel system at 28.9°. The heat of adsorption for the first layer was found to be considerably higher than the heat of liquefaction. The variation in the heat of adsorption with surface coverage was greater than that predicted by the BET theory.

Introduction

Previous studies in these laboratories² showed that bromine, at or above its boiling point, was adsorbed by silica gel to give Type III isotherms. Using the BET theory Brunauer, *et al.*,³ obtained a theoretical isotherm that fitted the experimental data by assuming that the heat of adsorption of bromine for the first layer was equal to the heat of liquefaction; *i.e.*, E_1 equaled E_L in the BET terminology. The investigation here reported was an experimental study of the heats of sorption of bromine on silica gel, attempting to determine quantitatively whether or not the assumption of Brunauer was correct. In order to test the postulate it was necessary that the measurements of the heats of adsorption be made at low relative pressures to preclude the possibility of multilayer formation. The experiments here reported were carried out at 28.9°.

Experimental

The problem involves the experimental determination of the heat evolved when one mole of gas is adsorbed by the solid surface as a function of the number of moles of gas already on the surface. An adsorption isotherm at the chosen temperature was first carefully determined. Then the heats evolved, due to a small increment of pressure increase of bromine, were measured as a function of the pressure. From the isotherm and the heat measurements it was possible to calculate the heat evolved per mole of gas adsorbed. A gravimetric apparatus similar to that described by Reyerson and Wertz⁴ and the same as used by Honig⁵ was used in this study. The quartz spiral of 18 mm. in diameter was carefully calibrated at the temperature of the experiments. The force constant was found to be independent of the total load up to an increase of 250 mg. The temperature coefficient of the force constant was found to be small but the spring extension depended markedly on the temperature. The glass tube supporting the spring was therefore thermostated by water jacketing and then circulating water from a ten-gallon thermostated bath was pumped through this jacket. The sample bulb was suspended from the quartz spiral by means of two glass fibers. The section of the tube containing the sample was also water jacketed and this was connected in series with the jacket surrounding the spiral. Thus the sample and spiral were maintained at the same temperature which could be kept constant to within $\pm 0.02^\circ$. The extension of the spiral was observed with a 10-cm. traveling microscope mounted on a massive steel pedestal. In order to check any expansion or contraction in this mounting framework or in the pedestal a glass rod 2 mm. in diameter was suspended inside of the quartz

spiral from the same hook. This provided an internal reference mark for all measurements.

The vapor pressure of the bromine in the system was controlled by a cryostat modeled after that of Scott and Brickwedde.⁶ This cryostat surrounded a long U tube which was placed between the breakoffsky containing the purified bromine and the tube containing the silica gel sample hanging from the spiral. The silica gel used in this study was taken from a larger sample that had been carefully purified by first treating it with concentrated nitric acid washing for several days with conductivity water and then electrolysing for a week. It was then oven dried at 120° and kept in sealed flasks. The bromine was a middle fraction taken in the vacuum distillation of a larger middle fraction. This was obtained by collecting the middle third while distilling through a tube containing phosphorus pentoxide. The bromine in each sample bulb was frozen by immersion in a liquid nitrogen bath after which the system was opened to a vacuum pump. The side arm to each sample tube was then sealed off and the tube, with a breakoffsky in place, sealed on to the sorption system. A small weighed glass bulb was filled with silica gel, 28-43 mesh, dried in an oven at 120° for 24 hours and then weighed to the nearest tenth of a mg. The bulb was then suspended from the spiral. The glass system already attached to the vacuum line was sealed off from the surroundings. A tube furnace slowly heated the section of the tube containing the silica gel to a temperature of 300°. The remainder of the tube was coated with soot and surrounded by infrared lamps. The furnace tube heating continued for 24 hours, at which time careful evacuation of the system was started. As soon as the pressure fell below 1 micron the infrared lamps were turned on and the sample temperature increased to 400°. Evacuation was continued for 24 hours after the heating together with additional flaming no longer raised the pressure above 1.0×10^{-5} mm. The system was then sealed off from the pumps and allowed to cool. A centrifugal pump began circulating water from the large thermostat through the jackets and a bath of Dry Ice and acetone placed around the tube of liquid bromine. Initial readings were taken and these were repeated after 24 hours to ensure that the system had reached a steady state. After breaking the seal to the bromine, readings were taken until consecutive readings checked. Each record of spring extension or reference point was the average of three readings having a deviation of no more than ± 3 microns. The first reading gave an adsorption value at the vapor pressure of the bromine in the Dry Ice-acetone-bath. The cryostat surrounding the "U" tube was then put into operation at a slightly higher temperature and the bromine distilled into the "U" tube. The temperature of the cryostat was controlled to $\pm 0.01^\circ$ by a platinum resistance thermometer used as one arm of a resistance bridge. Chloroform was used as the cryostating liquid and Dry Ice-acetone for cooling. A photocell was used in a thyatron phase shift apparatus as illustrated by Muller, Garman and Droz.⁷ As the cryostat cooled from the set temperature the unbalanced bridge caused light reflected from the galvanometer mirror to fall on the photo cell. This caused an increased electrical input to flow through a resistance heater. The system operated for both heating and cooling. With additional secondary controls the cryostat operated very effectively within the limits given above at a set temperature. By

(1) Adapted from a portion of the thesis of Robert A. Brand submitted to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the Ph D. degree.

(2) L. H. Reyerson and A. E. Cameron, *THIS JOURNAL*, **39**, 181 (1935).

(3) S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, *J. Am. Chem. Soc.*, **62**, 1725 (1940).

(4) L. H. Reyerson and J. E. Wertz, *THIS JOURNAL*, **53**, 234 (1949).

(5) J. M. Honig, Ph.D. thesis, University of Minnesota, 1952.

(6) R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **6**, 401 (1931).

(7) R. H. Muller, R. L. Garman and M. E. Droz, "Experimental Electronics," Prentice-Hall, Inc., New York, N. Y., 1942, p. 147.

setting the cryostat for a series of different temperatures it was possible to obtain an isotherm over the relative pressure range from zero to 0.45.

The amount of sorbent that could be used in a calorimeter of reasonable size coupled with the necessity of adding the gas in small increments placed several restrictions on the construction of the system. A calorimeter assembly, patterned after that used by Ward,⁸ was finally selected since it seemed well adapted for isothermal determinations where the heating period was limited to short time intervals. Three concentric copper cans were constructed of sheet metal seven hundredths of an inch thick. The outer can was ten inches in diameter and sixteen inches high. Each was insulated from the other by a half inch of kapok. The can assembly was placed in a masonite box fourteen inches square by twenty inches high. The outer can rested on compressed cork and the surrounding space was filled with ground cork. The top of the masonite box and the lid of the outer can were fastened together through a two-inch slab of cork. A thermoregulator, built for the purpose, was placed inside the outer can. This regulator could be set to control, by means of an electronic relay, the electrical input to a nichrome heater, wound directly on the outer can. The heater was non-inductively wound and alternating current used for heating. The heating rate was adjusted by a rheostat to obtain a minimum period of the on-off cycle. Water filled the inner can to within one inch of the top with no stirring. Tap water circulating through three-eighths-inch copper tubing imbedded in the ground cork provided the constant cooling for the calorimeter thermostat.

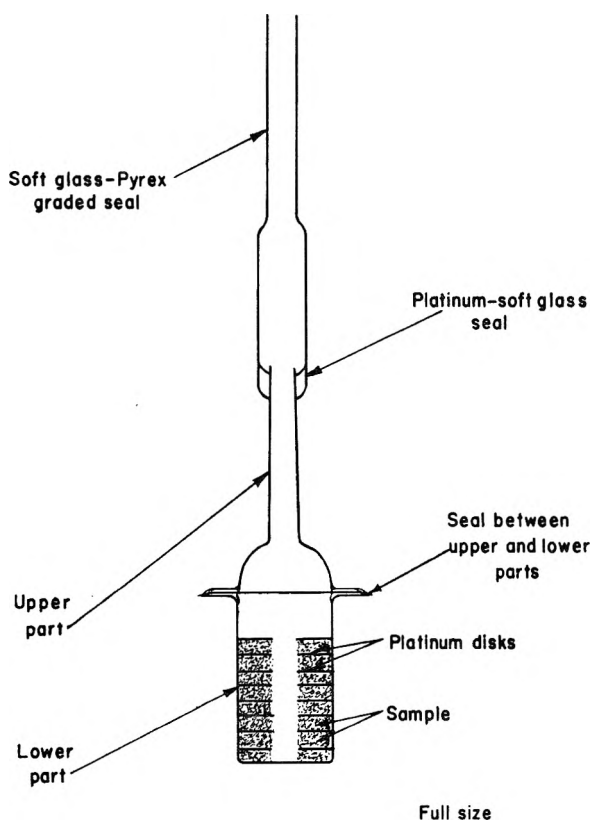


Fig. 1.—Calorimeter assembly.

A brass tube, of sufficient size to hold the half-pint Dewar flask containing the calorimeter, had a brass plate soldered on the bottom and a flange on the top. A smaller tube, with a brass disk on its top to support the Dewar, was set within the larger tube. The Dewar was held concentric to the tube by sponge rubber rings. This entire assembly, attached to the lid of the inner can, formed the calorimeter chamber. A thirty-junction copper-constantan thermel was used to determine the temperature rise of the calorimeter.

The measuring junctions were evenly distributed around the outside of the brass ring and insulated both from each other and the ring. The entire assembly was coated with formvar varnish. The brass ring, with the thermel junctions attached, was mounted next to the calorimeter within the Dewar. The reference junctions were placed in equally spaced holes drilled in a split ring. This ring was forced into the brass tube, outside of the Dewar, in such a manner that it expanded tightly against the wall, resulting in good thermal contact.

It was decided that an all platinum calorimeter would be best for the study. Dr. John E. Wertz of this Laboratory designed and then supervised its construction. Figure 1 schematically shows the way in which it was assembled. The platinum top was sealed to a soft glass tube and this in turn through a graded seal to a Pyrex tube that was then connected to the vacuum line and the bromine supply. The lower part was designed so that small amounts of silica gel could be poured around a bakelite rod, then covered by a platinum disk and pressed tightly into place. Eight successive fillings of about 4 mm. depth were covered by the platinum disks and tightly packed. The bakelite rod was then removed and the hole, left by the rod, provided a space for the bromine vapor to penetrate the sample rapidly. This part of the assembly was oven dried for 24 hours and then weighed to ± 1 mg. Previous weights of the platinum disks and the lower part of the calorimeter subtracted from the total weight gave the weight of the silica gel. The flanges of the upper and lower parts of the calorimeter had been previously rolled to a thickness of 0.010 inch by a pressure roller device, developed by Dr. Wertz. The two parts were clamped together, and, after protecting the upper glass seals against heat, the thin flange heated to a yellow heat by a high temperature flame just as it passed between pressure sealing rollers. This operation fused the two parts of the calorimeter together and the system proved to be gas tight when evacuated.

The whole system was degassed in the same manner as used for the sorption isotherm. The platinum calorimeter was placed in a brass sleeve and a heavy brass block with the ring containing the thermel above it. The whole was then placed in the Dewar and copper leads from the thermel were brought out through a bakelite tube to a twenty-four position thermocouple switch. The e.m.f. of the thermel was measured by a Leeds and Northrup White Single Thermocouple potentiometer using a type HS galvanometer mounted on a Mueller suspension as a null detector. An illuminated scale seven meters away was viewed through a surveyor's level. This scale could be read to ± 0.3 mm. which corresponds to about ± 0.01 microvolt. Electrical heating was used to calibrate the calorimeter. A heating element of 100 ohms resistance had been wound on the brass block that supported the platinum calorimeter in the Dewar and the current was supplied by a six-volt storage battery. The length of the heating period was controlled by a seconds pendulum clock adjusted to within ± 1 second a day by standard time signals. A half-hour drain through a dummy heater made it possible to use a steady current for calibration. Prior to the flow of current into the calorimeter the readings of the thermocouple were taken each minute for ten minutes and at the close of the heating period the readings were taken for 15 minutes. These readings gave both the fore-drift and the after-drift of the system. When Tian⁹ originally proposed this system of alternating thermel conductors and insulators as a thermostat for a calorimeter, he showed that for short period oscillations in the temperature of the outer can the amplitude of oscillation would be reduced by a factor of about one-hundredth in the next inner can. In the system here used the outer can was regulated to $\pm 0.01^\circ$. The variation in the inner water-bath should, therefore, be $\pm 0.000001^\circ$. Actually no short term variations were observed by measurements to $\pm 0.00002^\circ$ in following the drift of the calorimeter with respect to the water-bath. Fore- and after-drift readings gave consistent results that plotted to straight lines as did the plot of thermal readings against energy equivalent. After careful calibration the same manipulations were followed as to heat measurements when bromine was admitted to the silica gel at varying pressures. The bromine was added to the sample in the same way that it was added in determining the isotherm. However, a temperature controller as designed by Penther and

(8) A. H. F. Ward, *Proc. Cambridge Phil. Soc.*, **26**, 278 (1930).

(9) A. Tian, *J. chim. phys.*, **20**, 132 (1923).

Pompeo¹⁰ was added to the cryostat controls in order to quickly change its temperature to reach a new vapor pressure of bromine. A new temperature could be reached in from three to four minutes and the observed variation was $\pm 0.01^\circ$. The silica gel sample used in determining the isotherm weighed 0.711 g. Heats of sorption were measured on two samples of the gel. The first one weighed 6.46 g. and the second 6.557 g.

Experimental Results

The isotherm data are shown plotted in Fig. 2. Here the number of millimoles sorbed is plotted as a function of the relative pressure. The observed e.m.f.'s of the cryostat thermocouple were converted to temperatures using the table of Roeser and Dahl.¹¹ The cryostat temperatures were then converted to the vapor pressures of bromine from a composite plot of the vapor pressures of bromine taken from the data of several authors.¹²⁻¹⁶ The data from the several sources do not show too good agreement so that the curve as constructed gives a probable error of about three per cent. This uncertainty affected the plotting of the isotherm but made no difference in the evaluation of the heats of sorption. This was so because the amounts sorbed, as well as the heats evolved, were measured as functions of cryostat temperatures. The amounts of bromines sorbed were determined by the net extension of the quartz spiral spring for successive changes in the vapor pressure of bromine. This extension of the spring multiplied by its determined sensitivity gave the increase in sample weight. The proper buoyancy corrections, due to changes in gas density, were made. The maximum temperature used in setting the cryostat was 9.97° . Since P_0 for bromine at 28.9° is 251.4 mm. the upper P/P_0 value used in the isotherm was 0.4368.

Heats of sorption were measured on two different samples of silica gel. The results of both sets of determinations were plotted as shown in Fig. 3. Calorimeter calibrations were carried out before each of the heat runs. Here the temperature rise of the calorimeter was plotted as a function of the electrical heat input. A reasonably good straight line was found for the calibration. The magnitude of the relative error between the various heat measurements can be estimated from the calibration data to be $\pm 2\%$. The error in the determination of the amount sorbed per gram of sample was found to be ± 0.0005 millimole per gram. The error can be estimated to be ± 0.0003 millimole per gram if the readings are taken from the smooth isotherm. The average number of millimoles sorbed per gram for a calorimetric determination was 0.015, giving a probable error of $\pm 2\%$. This together with the estimated error for heat determinations gave a total probable error in an individual value of the heat of sorption of $\pm 3\%$. Figure 3 was con-

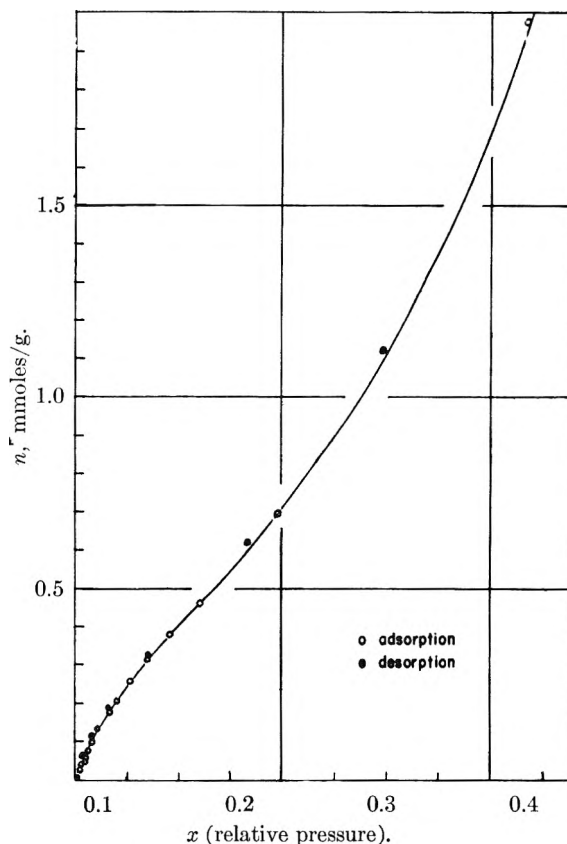


Fig. 2.—Sorption isotherm, bromine on silica gel at 28.9° .

structed by empirical selection of a smooth curve where the sum of the residuals was equal to zero. A probable error was determined to be $\pm 3\%$ from the sum of the absolute values of the residuals. This is in good agreement with the estimated experimental error. The relative vapor pressures of bromine used in the heat determinations ranged from just above zero to just under 0.12. The actual energy in calories, as measured, ranged from 0.531 to 2.83 small calories. Most of the determinations were actually in the neighborhood of 1 small calorie.

Discussion

The isotherm of the sorption of bromine on silica gel at 28.9° is definitely of the sigmoid or Type II of the BET theory. The earlier work from this Laboratory indicated Type III isotherms at 58 and 79° . The isotherms, previously measured, appeared to be convex toward the pressure axis at all points. There is some question as to the correct shape of the early isotherms at the lowest pressures because the available quartz spirals did not have the present high sensitivity. There is no doubt but that the present isotherm is concave to the pressure axis in the low relative pressures region and shows an inflection between a relative pressure of one and two tenths becoming convex at higher pressures. If one assumes as Brunauer did that $E_1 = E_L$ for Type III isotherms and then uses a linear form of the BET theory, one finds, upon plotting the earlier results, that an approximate straight line exists only for relative pressures above 0.15. In the case of the present isotherm, de-

(10) C. J. Penther and D. J. Pompeo, *Electronics*, **14**, No. 4, 20 (1941).

(11) W. F. Roeser and A. I. Dahl, *J. Research Natl. Bur. Standards*, **20**, 337 (1938).

(12) C. Cuthbertson and M. Cuthbertson, *Proc. Roy. Soc. (London)*, **A85**, 306 (1911).

(13) F. Henglein, G. V. Rosenberg and H. Muchlinski, *Z. Physik*, **11**, 1 (1922).

(14) W. Ramsay and S. Young, *J. Chem. Soc.*, **49**, 453 (1886).

(15) T. Isnardi, *Ann. Physik*, **61**, 264 (1920).

(16) F. E. C. Scheffer and M. Voogd, *Rec. trav. chim.*, **45**, 214 (1926).

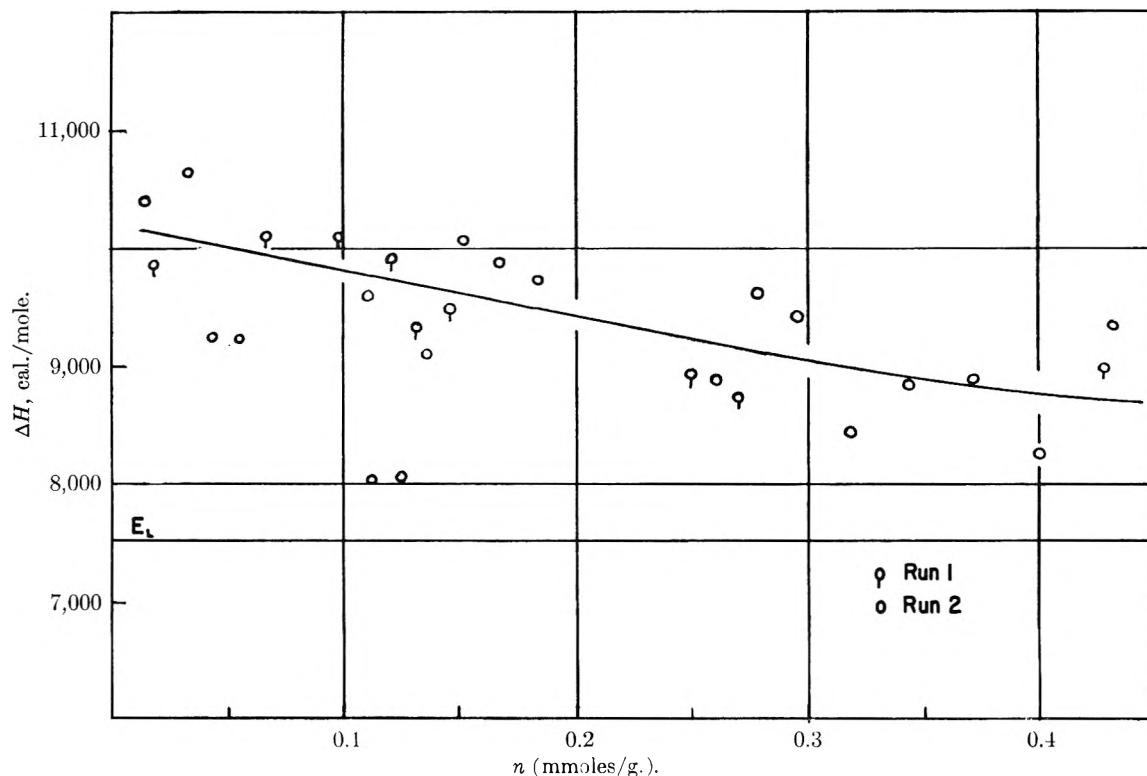


Fig. 3.—Heats of adsorption, bromine on silica gel at 28.9°.

viations certainly exist below a relative pressure of 0.3. The present evidence from the isotherms alone does not appear to justify the assumptions made by Brunauer.

The calorimetrically measured heats as determined in this study lie somewhere between the differential heats of sorption and the isothermal heats. As Brunauer points out it is difficult to evaluate to what extent the external work is transferred to the calorimeter as heat. This difference will be small in this case and in any case will not vitiate the conclusion that the heats of sorption of bromine on silica gel at 28.9° are definitely greater than the heat of liquefaction. In the low pressure ranges the difference amounts to about 3 kcal. and at the highest pressures measured it still is about 1 kcal. greater. The gradual fall in the heat liberated during the sorption process, as the amount sorbed increases, points strongly to a non-uniform sorption surface. Partial molal entropy of the adsorbed phase was calculated from the calorimetric

data. At the lowest relative pressure the partial molal entropy was only slightly above that of liquid bromine and after that the values corresponded very closely with that of the liquid. One can interpret this as meaning that there is mobility in the first layer and that the molecules of adsorbed bromine have about the same number of degrees of freedom as they do in the liquid. For the type of sorptions here reported it is evident that a better model for the adsorbed phase is needed than that offered by the BET theory.

DISCUSSION

W. B. INNES.—Is any information available on the surface area of the gel used for this work? If this is a normal type gel with an area of 500 sq. m./g. and Br₂ has a normal molecular cross-section (21 sq. Å.), only about 15% of the surface is covered at a relative pressure of 0.2.

Do you think constitutional water plays a role in causing decreasing heat of adsorption with increasing coverage?

L. H. REYERSON.—The silica gel used was of the normal type.

WATER VAPOR SORPTION BY ALUMINUM SOAPS¹BY JOHN H. GROSS² AND WALTER H. BAUER*Department of Chemistry, Walker Laboratory, Rensselaer Polytechnic Institute, Troy, New York**Received March 5, 1954*

Water vapor sorption isotherms have been obtained at 25 and 30° for aluminum distearate, aluminum dilaurate, aluminum di-2-ethylhexoate, aluminum dilaurate coprecipitated with lauric acid and aluminum dilaurate coprecipitated with aluminum hydroxide. The sorption isotherms were found to be sigmoid, of Type II and they showed hysteresis loops extending to the lowest pressures. Fit of the BET equation to the data was found in some cases. Calculations of surface area and energy of adsorption were made. It was concluded that the sorption process involves monolayer and multilayer adsorption with capillary condensation, and that part of the sorbed water swells the aluminum soap crystallites, attaching to the soap polymer chains by hydrogen bonding. No evidence was found for hydrate formation.

Introduction

Aluminum soaps prepared by precipitation from aqueous sodium soap solutions with aluminum salts may consist of the monohydroxy di-fatty acid salt, of the aluminum disoap together with free fatty

Experimental

Materials.—Water used as adsorbate was triply distilled and freed from dissolved air. The soaps used were three aluminum laurates of varying aluminum to fatty acid ratio, aluminum stearate, aluminum caprylate and aluminum 2-ethyl hexoate. Composition of the soaps and per cent.

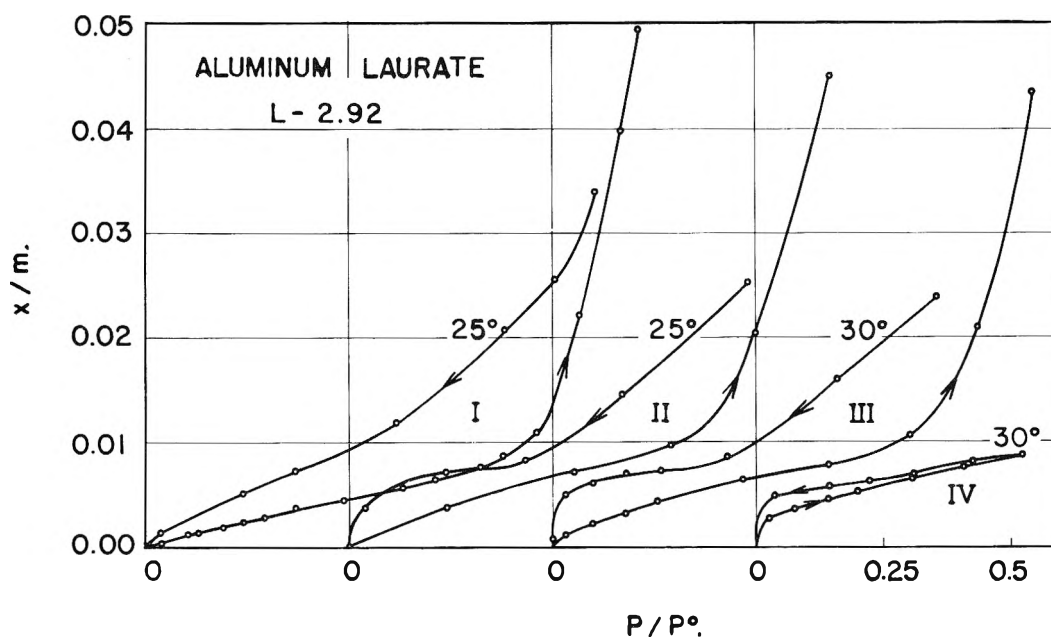


Fig. 1.—Sorption isotherms of water on aluminum laurate, sample L-2.92. In Figs. 1-6 x/m is grams water adsorbed per gram of soap, and p/p_0 is the ratio of the water pressure to the vapor pressure of pure water at the indicated temperature.

acid,³ or of the disoap together with aluminum hydroxide,⁴ depending upon the amount of hydroxide present in the sodium soap solution in excess of that required to form the sodium soap from the acid. Water is strongly sorbed by these soaps, and the nature of the sorption process is of interest because of the reducing effect of sorbed water on the thickening power of the soaps in hydrocarbon gels. In view of the very limited previous study of water sorption by aluminum laurate⁵ it appeared desirable to investigate more completely the sorption of water by aluminum laurates of various compositions and by aluminum soaps prepared from other fatty acids.

(1) This study was conducted in collaboration with the Chemical Corps Technical Command, Army Chemical Center, Maryland, and under contract with the Chemical Corps.

(2) John H. Gross, Ph.D. Dissertation, Rensselaer Polytechnic Institute, Troy, New York, June, 1949.

(3) W. W. Harple, S. E. Wiberley and W. H. Bauer, *Anal. Chem.*, **24**, 635 (1952).

(4) A. E. Alexander and V. R. Gray, *This Journal*, **53**, 23 (1949).

(5) G. W. Shreve, H. H. Pomeroy and K. J. Mysels, *ibid.*, **51**, 963 (1947).

weight losses on evacuation are shown in Table I. Data concerning the preparation and composition of the soaps have been previously reported.³

TABLE I
CHARACTERISTICS OF ALUMINUM SOAPS

Sample designation	Calcd. moles acid/mole aluminum based on actual Al analysis	Wt. % fatty acid distillation loss to reservoir at liquid N ₂ temp.
Aluminum laurate, L-2.92	2.92	24.1
Aluminum laurate, L-2.12	2.12	3.8
Aluminum laurate, L-1.48	1.48	0.0
Aluminum stearate, S-2.03	2.03	0.7
Aluminum caprylate, C-2.02	2.02	0.9
Aluminum 2-ethylhexoate, EC-1.93	1.93	1.3

Apparatus and Procedure.—The sorption balances employed were of the type developed by McBain and Bakr,⁶

(6) J. W. McBain and A. M. Bakr, *J. Am. Chem. Soc.*, **48**, 690 (1926).

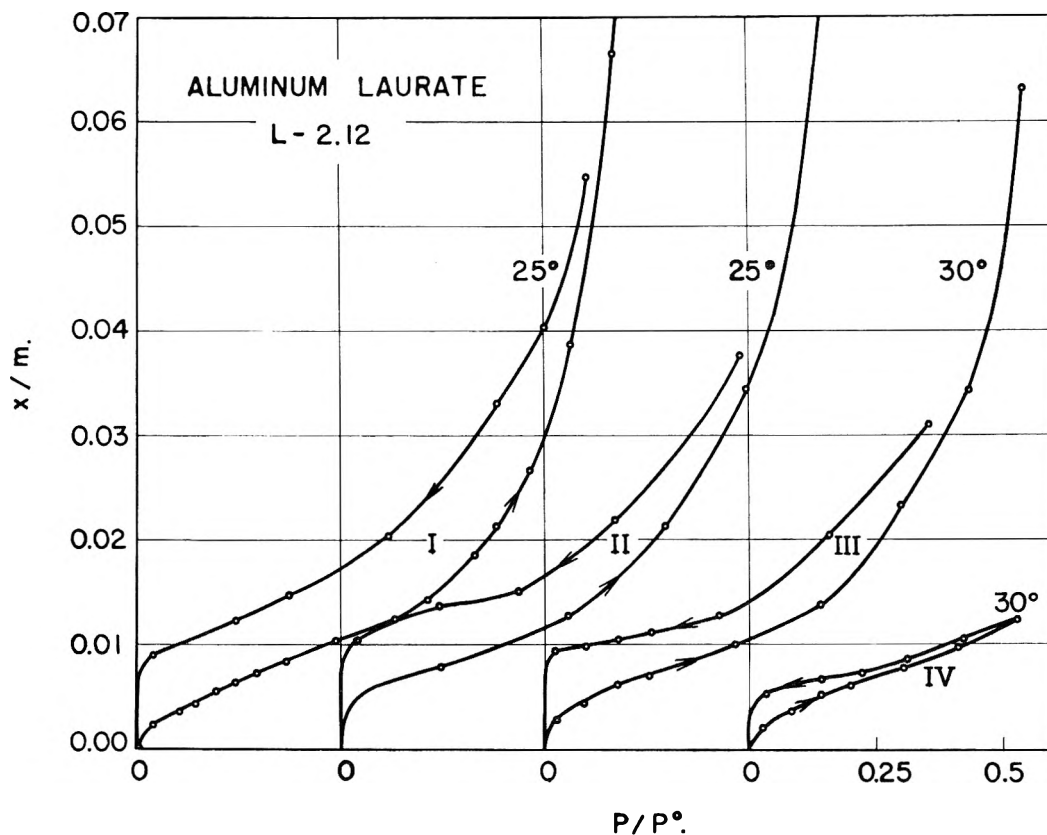


Fig. 2.—Sorption isotherms of water on aluminum laurate, sample L-2.12.

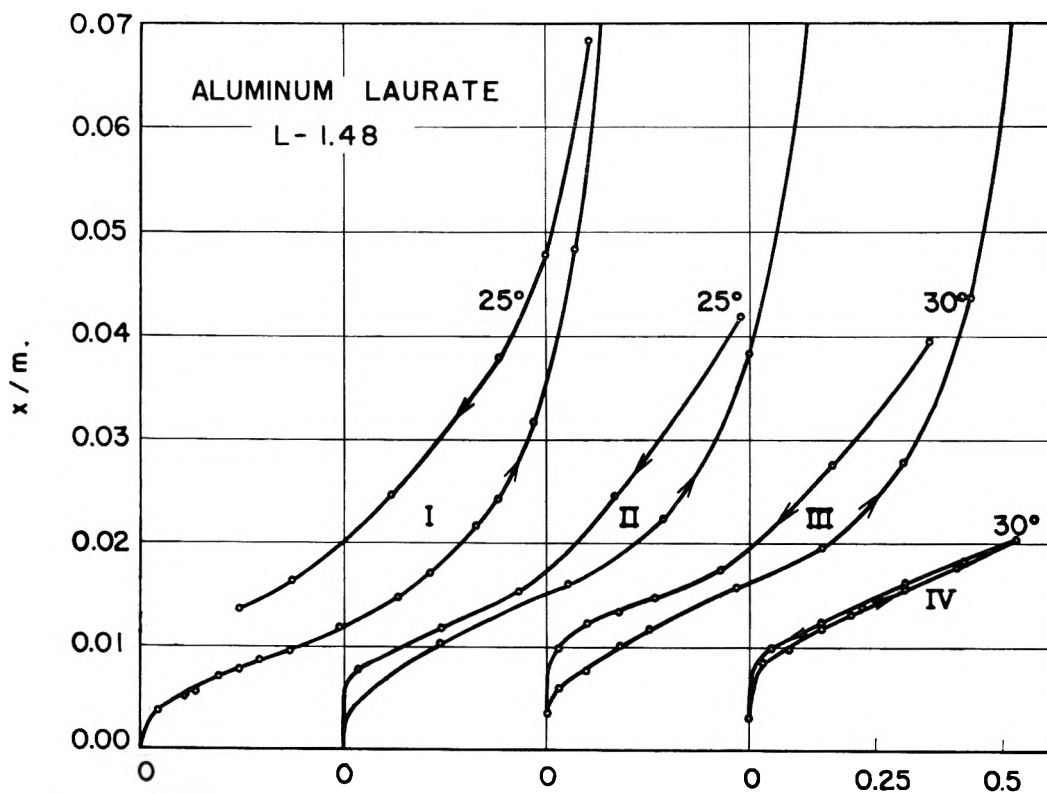


Fig. 3.—Sorption isotherms of water on aluminum laurate, sample L-1.48.

and were modifications of the apparatus described by Spitzze and Hansen.⁷ Six balance tubes were used in pairs, each pair being attached to a vacuum manifold and to a water

reservoir whose temperature was controlled by a thermostat. Each of the tubes, which were mounted in an air-bath, contained a sample bucket hung from a quartz spiral. Additional water reservoirs were provided so that temperatures from 0 to -195° could be maintained about water with-

(7) L. A. Spitzze and L. A. Hansen, *Ind. Eng. Chem.*, **34**, 506 (1942).

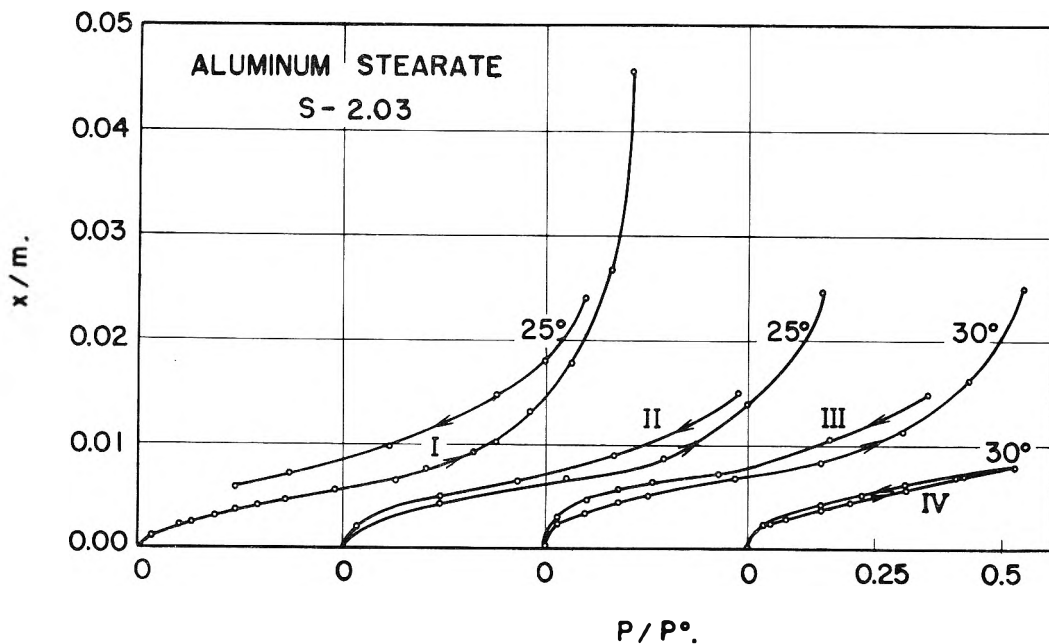


Fig. 4.—Sorption isotherms of water on aluminum stearate, sample S-2.03.

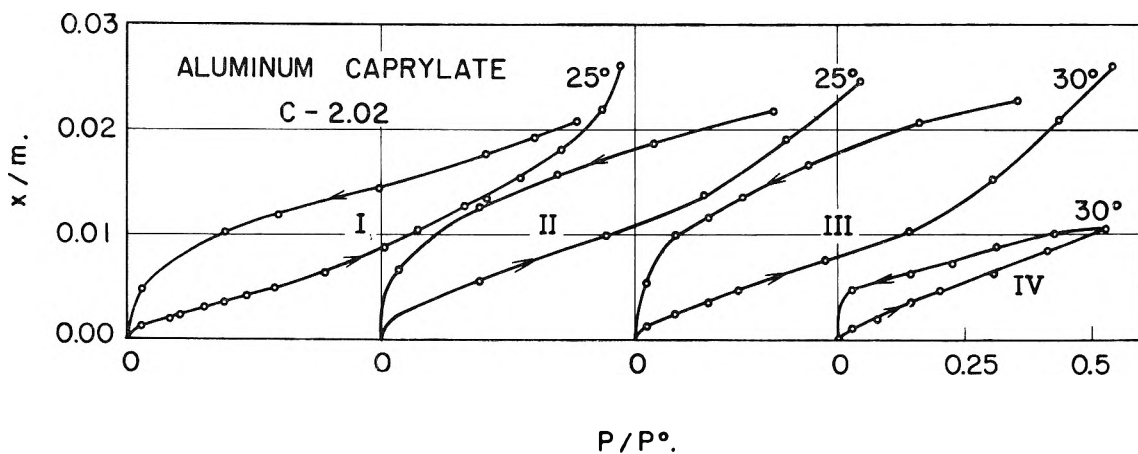


Fig. 5.—Sorption isotherms of water on aluminum caprylate, sample C-2.02.

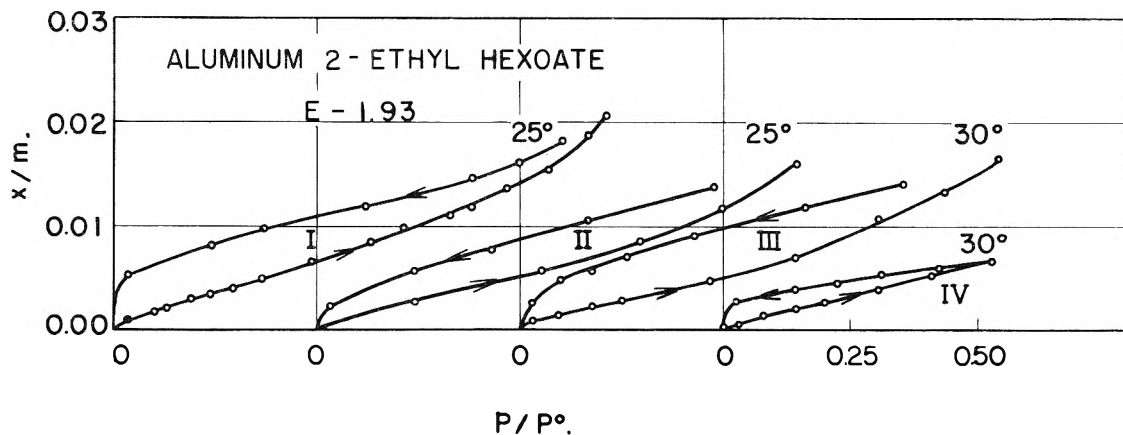


Fig. 6.—Sorption isotherms of water on aluminum 2-ethyl hexoate, sample E-1.93.

drawn from the sorption sections. Air-bath temperatures were controlled with a maximum variation of $\pm 0.02^\circ$. The quartz spirals varied in sensitivity from 0.01157 to 0.04155 g. per cm. Extension was measured with a precision cathetometer. Pyrex sample buckets were prepared by the method of Cameron.⁸ Temperatures of the water in

the reservoirs below 0° were obtained by placing about the reservoirs Dewar flasks containing ice-salt solutions, solid carbon dioxide-cellosolve mixtures, or liquid nitrogen. Water was introduced to the balance systems containing the dried soap samples from capsules containing air-free water which were broken after prolonged evacuation at 10^{-6} mm. and after the tubes were sealed off from the pumping system. Slow distillation of fatty acid⁹ occurred to the

(8) A. E. Cameron, *J. Am. Chem. Soc.*, **53**, 2646 (1931).

auxiliary reservoirs at liquid nitrogen temperatures, to the extent shown in Table I.

Results and Discussion

For each of the six soaps, two sorption isotherms were obtained at 25.0° and one at 30.0° over the range of p/p_0 from 0 to 0.95, and a final isotherm was then obtained at 30.0° over the range of p/p_0 from 0 to 0.528. The results are shown in Figs. 1-6. The isotherms show the sorption behavior of the soaps to be similar. A common property is a sigmoid curve with a hysteresis loop extending in a complete isotherm back to the lowest values of p/p_0 at which measurements could be taken. Water responsible for hysteresis enters the soap throughout the full length of the sorption cycle, as demonstrated by the shape of the isotherms carried only to $p/p_0 = 0.528$. In this range, capillary condensation is not expected, but entry of water into the soap crystallite may be postulated. At each temperature the amount of water adsorbed increases in the second hydration-dehydration cycle indicating that a change in the sorptive structure of the soap occurs in each cycle. The shift in isotherms cannot be ascribed to the loss of fatty acid, since the isotherms of aluminum laurate L-1.48, which showed constant dry weight, underwent considerable shifts from the first to the second cycle at each temperature.

All of the isotherms are of the sigmoid Type II class, indicating that multilayer adsorption takes place, and some of the hysteresis may be ascribed to capillary condensation. The persistence of hysteresis to low pressure regions is not believed to be based on capillary condensation.⁹ It is suggested that water may swell the soaps, penetrating the crystal lattice along the length of the polymeric aluminum soap molecules, and hydrogen bonding at the recurring aluminum oxygen linkage regions of the proposed structures.^{4,10}

A test was made of the applicability of the BET equation to the sorption data obtained for the six soaps. In four cases, that of aluminum laurates L-2.12, L-1.48, aluminum 2-ethylhexoate, EC-1.93, and aluminum stearate, S-2.03, a good fit to a straight line was found when $p/[(x/m)(p_0 - p)]$ was plotted versus p/p_0 over the range from $p/p_0 = 0.05$ to 0.35. In Table II are given the calculated values of the surface area per gram, and of

the energy of adsorption for the soaps treated by means of the BET equation.

TABLE II
SURFACE AREA AND $E_1 - E_L$ FROM BET EQUATION

Soap sample	Surface area at 25° m. ² /g. (H ₂ O = 10.5 Å./molecule)	$E_1 - E_L$, cal. net energy of adsorption
Aluminum laurate, L-2.12	33.6	1130
Aluminum laurate, L-1.48	32.5	1450
Aluminum 2-ethylhexanoate, EC-1.93	33.8	510
Aluminum stearate, S-2.03	15.0	1650

Variations with the temperature of these quantities are larger than would be expected from the 5° temperature change, and the calculated quantities must be considered to be approximations only. However, the values found for the energies of adsorption, ranging from 500 to 1900 cal. per mole of water are somewhat higher than those usually found for physical adsorption, but they do not approach the energies found in clear cases of chemisorption. Babbitt¹¹ has shown that if water molecules are held to an adsorbent by two hydrogen bonds, the energy required to remove the molecule is 1350 cal. per mole higher than the heat of vaporization of liquid water. This value is in the region of the values of the net energies of adsorption found and indicates that sorption of water by aluminum soaps may involve hydrogen bonding.

Conclusions

From the shape of the isotherms, the hysteretic behavior, and the increase in sorptive capacity for water after each desorption cycle, it is concluded that monolayer and multilayer adsorption takes place, together with capillary condensation, when water is sorbed by aluminum soaps. Permanent structure modification of the soap crystallites occurs in sorption-desorption cycles, possibly because of penetration by water molecules. No evidence for formation of hydrates was found, but net energies of adsorption calculated were consistent with the existence of hydrogen bonding of water to the aluminum soaps molecules.

Acknowledgment.—The authors are indebted to Henry Raich and Grant K. Rauscher for use, for a sorption study, of the aluminum soaps discussed in this report.

(9) E. Ott, "Cellulose and its Derivatives," Vol. 5, "High Polymers," Interscience Publishers, Inc., New York, N. Y., 1943.

(10) C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).

(11) J. D. Babbitt, *Can. J. Research*, **20A**, 143 (1946).

THE PHYSICAL STRUCTURE OF ASBESTOS

BY G. J. YOUNG AND F. H. HEALEY

*Surface Chemistry Laboratory, Lehigh University, Bethlehem, Penna.**Received March 5, 1954*

In the initial phase of a study of the surface chemistry of chrysotile asbestos, nitrogen and water vapor isotherms were measured on samples outgassed at room temperature. Neither isotherm showed hysteresis, but the area available to water vapor was found to be almost twice that available to nitrogen. Additional detailed studies of the gases A, CO, C₂H₂, C₄H₁₀, (CH₃)₃N, (CH₃)₂NH and NH₃ showed that only ammonia followed the anomalously high adsorption found for water vapor. Activation at increasing temperatures increases the available areas up to about 425° where the water and nitrogen areas agree. Above this temperature the surface structure apparently changes (at temperatures below that at which the X-ray pattern changes) as evidenced by area decrease and, finally, at still higher temperatures the internal structure breaks down. These results have been explained by the hypothesis that asbestos has an internal capillary structure. It is proposed that entrance to these capillaries is blocked by firmly bound water, through which water vapor and ammonia, but not the other gases, can diffuse. Adsorption measurements on other similar fibrous minerals, anthophyllite and tremolite, do not show the same behavior. It is possible that this internal capillary structure may be identified with the apparent hollow tube structure suggested by electron photomicrographs. The filling of the capillary structure with adsorbed water vapor is strikingly illustrated by calculations of surface areas by the Harkins absolute method from heat of immersion data at various surface coverages.

Introduction

Asbestos is a generic name for a group of minerals possessing a crystalline fibrous structure which are commonly classified under three varieties: anthophyllite, amphibole and serpentine. Chrysotile, a serpentine mineral, accounts for the majority of asbestos used commercially. Yet, in spite of its wide usage there is a sparsity of information concerning its surface properties.

In a general study of the surface chemistry of chrysotile asbestos it became necessary, in order to explain certain apparent anomalous results, to examine not only the surface properties but also the physical structure. Although much is known about the crystal lattice structure from X-ray diffraction data, relatively little information except that suggested by electron microscope examinations¹⁻⁴ has been reported concerning the physical structure of the asbestos fibers. Such information is important for a proper understanding of the role played by asbestos in its use as a filler for building materials and as a catalyst support.

Experimental.—The asbestos used in this investigation was a sample of Canadian Johns Manville grade 7-R, a commercial short-fiber asbestos. This sample was composed mainly of chrysotile with a small amount of native impurities present, and was comparable in its adsorption characteristics to chrysotile asbestos from other sources. Adsorption measurements were carried out on this sample in the as-received state and also after washing with water and degreasing with purified benzene. The only effect of washing and degreasing was to decrease the surface area slightly due probably to the removal of some "fines" in the washing process. A negligible amount of soluble material, primarily soluble chlorides, was extracted with boiling water from the washed and degreased sample. The surface areas of the 7-R asbestos, long fiber chrysotile, and other minerals used for comparison varied according to source and state of subdivision.

A standard volumetric gas adsorption apparatus was used in the adsorption studies of all gases employed with the exception of water vapor and *n*-butane. For water vapor adsorption a modified Orr apparatus⁵ was used. The water vapor adsorption results from the volumetric apparatus were compared, in some cases, to results from gravimetric studies using a series of desiccators containing saturated

salt solutions to give the desired relative pressures. Adsorption of water vapor in the gravimetric method occurred in the presence of atmospheric air in the desiccators. The results of the two methods agreed exactly indicating that water vapor adsorption phenomena observed in the adsorption apparatus in the absence of air would occur in the same manner under atmospheric conditions. *n*-Butane was found to be slightly soluble in the usual high-vacuum stopcock lubricants such as Apiezon N. Therefore, a special volumetric apparatus was designed for this gas, employing a Hoke metal valve as the only stopcock in the adsorption system. The metal valve required no lubricant.

The gases used in this investigation were either of C.P. or 99.9% purity grade. All the gases except helium were further purified by condensing and fractionating into the storage bulb. Prior to this final step, argon and nitrogen were passed over heated copper gauze and acetylene was passed through activated charcoal traps at -70°. Helium was passed through activated charcoal at -195°.

The heat of immersion calorimeter and the techniques employed have been described in a previous publication.⁵

Results and Discussion.—The results of gas adsorption measurements on 7-R asbestos are given in Table I. The asbestos samples used here were prepared by evacuation at 10⁻⁵ mm. at 25° for 24 hours and are referred to as "unactivated." Evacuation at this temperature for longer periods produced no change in surface area. The *V_m* values were calculated by use of the conventional BET equation. The effective areas occupied by the adsorbed molecules were determined from adsorption on a sample of rutile assuming the area occupied by the nitrogen molecule to be 16.2 Å.² The packing of the gas molecules on the rutile surface must be similar to the packing on the asbestos surface since

TABLE I
RESULTS OF ADSORPTION OF SEVERAL GASES ON
UNACTIVATED ASBESTOS

Gas	Temp., °C.	<i>V_m</i> , ml./g.	Apparent area of adsorbed molecule, Å. ²	Surface area, m. ² /g.
N ₂	-195	2.22	16.2	9.7
A	-195	2.26	15.8	9.6
CO	-195	2.16	16.8	9.8
C ₂ H ₂	-78	1.68	21.4	9.7
C ₄ H ₁₀	0	0.77	47.0	9.7
(CH ₃) ₃ N	0	1.16	30.6	9.6
(CH ₃) ₂ NH	0	1.28	28.7	9.9
NH ₃	-33	4.26	15.4	17.6
H ₂ O	23	6.17	10.6	17.6

(1) J. Turkevich and J. Hillier, *Anal. Chem.*, **21**, 475 (1949).

(2) T. F. Bates, L. B. Sand and J. F. Mink, *Science*, **111**, 512 (1950).

(3) W. Noll and H. Kircher, *Naturwissenschaften*, **37**, 540 (1950).

(4) W. Noll and H. Kircher, *ibid.*, **39**, 188 (1952).

(5) A. C. Zettlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *This Journal*, **57**, 649 (1953).

agreement in surface areas determined from adsorption of the various gases were obtained for both surfaces except for the adsorption of water vapor and ammonia on asbestos. Typical Type II adsorption isotherms were obtained for all gases and no adsorption-desorption hysteresis was observed. It may be noted from Table I that the adsorption results for all gases except ammonia and water vapor gave a surface area of *ca.* 9.7 m.²/g., while these latter two gases gave an area of 17.6 m.²/g. The possibility of specific interaction of water vapor and ammonia with the asbestos surface is ruled out because of the reversibility of the adsorption, the smooth Type II isotherms obtained, and the wide difference in V_m values between the two gases. The alternative, that a portion of the asbestos surface is available to water and ammonia and not to the other gases, seems more probable. The criterion for entrance to this restricted portion of the surface appears to be one of the chemical nature of the molecule (*e.g.*, extreme polarity).

Surface areas were then determined by nitrogen and water vapor adsorption for asbestos activated under various conditions. The results of this study are shown in Fig. 1. It is seen that, while the surface areas determined from nitrogen and water vapor adsorption differed at low activation temperatures, agreement is obtained for samples activated at higher temperatures. Indeed, at the maximum surface area the same surface is available to both gases. Samples activated at *ca.* 425° gave a maximum surface area and are referred to as "activated."

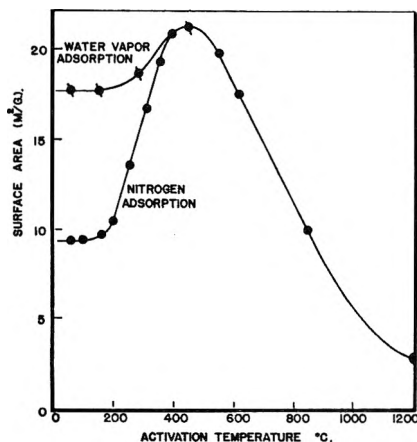


Fig. 1.—Adsorption on asbestos at various activations.

X-Ray diffraction patterns of samples heated to 500° for one hour at 10^{-5} mm. indicated that no change in the bulk chrysotile structure occurred. It is concluded, therefore, that the decrease in surface area for samples activated at temperatures greater than 450° results initially from alteration of the surface structure only. At much higher temperatures, the chrysotile structure is undoubtedly altered. The weight loss on ignition at 1200° for five hours was approximately 13%.

The new surface made available to nitrogen adsorption upon activation of chrysotile was, at least in part, in the form of capillaries. This conclusion was indicated by the adsorption-desorption hysteresis observed in the nitrogen isotherms. These

results are illustrated in Fig. 2 which gives nitrogen adsorption and desorption isotherms on unactivated and activated chrysotile. The sample activated at 425° gave the largest hysteresis loop and therefore possesses the greatest amount of capillary structure. The average diameter for these capillaries was calculated by determining the change in the dead space volume available to helium in a large sample of chrysotile upon activation. It was assumed that helium, like nitrogen, could not enter the capillary structure until after the sample had been activated. The computed average internal diameter of the capillaries was 160 Å. assuming them to be round and having a surface roughness of one.

It was now pertinent to inquire as to the reason nitrogen could not enter the capillary system of the unactivated sample and why ammonia and water vapor gave almost double the nitrogen surface area for the unactivated sample. The results of adsorption experiments on activated asbestos given in Table II show that activated chrysotile can be restored to the unactivated state by saturation with

TABLE II
ADSORPTION ON ACTIVATED ASBESTOS

Treatment	Nitrogen area, m. ² /g.	Water vapor area, m. ² /g.
Unactivated	9.7	17.6
Activated	21.3	21.9
Activated, then exposed to atmosphere (<i>ca.</i> 50% R.H.) for 48 hr., then evacuated at 25° for 24 hr.	21.4	...
Activated - saturated with water vapor-evacuated at 25° for 24 hr.	9.8	17.8

water vapor. Indeed, these results suggest that entrance to the capillaries is prevented by sorbed water which may be removed by activation at 425°. A single sample can be activated repeatedly and restored to the original condition by saturation with water vapor provided that the activation temperature is not sufficiently high to destroy the chrysotile structure. Since only water vapor is necessary to restore the activated asbestos to the unactivated state where the internal capillary structure is not available to nitrogen adsorption, it must be sorbed water in some form that prevents the entrance of nitrogen molecules to this part of the surface. The hypothesis of sorbed water plugs explains the larger adsorption of water vapor and ammonia on the unactivated sample on the basis that these plugs would be permeable to these polar gases but not to non-polar gases. The water plugs do not fill the length of the capillaries as indicated by the fact that the surface area as determined by water vapor or ammonia on the unactivated sample is intermediate between the external surface area of 9.7 mg.²/g. and the total surface area of 21.9 m.²/g. Capillary forces in addition to strong adsorption forces, or possibly chemical bonds, must prevent the removal of these water plugs at 25°.

Recent electron photomicrographs of chrysotile¹⁻⁴ suggest that the individual fibers are in the form of hollow cylindrical tubes. Electron photo-

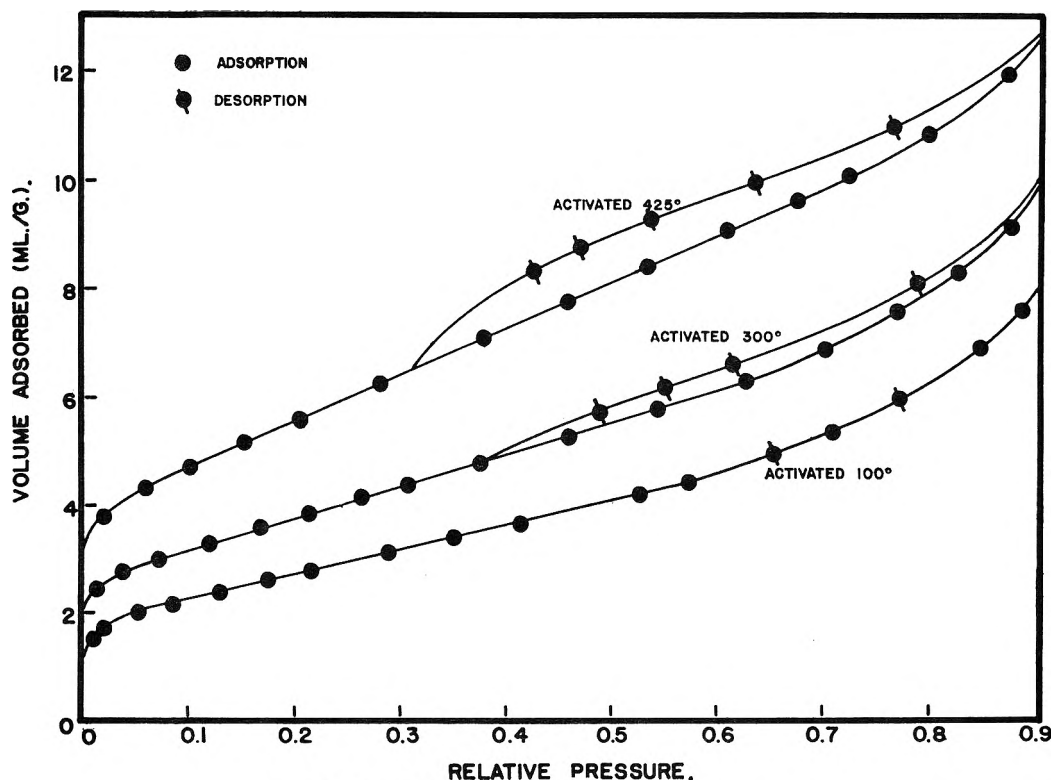


Fig. 2.—Adsorption of nitrogen on asbestos.

micrographs of 7-R asbestos³ reveal the same chrysotile structure. The average external diameter of single fibers of the 7-R was *ca.* 350 Å, and the average internal diameter of the apparent hollow section was *ca.* 150 Å. If the entire external surface of the individual fibers of the size indicated in the electron photomicrographs were available to adsorbed molecules, the surface area would be several times that determined experimentally. Thus, the adsorption results on 7-R asbestos indicate that the majority of fibers are bound in fiber bundles and that adsorbed molecules cannot reach all external surfaces of the individual fibers. The capillary structure of chrysotile asbestos appears to be associated with the apparent hollow sections of the individual fibers as suggested by electron photomicrographs rather than interstices in the fiber bundles. The average diameter of the capillaries as determined by helium densities is in good agreement with the average diameter of the apparent hollow sections of the individual fibers shown in electron photomicrographs. In addition the adsorption results on anthophyllite and tremolite (an amphibole)

given in Table III indicate that the same amount of surface is available to both water vapor and nitrogen adsorption.

Anthophyllite and tremolite are similar to asbestos in that they have a fibrous structure, but no apparent hollow structure within the individual fibers.⁷ The agreement in nitrogen and water surface areas for these minerals indicate that fiber bundles do not, in themselves, lead to an effective capillary structure.

The data so far presented appear to be explained only on the hypothesis that an internal capillary structure exists in chrysotile. It was deemed necessary to test this hypothesis further. This was accomplished from calculations of the surface area by the Harkins absolute method⁸ for various amounts of water vapor adsorbed on the surface.

Heats of immersional wetting of unactivated asbestos in water at 25° with various amounts of adsorbed water vapor on the asbestos surface have been given⁵ as a function of the volume adsorbed. The heat of wetting curve falls to the value for the heat of wetting of a bulk water surface, 118 ergs/cm.², soon after monolayer coverage. Thus the surface area of unactivated samples with adsorbed films of relative pressures greater than *ca.* 0.4 may be calculated by the Harkins absolute method. This is of special interest in the case of asbestos since according to the proposed capillary structure, the capillaries should be completely filled at high relative pressures thus showing a decrease in the surface area available in the heat of immersion determinations.

TABLE III

ADSORPTION ON FIBROUS MINERALS EVACUATED AT 25° FOR 24 HOURS

Sample	Nitrogen area, m. ² /g.	Water vapor area, m. ² /g.
7-R Asbestos	9.7	17.6
Chrysotile (pure)	8.1	21.4
Anthophyllite	20.0	20.8
Tremolite (fibrous)	3.1	3.3

(6) Obtained by Professor T. F. Bates at Pennsylvania State University.

(7) *Trans. Can. Inst. Mining and Met.*, **54**, 151 (1951).

(8) W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952.

The filling of the capillaries is strikingly illustrated in Fig. 3 which gives the surface area as calculated by the Harkins absolute method from heat of immersion data for various relative pressures of the adsorbed film. At lower coverages, $p/p_0 = 0.4$ to 0.6, the surface area is the same as was given by water vapor adsorption, *e.g.*, the external area plus that internal area not occupied by the water plugs. The decrease in surface area from $p/p_0 = 0.6$ to 0.85 is due to the filling of capillaries. The range in relative pressure over which this occurs indicates a size distribution for the capillary diameter. At relative pressures over 0.90 the capillaries are completely filled and thus the area available is only the external area as was given by nitrogen adsorption. This evidence offers excellent support for the proposed capillary structure for chrysotile.

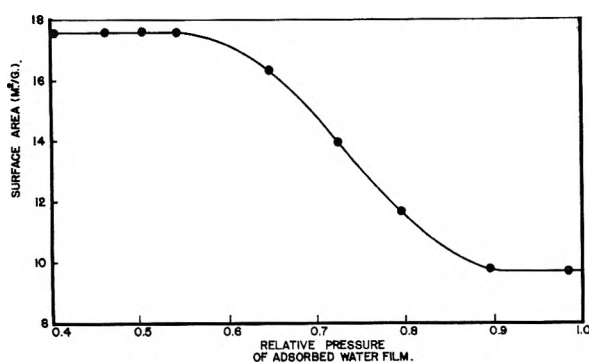


Fig. 3.—Surface area of asbestos by Harkins' absolute method.

Heats of wetting values were also determined for emersion of activated asbestos in water. This value is 850 ergs/cm.² as compared to 420 ergs/cm.² for the unactivated surface. This amounts to 1235 ergs/cm.² for the wetting of the capillary surfaces and the filling of the capillaries based on a square centimeter of capillary surface. This value is considerably higher than heat of wetting values for the usual solid surface. Indeed, if the adsorbed water is held this strongly in the capillaries by surface and capillary forces, it is not surprising that the water plugs are not completely removed by evacuation alone.

The conclusions concerning the physical structure of chrysotile asbestos as implied by the results of this investigation may be summarized as follows.

1. The individual fibers in chrysotile are for the most part bound in fiber bundles; thus, a large portion of their external surface is not available to adsorbed molecules.

2. Chrysotile has an internal capillary structure.

3. These capillaries appear to be within the individual fibers themselves; indeed it is possible that the capillaries may be identified with the apparent hollow tubular structure shown by electron photomicrographs.

4. The capillaries appear to be blocked in some manner with strongly sorbed water plugs. These plugs are permeable to water vapor and ammonia but not to less polar gases.

5. The water plugs are removed by activation at 425° at 10⁻⁵ mm. pressure. There is no change in the bulk chrysotile structure after heating to temperatures up to 500°; however, changes in the surface occur at temperatures greater than *ca.* 450°.

6. The water plugs may be re-formed in samples activated at less than 425° by saturation with water vapor.

Experimental work has been extended to other serpentine minerals but has not yet been completed. Antigorite, having the same chemical composition as chrysotile but no fibrous character as revealed by electron photomicrographs, also shows anomalous sorption of water vapor. Since no hysteresis sets in with high temperature activation, it appears that the explanation for antigorite must be different than that for serpentine.

Acknowledgment.—The authors gratefully acknowledge the financial support and the aid in obtaining adsorbent samples provided by the Armstrong Cork Company. We also wish to thank Professor A. C. Zettlemoyer for many stimulating discussions of this research.

DISCUSSION

F. M. FOWKES.—(1) Do you have measurements of the amount of water in the "plugs," such as the change in weight on activation? Does this correspond to the amount of water indicated by the difference in surface areas of water before and after activation? (2) One might expect the "plugs" to slow adsorption. Do rates of attainment of equilibrium indicate this? (3) Why does dimethylamine give the same area as the non-polar gases instead of the larger area obtained with ammonia?

G. J. YOUNG.—Taking your points in order: (1) The weight loss on activation has been measured up to 425°. If this weight loss is attributed solely to loss of adsorbed water, then considerably more water is lost than would be indicated by the area difference before and after activation assuming monolayer coverage. This result would be expected since the plugs are undoubtedly several water layers thick.

(2) The rates of adsorption of both ammonia and water are slower than for the other gases used in this study. However, no large differences in the rates of adsorption of ammonia and water on activated and unactivated 7-R were observed.

(3) Dimethylamine has a smaller dipole per unit volume than either ammonia or water. This may explain why this gas, which is relatively polar, cannot pass the water "plugs" to enter the capillary structure.

F. L. PUNDSACK.—It has been our experience that the commercial 7R type of asbestos used in this work is a heterogeneous material which contains appreciable amounts of magnetite and the magnesium hydroxide mineral brucite along with minor amounts of other extraneous minerals. Of the serpentine fraction of the sample, there seems to be some question among mineralogists and crystallographers as to whether or not this fraction is a mixture of the platy variety of serpentine along with the fibrous variety, chrysotile. In view of this uncertainty in the sample, were any analyses made of the material used in this work, or were any attempts made to separate the extraneous components?

G. J. YOUNG.—The 7-R samples were washed and degreased to remove soluble materials. No further attempt was made to separate the remaining components. However, the adsorption results on 7-R agreed essentially with the results obtained on several hand picked samples of pure chrysotile. This appears to indicate that a major portion of the 7-R is chrysotile, although admittedly there could be a relatively large amount of antigorite present.

THE SURFACE PROPERTIES OF CHRYSOTILE ASBESTOS

BY F. H. HEALEY AND G. J. YOUNG

Surface Chemistry Laboratory, Lehigh University, Bethlehem, Penna.

Received March 5, 1954

Thermodynamic functions for the adsorption of gases on unactivated and activated chrysotile asbestos indicate that the unactivated asbestos surface is homogeneous to water vapor adsorption but is heterogeneous to argon adsorption. Distribution curves for the adsorption site energies of the activated and unactivated asbestos surface were calculated from the isosteric heats for argon adsorption. These curves indicate that the surface of the capillary structure made available on activation is of lower energy in regard to non-polar gas adsorption than the external surface of the fibers. Heats of immersion for the asbestos-water system support the conclusion that the unactivated asbestos surface is homogeneous for polar gas adsorption.

Introduction

The previous paper¹ presented evidence which suggested that chrysotile asbestos consists of hollow tubular fibrils bound together in fiber bundles. It was hypothesized that the internal capillaries were blocked by plugs of sorbed water. The water plugs could be removed by activation at 425° and restored by saturation with water vapor. Non-polar gases were unable to penetrate the plugged capillaries and were adsorbed only on the external surface of the unactivated asbestos. It was thus possible to study separately the surface properties of the two types of surfaces. The present paper presents some thermodynamic functions obtained for the adsorption of argon and water vapor on activated and unactivated chrysotile asbestos.

Experimental.—The asbestos used in this investigation was a sample of Canadian Johns Manville grade 7-R, the same as in the previous paper.¹ An "activated" sample is one that has been heated to 425° for one hour under a vacuum of 10⁻⁵ mm., giving a maximum surface area. "Unactivated" refers to samples evacuated at 25° for 24 hours.

A standard BET-type volumetric apparatus was used for argon adsorption. The purification of gases has been reported previously.¹

Results and Discussion.—The isosteric and equilibrium heats of adsorption for water vapor on unactivated asbestos, determined from adsorption isotherms at 15 and 23°, have been published.² These curves are nearly linear at the lower surface coverages and exhibit maxima in the vicinity of V_m . The absolute entropy of the adsorbed state, S_s , and the corresponding entropy values calculated from the isosteric heats, \bar{S}_s , are presented in Fig. 1.

The general shape of the enthalpy and entropy curves is indicative of a fairly homogeneous surface. This conclusion is confirmed further by determination of the equilibrium constant, $K = \theta / [(1 - \theta)p/p_0]$, as suggested by Graham.³ Values for K were constant at 66 ± 8 , though exhibiting a slight downward trend, over the relative pressure range of 0.001 to 0.07 (*i.e.*, from $\theta = 0.07$ to $\theta = 0.8$) thus indicating a surface relatively homogeneous to water vapor adsorption. The values of the equilibrium constant did not give evidence of interactions between adsorbed molecules at as low coverages as did the isosteric heat curves.

The maximum in the isosteric heat curve is more pronounced than generally encountered. It appears reasonable that the first molecules adsorbed

on the surface are separated by a sufficient distance so that there is little nearest neighbor interaction. The isosteric heat at low coverages, therefore, will result only from surface forces and will be constant if the surface is homogeneous. At higher coverages the molecules are in closer proximity and hydrogen-bonding results. Since hydrogen-bond formation represents considerably more energy than the usual molecular interactions, a substantial contribution to the heat of adsorption is to be expected. The isosteric heat values therefore are greater than the initial values (at low coverages) by *ca.* 4 kcal. at the maximum, a reasonable value for hydrogen-bond formation in two dimensions.

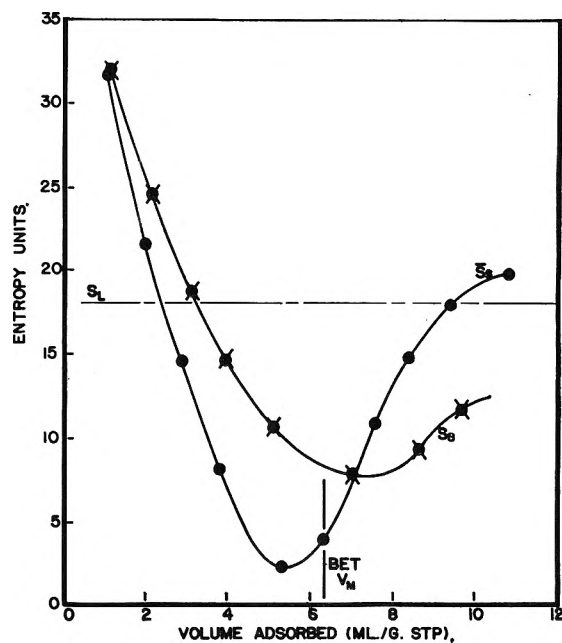


Fig. 1.—Entropy of water vapor in the adsorbed state on asbestos.

The entropy values S_s and \bar{S}_s cross at a minimum in the S_s curve as pointed out by Hill.⁴ The entropy of the adsorbed state, S_s , for water vapor on asbestos at V_m is lower than the entropy of liquid water, S_L . This is indicative of strong binding and little mobility. Indeed this is not unreasonable if the adsorbed molecules at V_m are restricted by hydrogen-bond formation as well as surface adsorption forces.

(1) G. J. Young and F. H. Healey, *THIS JOURNAL*, **58**, 81 (1954).

(2) A. C. Zettlemyer, G. J. Young, J. J. Chessick and F. H. Healey, *ibid.*, **57**, 649 (1953).

(3) D. Graham, *ibid.*, **57**, 665 (1953).

(4) T. L. Hill, P. H. Emmett and L. G. Joyner, *J. Am. Chem. Soc.*, **73**, 5105 (1951).

Isosteric heats of adsorption were determined for argon on both activated and unactivated asbestos from isotherms at -195 and -183° . These heat curves were typical of heat curves for a heterogeneous surface in contrast to water vapor adsorption on the unactivated surface which indicated homogeneity. Indeed it appears that while the surface force field contributed by polar van der Waals forces is nearly homogeneous for the unactivated asbestos surface, the surface force field contributed by non-polar van der Waals forces is largely heterogeneous. Distribution curves for the adsorption site energies for argon on activated and unactivated asbestos were calculated from the isosteric heat curves and are presented in Fig. 2. The distribu-

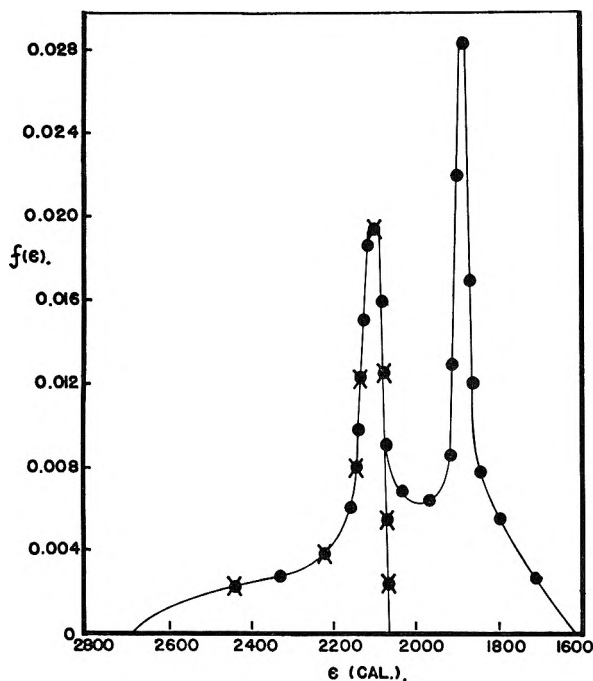


Fig. 2.—Site energy distribution for argon adsorption on asbestos: ●, unactivated; ●, activated at 425° .

tion function, $f(\epsilon) = dv/dq_{st}$, suggested by Morrison and Drain⁵ was used. These authors assumed that the decrease in the heat of adsorption was due solely to surface heterogeneity. This assumption was found not to be entirely valid for their heat data, which was at 0°K ., and it is certainly more approximate for our data at a higher temperature where nearest neighbor interactions are more in evidence. However, these curves do give a relative

(5) L. E. Drain and J. A. Morrison, *Trans. Faraday Soc.*, **48**, 316 (1952).

comparison of the potential field suffered by an argon atom on adsorption on the activated and unactivated surfaces.

It is seen from Fig. 2 that the adsorption sites available on the unactivated sample are not altered on activation. It is remarkable that the same site energy distribution is followed by the initial portion of the curve for the activated sample as for the unactivated sample. Further, activation appears to create only sites of lower energy. In the previous paper,¹ it was suggested that the asbestos fibrils were hollow cylindrical tubes and that the internal capillaries were blocked by sorbed water plugs. It was hypothesized that the interior of the hollow cylinders became available to the adsorption of non-polar gases like argon only by activation which removed the water plugs. Thus the surface of the internal capillary structure is represented by the latter portion of the distribution curve for the activated sample. The surface of the capillaries must therefore exert a lower potential field to a non-polar molecule than the external surface of the fibers. This would imply a structural array for the interior of the capillaries different from that of the exterior of the fibrils. The high heat of wetting by water on the capillary surface¹ and the low adsorption energies for argon suggest that the interior of the capillary walls may be composed of highly polar structural groups or atoms.

The heats of wetting by water of unactivated 7-R asbestos with varying amounts of adsorbed water vapor on the surface already have been published.² The heat of wetting is approximately a linear function of V_m . Thus, the heat of wetting depends primarily on the amount of bare surface available and not on which portion of the surface is covered. The adsorption energy, $U_0 - U/N_s$, of the surface is approximately constant. This is additional evidence of surface homogeneity. A slight concavity of the heat of wetting curve toward the axis should be expected if nearest neighbor interactions occur. Calculation shows that the amount of curvature to be expected is small and of the order of magnitude of the experimental error in determining the heats of wetting. That the heat of wetting data are reasonably consistent with adsorption results has been established.²

Acknowledgment.—The authors wish to express their appreciation to the Armstrong Cork Company for financial support and helpful criticism from the research staff. We are also indebted to Professor A. C. Zettlemoyer for helpful discussions in the interpretation of our results.

THE HEATS OF IMMERSIONAL WETTING OF RUTILE AND GRAPHON IN ORGANIC LIQUIDS

BY F. H. HEALEY, J. J. CHESSICK, A. C. ZETTEMAYER AND G. J. YOUNG

Surface Chemistry Laboratory, Lehigh University, Bethlehem, Pa.

Received March 5, 1954

The heats of immersion of a heteropolar hydrophilic solid, titanium dioxide (rutile), and of a homopolar hydrophobic solid, Graphon, have been measured in water and in a series of organic liquids differing in functional group, chain length or chain branching. The heat values for rutile were found to depend upon the functionality of the wetting liquid; however, except for water, the values for Graphon were almost the same for all the liquids. Both the heats of immersion and the net heats of adsorption found with rutile for a series of *n*-butyl derivatives and including a series of hydrocarbons were linear and parallel functions of the dipole moment. From the slope of the lines the average electrostatic field strength of the rutile surface at the position of the dipole was calculated to be 3.2×10^6 e.s.u. From this value, the distance from the rutile surface to the dipole center was estimated to be 3.0 Å. Variations in the chain length of *n*-alcohols or hydrocarbons had no appreciable effect on the heats of immersion of either solid. Increased branching of the carbon chain, in passing from *n*-butyl and *i*-butyl alcohol also had no effect; however, *t*-butyl alcohol had a 10% lower value.

Introduction

A number of investigators¹⁻⁴ have reported heats of immersion for a variety of solids in organic liquids. Nevertheless, the need remained for clarifying the discrepancies between some of these values and for an orderly accounting of the effect of changes in functionality and chain length of the liquid with non-porous solids of widely different polarity.

The two solids chosen for this investigation represent examples of well-defined but widely different surfaces: Graphon,⁵ which possesses a homopolar, hydrophobic surface, and rutile⁶ which possesses a heteropolar, hydrophilic surface. The organic liquids included a homologous series of hydrocarbons and alcohols and several different butyl derivatives; water was included for comparison.

From the measured heats of immersion interesting conclusions about the adsorption process were developed. In particular, a method was evolved for experimentally evaluating the surface force field of a solid.

Experimental

Apparatus.—The calorimeter, associated equipment and general techniques were the same as those previously reported⁷ except for the following changes. For the measurements with organic liquids a calorimeter employing a hard maple head was used. The calorimeter head was fitted with two entrance tubes equipped with ground glass joints. Nitrogen, which had been dried over P₂O₅, was passed through the calorimeter for several hours prior to the admission of the organic liquid. After drying and distilling the organic liquids, in the manner described below, the liquid was transferred under anhydrous conditions through one of the inlet tubes of the calorimeter. The apparatus was installed in the air-bath and then, after a suitable rating period was attained (usually within one hour), the thin-wall sample tube was broken. The rise in temperature was measured by the change in resistance of a thermistor.⁷ Electrical calibrations were made after each run.

Solids.—The titanium dioxide (rutile), du Pont Ti-Pure R-300, Lot 5550, was activated at 400° and 1×10^{-5} mm. pressure for 2 hours before sealing off. The surface area

as measured by nitrogen adsorption by the conventional B.E.T. method was 7.3 m.²/g.

The Graphon, Lot No. L-2808, supplied by the Godfrey L. Cabot Company, had a surface area as given by nitrogen adsorption of 95 m.²/g. The standard activation conditions were 25° and 1×10^{-6} mm. pressure for 24 hours.

Liquids.—The straight chain alcohols were Baker Analyzed Reagents; isobutyl alcohol, *t*-butyl alcohol, *n*-butyl chloride, *n*-butylamine and butyric acid were obtained from the Matheson Company. The hydrocarbons were obtained from Phillips Petroleum Company with hexane and heptane designated as "Pure Grade" and octane as "Research Grade."

Drying of Liquids.—Harkins and Dahlstrom⁸ had reported that traces of water caused a considerable increase in the heat of immersion of TiO₂ (anatase) in benzene. All liquids in the present investigations were carefully dried before fractional distillation through a packed column into a specially constructed receiver designed for anhydrous transfer. Magnesium sulfate was used as the drying agent for the alcohols, amine, chloride and acid. Several of the alcohols were also distilled over magnesium turnings, but this treatment did not produce a change in the heat values.

The hydrocarbons were washed with sulfuric acid, potassium hydroxide and water, followed by preliminary drying with calcium chloride. They were then stored for several weeks over sodium, and fresh sodium was added every few days. Immediately prior to use they were shaken with anhydrous magnesium sulfate and fractionally distilled over sodium.

To observe the effect on the heat of immersion of trace water and other impurities, measurements were also made with the straight-chain alcohols in the state as received; a comparison of results is given in Table I. For convenience the values will be given as positive throughout the paper although all wetting processes were exothermic.

TABLE I

EFFECT OF DRYING AND DISTILLATION OF NORMAL ALCOHOLS ON HEATS OF IMMERSIONAL WETTING OF RUTILE AND GRAPHON AT 25°, ERGS/CM.²

Liquid	Rutile		Graphon	
	Un-treated	Dried and distilled	Un-treated	Dried and distilled
Methanol	420 ± 10	426 ± 11		
Ethanol	351 ± 26	397 ± 3		
<i>n</i> -Butanol	390 ± 3	410 ± 1	115	114 ± 7
<i>n</i> -Pentanol	456 ± 9	413 ± 8	120	120

The deviations given in Table I represent the average experimental deviation of two to four runs. Where no deviation is given only a single observation was made. The data show that with rutile, the purification of the liquid generally did affect the heat of immersion, whereas with Graphon no effect was observed. Since the hydrophilic rutile surface undoubtedly adsorbs both alcohol and any

(1) K. Andress and E. Berl, *Z. physik. Chem.*, **122**, 81 (1926).
 (2) G. E. Boyd and W. D. Harkins, *J. Am. Chem. Soc.*, **64**, 1190 (1942).
 (3) E. Hutchinson, *Trans. Faraday Soc.*, **74**, 1598 (1952).
 (4) F. E. Bartell, *This Journal*, **68**, 36 (1954).
 (5) T. L. Hill, R. H. Emmett and L. G. Joyner, *J. Am. Chem. Soc.*, **73**, 5102 (1951).
 (6) L. E. Drain and J. A. Morrison, *Trans. Faraday Soc.*, **48**, 316 (1952).
 (7) A. C. Zetlemoyer, G. J. Young, J. J. Chessick and F. H. Healey, *This Journal*, **57**, 649 (1953).

(8) W. D. Harkins and R. Dahlstrom, *Ind. Eng. Chem.*, **22**, 897 (1930).

water when present, while the hydrophobic Graphon adsorbs only alcohol, the difference in the behavior of the two surfaces is readily explained.

The heat of immersion of rutile in water amounted to 550 ergs/cm.²; therefore, it was rather surprising that the heat of immersion values for this solid in the first three alcohols showed an increase in average heat after drying. This increase is believed to result from the exothermic heat of solution of water in alcohol; this heat must be supplied in order to adsorb the water from solution.

While the change in heats of immersion produced by purification of the alcohols did not exceed 15%, drying of the hydrocarbons had a profound effect on the value for rutile immersion. For example, the heat of immersion of rutile in heptane dried with calcium chloride was 292 ergs/cm.². The heat value was reduced to 218 when heptane stored over sodium for several weeks was used. The lowest value found experimentally was 144 ergs/cm.²; the heptane used was stored over sodium for several months, shaken well with anhydrous magnesium sulfate and distilled over sodium. Water is, of course, preferentially adsorbed from non-polar solvents by hydrophilic solids and thus would be expected to produce marked effects. With Graphon, which adsorbs the hydrocarbons in preference to water, no change in the heat of immersion was produced by varying the conditions for drying the organic liquids.

Results and Discussion

The present measurements were made to evaluate the effects of polarity, chain length and chain branching of organic molecules on the heat of immersion for two types of solid surfaces. The results obtained, together with the average experimental deviation of the measurements, are given in Table II for the two solids, rutile and Graphon.

TABLE II
HEATS OF IMMERSIONAL WETTING OF RUTILE AND GRAPHON
AT 25°, ERGS/CM.²

Liquid	Rutile	Graphon
Water	550 ± 18	32.2 ± 0.1
Methyl alcohol	426 ± 11	102 ± 2
Ethyl alcohol	397 ± 3	110 ± 4
<i>n</i> -Butyl alcohol	410 ± 1	114 ± 5
<i>n</i> -Amyl alcohol	413 ± 8	120 ± 0
Isobutyl alcohol	415 ± 7	115 ± 1
<i>t</i> -Butyl alcohol ^a	373 ± 17	102 ± 4
<i>n</i> -Butylamine	330 ± 40	106 ± 6
<i>n</i> -Butyl chloride	502 ± 8	106 ± 2
Butyric acid	506 ± 11	115 ± 1
Hexane	135 ± 1	103 ± 3
Heptane	144 ± 9	112 ± 2
Octane	140 ± 5	127 ± 0

^a Measured at 27° to avoid solidification of the liquid.

Effect of Polarity of Liquid.—The immersion process involves in essence the transfer of molecules from the bulk liquid to the region influenced by the surface force field of the solid. Depending on the structural features of the liquid molecules and the nature of the solid surface, this transfer may involve, in addition to the changes in the forces exerted on the liquid molecules, the changes in the orientation of these molecules, and in the degree of association of the liquid, as, for example, the amount of hydrogen bonding. When the immersion process involves only physical forces exclusive of adsorption it is considered that no changes occur in the solid surface.

A comparison of the results for the two surfaces in Table II shows that for all the polar liquids the

heats were markedly higher for rutile. For the non-polar liquids, on the other hand, the difference between the two solids was much smaller. Furthermore, while the heat of wetting of rutile varied considerably with the type of polar group, the values obtained with Graphon for the various liquids, other than water, are strikingly similar. Others^{1,4} have reported this similarity in the heats of immersion of carbon surfaces in organic liquids and the lower heat with water. Bartell's results with graphite for a number of different liquids agree well in magnitude with the results reported here.

The extremely non-polar solid Graphon⁹ would interact with the liquid molecules principally through dispersion forces. Since these forces are additive, an adsorbed molecule would tend to lie flat in order to provide the maximum amount of contact with the surface.¹⁰ With the solid in direct contact with the liquid, the polar group might be oriented away from the non-polar surface toward the polar liquid phase. With a close-packed layer of non-branched carbon chains both flat and perpendicular orientations would approach the same number of atomic contacts per square centimeter of surface. For the non-polar liquids there would be no such orienting tendency and the molecules might lie flat on the Graphon surface.

For a heteropolar surface and a polar molecule the polar van der Waals forces would make a significant contribution to the interaction energy. Since all of the straight chain butane derivatives used in this investigation possessed dipoles at their periphery, these dipoles could approach the surface closely and exert an orienting effect on the molecule. The energy of interaction between the electrostatic field of the surface, E , and the dipole moment of the molecule, μ , is given by

$$E = -F\mu \quad (1)$$

where F is an exponential function of r , the distance from the surface. If it is assumed as a first approximation that for the *n*-butane derivatives in Table II, the polarizabilities, distance from surface to dipole and cross-sectional area are the same, then the interaction energy per square centimeter of surface should be a linear function of the dipole moment.

Figure 1 contains a plot of the heat of immersion of rutile as a function of the dipole moment of these 4-carbon, straight-chain liquids. The dipole moments are those of Smyth.¹¹ It is seen that, with the exception of butyric acid, there is a linear increase in the heat of immersion with increasing dipole moment. The intercept was taken as the average value of the heat of immersion in the non-polar hydrocarbons, corresponding to zero moment. It is particularly striking that a single straight line corresponds, within experimental error, to the values obtained not only with the polar liquids, but with the non-polar liquids as well. Thus differences in dipole moment are sufficient to ex-

(9) Approximately $1/1000$ of the surface sites on Graphon have been estimated to have hydrophilic character: G. J. Young, J. J. Chessick, F. H. Healey and A. C. Zettlemoyer, *THIS JOURNAL*, **58**, 313 (1954).

(10) J. H. de Boer, "Advances in Catalysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1950.

(11) A. Weissberger, "Physical Methods of Organic Chemistry," Part II, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1614.

plain the major differences in the heats of immersion of rutile in these liquids.

The deviation of the heat value for butyric acid might be due to the higher polarizability of the carboxyl group in comparison to the other polar groups. However, it is interesting to note that Harkins¹² gives the relative heat of wetting of TiO₂ (anatase) by butyric acid as 0.77 of the heat of wetting by water. Our value for water was 550 ergs/cm.² and 0.77 of this is 424 ergs/cm.², which agrees remarkably with the value of 427 ergs obtained from the line in Fig. 1. It is possible, therefore, that our experimental value for this acid is too high.

The heat of adsorption is related to the heat of immersion by the equation¹²

$$h_{D(VSF)} = h_{E(SL)} - h_{E(SL)} + n\lambda \quad (2)$$

where the symbols are the same as those used by Harkins: *i.e.*, $h_{D(VSF)}$ is the heat of desorption of the adsorbed film per cm.² of solid surface, $h_{E(SL)}$ is the heat of emersion per cm.² of the solid into the vapor at a particular equilibrium pressure, and $n\lambda$ is the heat of vaporization of the n moles adsorbed per cm.² at this equilibrium pressure. Heats of desorption and emersion are used in order to give positive values consistent with the thermodynamic conventions of Harkins. If the equilibrium pressure is that of the saturated vapor, the equation may be reduced for these liquid-solid systems which have duplex films and zero contact angle, to the form

$$h_{D(VSe)} = h_{E(SL)} - h_L + n\lambda \quad (3)$$

where $h_{D(VSe)}$ refers to the heat of desorption of the film in equilibrium with the saturated vapor, and h_L is the enthalpy per cm.² of liquid surface. The restriction of equation 3 to systems having zero contact angles is sometimes overlooked,⁴ but it is only for such systems that it is valid to assume that the heat of emersion of the adsorbed film per cm.² of solid surface is equal to the enthalpy of the liquid surface. For systems which exhibit finite equilibrium contact angles, there is no evidence to show that the solid surface is completely covered by the adsorbed film. Equation 3 is therefore applicable to all the systems in the present investigation except Graphon-water, which has been treated previously⁹ by use of equation 2.

Since the values of n were not determined, the net heats of desorption, $h_{D(VSe)} - n\lambda$, were calculated by equation 3 for the liquids given in Fig. 1. The values of h_L were obtained from the surface tensions γ_L , and the temperature coefficients of the liquids by the relation

$$h_L = \gamma_L - T \left(\frac{\partial \gamma_L}{\partial T} \right) \quad (4)$$

These net heats of desorption are plotted on the lower line of Fig. 1. These heats were also a linear function of the dipole moment of the liquid and indeed the slopes of the two lines in Fig. 1 are essentially identical. This parallelism follows from the similarity in the h_L values which varied only between 47 and 65 ergs/cm.². The average value for the five liquids was 54 ergs/cm.². Thus the

(12) W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952.

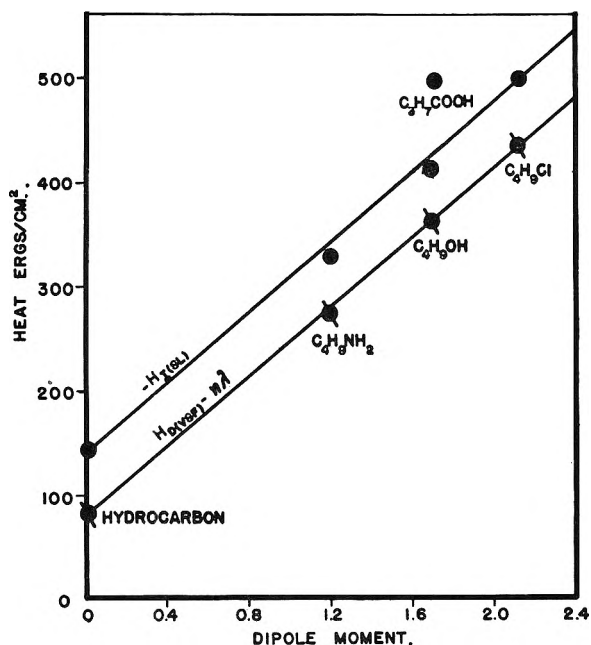


Fig. 1.—Heats of immersion and adsorption at 25° for rutile as a function of the dipole moment of the wetting liquid.

arguments presented above for the linear relation between the heat of adsorption and the dipole moment of the adsorbate apply within experimental error to the heats of immersion.

Equation 1 was derived for the energy of interaction of a dipole with a planar solid in a vacuum. If the linear relationship found is not fortuitous but is actually related to the polar van der Waals energy of adsorption as expressed by equation 1, then the slope of the line in Fig. 1 is a quantitative measure of the strength of the electrostatic field emanating from the surface of rutile immersed in the liquids. Assuming that the area occupied per molecule is of the order of 20 Å.² and that the net heat of adsorption arises primarily from the molecules in the first adsorbed layer, the surface concentration would be 5.0×10^{14} molecules per cm.². Dividing this figure into the slope of Fig. 1 gives a field strength of 3.2×10^5 e.s.u. De Boer¹⁰ has calculated the field at a distance of 2.7 Å.² from the surface of NaCl to be 2.15×10^5 e.s.u., so the agreement in magnitude is excellent. The equation of Hückel¹³ for the field strength is

$$F = \frac{8\pi\epsilon}{r_c^2} \exp - \pi\sqrt{2} \frac{r}{r_c} \quad (5)$$

where ϵ is the charge per electron. Using the value of 3.2×10^5 as F , and as r_c , which is defined as the shortest interionic distance in the crystal, the value 1.96 Å., the observed interionic distance of rutile as given by Pauling,¹⁴ the calculated value of r , the distance from the center of a surface ion is 2.2 Å., a reasonable value in view of the 2.7 Å. estimated by de Boer for an OH dipole on NaCl.

It would appear that the above experimental method of obtaining the strength of the electrosta-

(13) E. Hückel, "Adsorption und Kapillarkondensation," Akad. Verlagsgesellschaft, Leipzig, 1928.

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 365.

tic field at the surface of rutile, may prove useful with other heteropolar surfaces.

Effect of Chain Length.—It has been reported¹⁵ that the heat of wetting of BaSO₄ remained constant within about 2% in the normal alcohols containing 1, 2, 3, 4, 6 and 8 carbon atoms; the values ranged from 335 to 350 ergs/cm.². Other workers have reported a decrease in the heat of wetting with increasing chain length of normal alcohols. Thus, Harkins¹² reported a decrease of approximately 25% for TiO₂ (anatase) and 23% for SiO₂ in going from ethyl to butyl alcohol; Gaudechon¹⁶ found an over-all decrease of only 8% for the heat of wetting of Al₂O₃ in methyl and amyl alcohols, and the values for propyl and amyl alcohols agreed within 1%.

In the present work the polar liquids were the normal alcohols containing 1, 2, 4 and 5 carbons, and the non-polar liquids were hexane, heptane and octane. For both solids the data indicate that chain length alone has little, if any, effect on the heat of wetting. For rutile, the polar alcohols gave an average value of 412 ergs/cm.². The non-polar hydrocarbons gave an average value of 140 ergs/cm.². The maximum deviation in each case was about 3% and there was no evidence of any trend in the values. Thus, the results obtained for rutile are more in accord with the results reported by Ill'in, *et al.*, for the normal alcohols on BaSO₄.

There is a further striking point of agreement between the results of Ill'in with BaSO₄ and the present data for rutile. The average heat of wetting of BaSO₄ by the alcohols was 343 ergs/cm.² and by water 455 ergs/cm.², so that relative to water the alcohols had a value of 0.755. Our average value for rutile in the normal alcohols relative to that in water is 0.749. Thus, although the absolute values of the heats of immersion of the two solids differed by 25%, the relative interaction with the different liquids differed by less than 1%.

With Graphon, both the alcohols and hydrocarbons tended to show a slight increase in the heat of immersion with increasing chain length; however, the effects are not sufficiently pronounced to be considered definite.

Effect of Chain Branching.—To study the effect of the chain branching on the heat of immersion, *n*-butyl, isobutyl and *t*-butyl alcohols were used. From the data in Table II it can be seen that with

both Graphon and rutile there was no noticeable difference between the values for *n*-butyl and isobutyl alcohols; however, *t*-butyl alcohol gave a smaller heat of immersion. Since with rutile the heat effect appears to be principally a function of the number and strength of the dipoles which can be accommodated per cm.² of surface, the simple end-branching of isobutyl alcohol does not seem to affect the packing of the molecules. The decreased heat with *t*-butyl alcohol could be attributed to the necessarily decreased surface concentration of dipoles.

In summary, the results show that the heat of immersion of Graphon is essentially unaffected by the structural features of the liquid molecules, whereas the heats of immersion of rutile vary directly with the dipole moment of the liquid when other factors such as polarizability and surface concentration of dipoles can be assumed similar. Increasing the length of the carbon chains of polar or non-polar liquids has no appreciable effect on the heats of immersion.

Acknowledgment.—The authors wish to express their appreciation for the financial support provided by the Office of Ordnance Research, Ordnance Project No. TB2-0001 (457), Contract No. DA-36-034-ORD-935.

DISCUSSION

F. M. FOWKES.—In considering the energy of interaction of water and alcohols with rutile, shouldn't the hydrogen-bonding of the hydrogen on the OH groups to the oxygen of the solid surface be included? This may be the major type of interaction, and differs from dipole interaction with a fixed field.

A. C. ZETTLEMOYER.—It does not appear that hydrogen-bonding between alcohol and the rutile surface occurs since the alcohol value lies on the same line as the chloride, and recent values we have obtained with the aldehyde and nitro derivatives.

A. C. ZETTLEMOYER.—The heat effects in the monolayer are of direct interest, and these values were calculated by Equation 3 with the reasonable approximation that the heat of immersion of the monolayer-covered solid would be essentially h_L , the enthalpy of the liquid surface. This approximation was experimentally verified with the system asbestos-water.

M. L. CORRIN.—It would be, I think, instructive to look at the heats of immersion when a monolayer rather than saturated film is on the solid. In this manner, much of the smearing-out which occurs in the duplex film will be avoided.

(15) B. A. Ill'in, A. V. Kiselev, V. F. Kiselev, O. A. Likhacheva and K. D. Scherbakova, *Doklady akad. Nauk U.S.S.R.*, **75**, 827 (1950).

(16) H. Gaudechon, *Compt. rend.*, **157**, 209 (1913).

AN ANALYTICAL EXPRESSION FOR CUMULATIVE PORE VOLUMES AND PORE SIZE DISTRIBUTIONS¹

By W. O. MILLIGAN AND C. R. ADAMS²

The Rice Institute, Houston, Texas

Received March 5, 1954

A new equation for representing pore size distributions has been applied to desorption isotherms and electron microscope data previously obtained for heat-treated (2 hr., 500°) dual oxide gels in the system BeO-In₂O₃. The new equation (constants defined later) $V - v_0 = h \tanh [k(R - r_0)]$ and its derivative, $dV/dR = hk \operatorname{sech}^2 [k(R - r_0)]$, have obvious advantages over equations commonly used to express pore size distributions. Although the Gaussian distribution is highly flexible, it suffers from two disadvantages. First, it cannot be integrated into a closed form of elementary functions, and it thus becomes tedious and difficult to compare calculated cumulative pore volumes with the experimental values obtained by the customary methods of determining pore size distributions. Furthermore, the Gaussian distribution is usually too wide at the top and too narrow at the bottom for many experimental distributions. The new equation, while still as flexible as the Gaussian distribution, possesses very simple closed expressions for both the differential and integral forms. Furthermore, it is narrower at the top and wider at the bottom than the Gaussian distribution, thus representing more closely many experimentally determined distributions which we have studied. Expressions similar to the Maxwellian distribution, while easily integrable, lack versatility in that the spread of the distribution cannot be controlled independently of the most frequent pore size. The new expression not only possesses a more simple integrated form but also may have its spread adjusted independently of the other parameters. The new function is easily fitted to the experimental data by numerical and/or graphical methods. It has been successfully applied to eleven gels in the system BeO-In₂O₃, which possess distributions having most frequent pore sizes ranging from 133 to 26 Å. and a variation in spread of a factor of 10.

Introduction

Most of the commonly occurring distribution functions have been used to represent pore size distributions. Many of them, however, are restricted in either of two respects: (a) they are insufficiently versatile to cover both sharp and broad distributions of different size ranges, or (b) they are cumbersome and tedious to handle either in the integrated or differentiated form. The Gaussian distribution, widely used to represent pore size distributions, cannot be integrated into a closed form, thus making it difficult to compare calculated cumulative pore volumes with the experimentally measured values. Furthermore, it is usually too wide at the top and too narrow at the bottom to fit well most experimental distributions. The Maxwellian distribution, along with the Gaussian distribution, has been used by Shull³ to represent pore size distributions, but this equation lacks versatility in that the spread cannot be controlled independently of the most frequent pore size.

The equation proposed here

$$dV/dR = hk \operatorname{sech}^2 [k(R - r_0)]$$

where

- V = cumulative pore volume of all pores having radii equal to or less than R
- $2h$ = total pore volume excluding adsorption
- k = factor determining the sharpness of the distribution
- r_0 = most frequent pore radius
- v_0 = cumulative pore volume of all pores having radii equal to or less than r_0

possesses wide versatility in that the spread, amplitude and position of the distribution can be varied independently. Furthermore, the integrated expression

$$V - v_0 = h \tanh [k(R - r_0)]$$

possesses a very simple closed analytical form, and

(1) Presented before the twenty-eighth National Colloid Symposium which was held under the auspices of the Division of Colloid Chemistry of the American Chemical Society in Troy, New York, June 24-26, 1954.

(2) Ethyl Corporation fellow in chemistry at The Rice Institute, 1953-1954.

(3) C. G. Shull, *J. Am. Chem. Soc.*, **70**, 1405 (1948).

calculated cumulative pore volumes can be easily compared with the experimental values. In Fig. 1 the distribution, $dV/dR = hk \operatorname{sech}^2 [k(R - r_0)]$, is shown with a Gaussian distribution (dashed line) having the same height and area. It is seen that the new expression is closely similar to the Gaussian distribution. The main difference is that the new expression is a little sharper at the top and a little broader at the bottom, thus approximating more closely many experimental distributions.

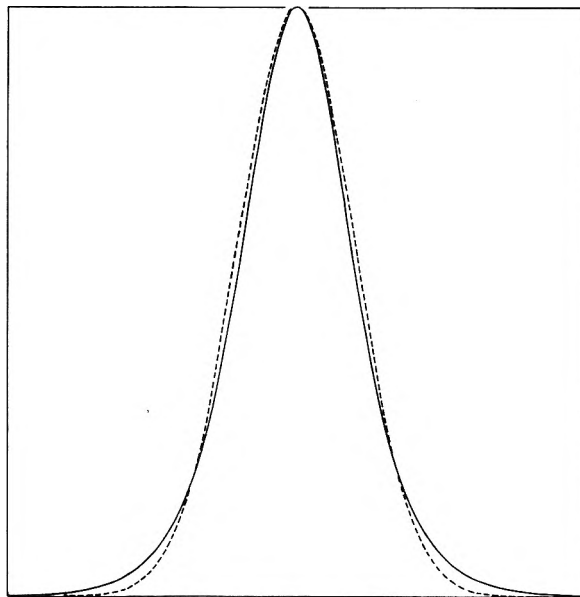


Fig. 1.—The distribution $dV/dR = hk \operatorname{sech}^2 [k(R - r_0)]$, (solid line), compared with a Gaussian distribution (dashed line) having the same height and area.

Since cumulative pore volumes are usually the only quantities accessible by methods commonly employed to determine pore sizes, it is desirable to work with the integrated form of the distribution function instead of the distribution function itself. The proposed equation is particularly adapted to such ends. The integrated expression may be fitted to the experimental values and the distribu-

TABLE I

10 MOLE % BeO-90 MOLE % In₂O₃, HEATED 500°

Electron micro- scopic pore size R, Å.	Pore volume, V, cc./g.		Electron micro- scopic pore size R, Å.	Pore volume, V, cc./g.	
	Obsd.	Calcd.		Obsd.	Calcd.
18	0.0452	0.0500	92	0.1731	0.1739
31	.0606	.0624	105	.2003	.2010
43	.0801	.0785	117	.2251	.2265
55	.1010	.0980	129	.2491	.2492
68	.1219	.1209	142	.2700	.2687
80	.1459	.1456	154	.2832	.2844

$$\sqrt{\Sigma(\Delta V)^2/n} = 0.002$$

Results and Conclusions

As an example of the agreement obtained with the new equation calculated and observed values for the cumulative pore volumes for the electron microscope results on the gel composed of 10 mole % BeO and 90 mole % In₂O₃, heat-treated at 500° for two hours are given in Table I. In Table II are given the most frequent pore size (r_0), the amplitude of the distribution (hk), the width of the distribution at half-height ($1.7628/k$), and the standard deviation of the calculated cumulative pore volumes as compared with the observed ones. Most of the deviation occurs at the extreme ends

TABLE II

Sample heated 2 hr., 500°		Most frequent pore radius		Amplitude		Width		Standard dev.	
Mole % BeO	Mole % In ₂ O ₃	des ^a r_0 , Å.	EM ^b	des	EM	des	EM	des	EM
0	100	133	120	0.00262	0.00230	104	129	0.006	0.006
10	90	83	98	.00303	.00222	88	129	.010	.002
20	80	78	78	.00317	.00296	88	73	.011	.008
30	70	78	84	.00467	.00388	84	99	.009	.007
40	60	86	84	.00892	.00452	44	101	.011	.010
50	50	96	82	.00968	.00684	44	75	.014	.019
60	40	100	101	.00569	.00376	66	105	.010	.007
70	30	85	96	.00689	.00540	73	96	.014	.013
80	20	86	77	.00566	.00436	63	85	.010	.012
90	10	70	66	.01103	.00800	44	63	.014	.017
100	0	32	26	.01347	.00360	12	59	.007	.008

$$\text{av.} = 0.011 \quad \bullet \quad 0.010$$

^a des = desorption isotherm. ^b EM = electron microscope.

tion function obtained analytically from the fitted equation.

Calculations

The integrated expression may be fitted by numerical and/or graphical methods. In the present case two parameters, k and r_0 , were found graphically and the other two, h and v_0 , were determined by the method of least squares. Cumulative pore volumes obtained for eleven gels in the system BeO-In₂O₃ by gas adsorption and electron microscope techniques already have been presented.^{4,5} The methods used in determining the parameters were as follows.

Approximate values of v_0 , k and r_0 were picked and the quantity $\tanh [k(R - r_0)]$ was plotted *vs.* $V - v_0$, using only absolute values of the two quantities so that the points below r_0 were "folded" back on the same graph paper as the points above r_0 . If the curves have a curvature upward (toward the $V - v_0$ axis), the value of k must be decreased. If the slope of the negative values is higher than the slope of the positive values, the value of r_0 must be decreased. Both the slope and curvature are very sensitive to the chosen values of k and r_0 so that correct values of k and r_0 are obtained in only about four graphings. In the authors' case special hyperbolic tangent graph paper was used, eliminating the necessity of obtaining from tables the values of the hyperbolic tangent. When the best values of k and r_0 had been obtained by the above methods the values of h and v_0 were obtained by the method of least squares.

(4) W. O. Milligan and C. R. Adams, *THIS JOURNAL*, **57**, 885 (1953).

(5) C. R. Adams and W. O. Milligan, *ibid.*, **58**, 219 (1954).

of the distributions. In Fig. 2 are shown in graphical form the results of the 10% BeO gel. The open points correspond to cumulative pore volumes obtained from two desorption isotherms at two dif-

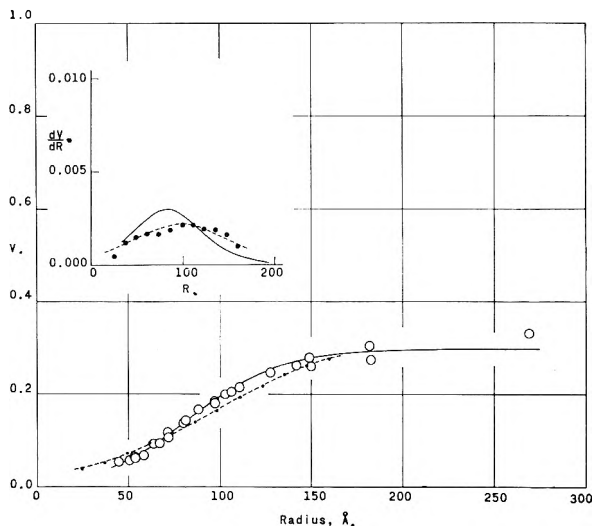


Fig. 2.—Calculated and observed cumulative pore volumes and pore size distributions for 10 mole % BeO-90 mole % In₂O₃, heated 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data. The points in the inset represented counted distributions from electron micrographs.

ferent temperatures.⁴ The closed points represent cumulative pore volumes obtained from electron micrographs.⁵ The curves are the calculated values using the new equation. The radius of the experimental points corresponds to the standard devia-

tion from the calculated values. In the inset are given the distribution functions obtained by various methods. The solid curve represents the analytical derivative of the new equation fitted to the desorption pore volumes by the method described. The points represent counted distributions obtained from high magnification electron micrographs. The dashed curve represents the new function fitted to the electron microscope pore volumes.

The over-all agreement is satisfactory. The largest deviations occur at the extreme ends of the distributions, where it would be expected that secondary effects, such as aggregation or clumping, would have a pronounced effect. In summary, the flexibility, ease of applicability, and the simple analytical forms of the new equation appear to justify its addition to the existing distribution functions.

COÖPERATIVE AND COMPETITIVE ADSORPTION IN THE PHOTOGRAPHIC PROCESS

BY T. H. JAMES AND W. VANSELOW

Communication No. 1648 from the Kodak Research Laboratories, Eastman Kodak Company, Rochester, N. Y.

Received March 5, 1954

The composition of the adsorption layer at the surface of the silver halide grain is determined by dynamic competition between the agents which can be adsorbed at any stage of the preparation and processing of the photographic emulsion. A brief review is given of some previous work on this subject, and new experimental results are reported. Uncharged pyrazolone merocyanine dyes are displaced by both silver ion and bromide ion from silver bromide, whereas the negatively charged sulfonated dyes are displaced by bromide ion and bound by silver ion. Bromide ion can displace some uncharged rhodanine merocyanines, and they can displace bromide ion. Adsorbed dyes can retard the rate of photographic development by an uncharged developing agent which is strongly enough adsorbed itself eventually to displace the dye. A strongly adsorbed dye can completely prevent development by a weakly adsorbed developing agent. A positively charged dye, or a neutral dye which can displace bromide ion, can accelerate the early stages of development by a negatively charged developing agent. Lead ion also can accelerate development by such an agent. Thiosulfate ion is adsorbed strongly by silver bromide. Several examples are given of the effect of an opposite charge in promoting adsorption, and of a like charge in displacing one adsorbed agent.

The surface conditions of the silver halide grains in a photographic emulsion are of major importance in determining their photographic behavior. These surface conditions are determined, at least in part, by adsorption of various agents present during the different stages of the preparation and processing of the photographic material. In the preparation of the emulsion, adsorption of gelatin, halide ion and certain impurities which may be present in the gelatin influence the rate of growth of the silver halide grains. Adsorption of the chemical sensitizers probably precedes the sensitizing reaction. For example, thiourea and many of its derivatives, which can act as effective chemical sensitizers, are strongly adsorbed by silver halide. Adsorption of optical sensitizers is a necessary condition for optical sensitization, although it is not a determining factor in the efficiency of sensitization. At least some of the antifoggants and stabilizers are adsorbed by silver halide. In the development process, adsorption of the developing agents by silver halide evidently precedes the development reaction in many instances. In the fixing process, adsorption likewise may play a role.

The actual composition of the adsorption layer or layers present on the surface of the silver halide grains at any given stage in the preparation or processing of the emulsion apparently is determined by a dynamic competition between the various agents present in the environment of the grain. The grain is formed in the presence of gelatin, and gelatin forms an adsorption layer 30 to 40 Å. in thickness which is rather tenaciously held by the silver halide surface.¹⁻³ Such an adsorbed gelatin layer is present at the stage of emulsion preparation at which chemical sensitizers or sensitizing dyes are added. However, both the sensitizing dyes and the thiourea chemical sensitizers are adsorbed by silver bromide, and gelatin does not prevent their adsorption. West, Carroll and Whitcomb⁴ have

shown that when a sensitizing dye is added to a suspension of silver bromide grains in gelatin, an equilibrium is established which is influenced, in general, by the amount of gelatin present, and they have shown by direct analysis that gelatin is actually displaced from the grain surface by a 2,2'-cyanine and a thiocarbocyanine dye. Conversely, James and Vanselow⁵ have shown that gelatin can displace certain sensitizing dyes, (e.g., a 3,3'-diethyloxycarbocyanine) from a silver bromide surface.

Thiourea and many of its derivatives are adsorbed by silver bromide in the absence of gelatin to form a monolayer.^{6,7} The monolayer formed prevents the adsorption of certain sensitizing dyes, such as 3,3'-diethyloxycarbocyanine ion. However, the more strongly adsorbed 3,3'-diethylthiocarbocyanine ion will displace some thiourea if added in sufficient excess, and, conversely, a solution of thiourea passed through a chromatographic column of silver bromide dyed by the thiocarbocyanine will completely displace the latter. It appears likely that thiourea can displace gelatin from silver bromide, since the thioureas readily displace the dyes which have been shown to displace gelatin.

Excess halide ion or silver ion can be adsorbed by the silver halide surface, but this adsorption corresponds to considerably less than monolayer coverage.⁸⁻¹⁰ The usual photographic emulsion is prepared in the presence of an excess of halide ions, and hence the silver halide grains should have some adsorbed halide ions on the surface. Such ions can influence the adsorption of various agents, such as the sensitizing dyes, and change in the concentration of excess halide in the surrounding solution can cause change in the amount of such agents adsorbed. As is well known,^{1,4,11,12} excess halide ion promotes

(1) S. E. Sheppard, R. H. Lambert and R. L. Keenan, *THIS JOURNAL*, **36**, 174 (1932).

(2) J. Pouradier and J. Roman, *Science et inds. phot.*, (2) **23**, 4 (1952).

(3) W. West, B. H. Carroll and D. L. Whitcomb, *J. Phot. Sci.*, **1**, 145 (1953).

(4) W. West, B. H. Carroll and D. L. Whitcomb, *THIS JOURNAL*, **56**, 0154 (1952).

(5) T. H. James and W. Vanselow, *J. Am. Chem. Soc.*, **73**, 5617 (1951).

(6) T. H. James and W. Vanselow, *THIS JOURNAL*, **57**, 725 (1953).

(7) T. H. James and W. Vanselow, *J. Phot. Sci.*, **1**, 133 (1953).

(8) E. J. W. Verwey, *Proc. Roy. Acad. Sci. Amsterdam*, **36**, 225 (1933).

(9) K. Astakhov and M. Suzdal'tzeva, *J. Phys. Chem. U.S.S.R.*, **6**, 1348 (1935).

(10) K. N. Davies and A. K. Holliday, *Trans. Faraday Soc.*, **48**, 1061 (1952).

(11) J. A. Leermakers, B. H. Carroll and C. J. Staud, *J. Chem. Phys.*, **5**, 878 (1937).

(12) T. H. James and W. Vanselow, *Science et inds. phot.*, (2) **23A**, 122 (1952).

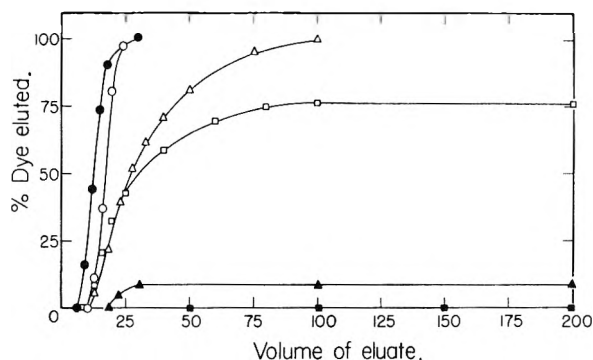


Fig. 1.—Chromatographic displacement of dye V, by acetone solutions of: Δ , acetone solution alone; \bullet , 10^{-3} M lithium bromide; \circ , 10^{-4} M lithium bromide; \blacksquare , 10^{-3} M silver nitrate; \blacktriangle , 10^{-4} M silver nitrate; \square , 10^{-5} M silver nitrate.

adsorption of the cyanine dyes, and excess silver ion tends to displace these dyes.

The literature cited shows that gelatin, the thio-urea sensitizers and the typical sensitizing dyes are not irreversibly adsorbed by silver bromide and that, at the proper concentration level, each can displace the other, at least in part. The present paper will deal with the effect of adsorption on photographic development, the adsorption of merocyanine dyes and thiosulfate ion, and with certain cooperative adsorption effects.

Experimental Procedure

The chromatographic experiments were carried out as previously described.⁶ Aged silver bromide with a specific surface of about 1400 sq. cm./gram was used at pAg 6.3. The chromatographic experiments and the pAg titrations were carried out at 25° . Photographic development tests were carried out at 20° , in a sensitometric developing machine with mechanical agitation. Exposures were made on an Eastman IIB Sensitometer, using a combination of Kodak Wratten No. 36 and Wratten No. 38A Filters to give blue-light exposure.

The dyes used were selected by B. H. Carroll, and were as follows

- I, 3,3'-diethylthiacarbocyanine chloride
- II, 3,3'-diethylloxycarbocyanine *p*-toluenesulfonate
- III, 1,1'-diethyl-2,2'-cyanine chloride
- IV, anhydro-3,3'-dicarboxymethylthiacarbocyanine hydroxide
- V, 4-[(3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-3-methyl-1-(*p*-sulfophenyl)-5-pyrazolone
- VI, 3-ethyl-5-[3-methyl-2(3H)-thiazolylidene ethylidene]-rhodanine
- VII, 5-[(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene]-3-*p*-sulfophenylrhodanine
- VIII, 4-[(3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-3-methyl-1-phenyl-5-pyrazolone
- IX, 4-[(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene]-3-methyl-1-(*p*-sulfophenyl)-5-pyrazolone
- X, 4-[(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene]-3-methyl-1-phenyl-5-pyrazolone

Experimental Results and Discussion

Adsorption of Merocyanine Dyes.—West, Carroll and Whitcomb⁴ observed an increase in the adsorption of rhodanine and thiohydantoin merocyanine dyes with increasing silver ion concentration, which they attributed to bonding action between silver ion and the sulfur of the C=S group. On the other hand, a pyrazolone merocyanine, 4-[(1,3,3'-trimethyl-2-indolenylidene)-ethylidene]-3-methyl-1-phenyl-5-pyrazolone, was adsorbed to a greater extent as the bromide ion concentration in-

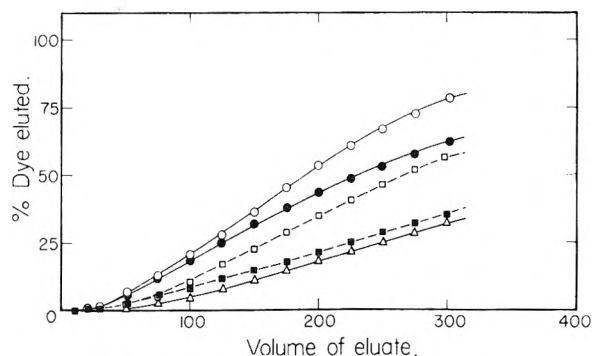


Fig. 2.—Chromatographic displacement of dye VIII by 50% ethanol solutions of: Δ , solvent alone; \square , 10^{-3} M potassium bromide; \blacksquare , 10^{-4} M potassium bromide; \bullet , 10^{-4} M silver nitrate; \circ , 10^{-3} M silver nitrate.

creased. Our chromatographic displacement experiments with the sulfonated pyrazolone dye V showed, however, that bromide ion displaced this dye and silver ion caused it to be more strongly adsorbed.¹² Further investigation seemed desirable. We compared two pairs of sulfonated and unsulfonated pyrazolone merocyanines, dyes V and VIII, and IX and X.

Figure 1 shows the percentage of dye V displaced from the silver bromide column by acetone solutions of silver nitrate and lithium bromide. Similar results obtained with 50% ethanol solutions of silver nitrate and potassium bromide confirm our previous findings with aqueous solutions that bromide ion displaces and silver ion binds the dye.¹² Other halides displace the sulfonated dye V in the order expected. The volumes of 0.001 M aqueous solution required to displace 30% of this dye were: KI, 70 ml.; KBr, 92; KCl, 138; water, 685; KF, 800; $NaNO_3$, 800. Figure 2 shows, however, that both silver ion and bromide ion displace the unsulfonated dye VIII. Similar results were obtained with the more weakly adsorbed unsulfonated dye X. The corresponding sulfonated dye IX was so weakly adsorbed by silver bromide of pAg 6.3 that only 4 ml. of 50% ethanol or of the silver nitrate or potassium bromide solutions displaced it from the column. However, if the column was treated with 0.001 M silver nitrate before the dye was added, the dye then was adsorbed so strongly that 100 ml. of silver nitrate solution failed to displace any of it. The preceding results are in agreement with the assumption that the unsulfonated pyrazolone dyes are adsorbed primarily by van der Waals forces, and adsorption of ions of either sign will tend to displace the dyes. Electrostatic attraction to the silver ions, however, is a major factor in the adsorption of the negatively charged sulfonated dyes.

Chromatographic experiments with dye VI and rhodanine merocyanines confirm the findings of West, Carroll and Whitcomb that silver ion increases the adsorption of these dyes. Bromide ion tends to displace them. Conversely, dye VI displaces bromide ion from silver bromide. Samples of precipitated, aged silver bromide were titrated with dye solution, and the changes in pAg in the solution determined. Table I gives the results obtained with 9 g. of silver bromide used in 100 ml. water at 25° . The dye was added in 0.001 M

ethanol solution. A control titration with pure ethanol showed no significant change in pAg in the amounts added. Approximately 6 micromoles of dye was required to form a monolayer on the silver bromide sample, and the maximum displacement of bromide ion occurred at this point.

TABLE I

TITRATION OF SILVER BROMIDE WITH MEROCYANINE DYE

Dye added, μ moles	pAg	$[Ag^+] \times 10^5$	Br^- liberated, μ moles	Br^-/dye
0	6.30	0.500	0.000	
2	6.45	.355	.044	0.022
4	6.98	.105	.395	.099
6	7.36	.044	1.104	.184
9.5	7.35	.045	1.116	.117

Adsorption of Developing Agents.—Sheppard and Meyer¹³ suggested that adsorption of developing agents by silver halide is an important step in the development process, and this suggestion receives considerable support. The often-observed dependence of development rate on a fractional power of the developing-agent concentration^{14,15} is most easily explained on the assumption that adsorption precedes development, and chromatographic experiments have demonstrated such adsorption for a number of developing agents.^{5,16} The pH-dependence of the chromatographic experiments indicates that many developers, as used in practice, can displace gelatin from the silver halide grain. However, significant retardation of development by gelatin can occur. Adsorbed gelatin markedly decreases the rate of reduction of exposed or unexposed silver chloride by the weakly adsorbed hydroxylamine.¹⁷ The rate of this reaction decreases with increasing addition of gelatin until the amount of gelatin added is sufficient to produce an adsorbed layer about 40 Å. thick. Beyond this, the rate becomes almost independent of gelatin addition.

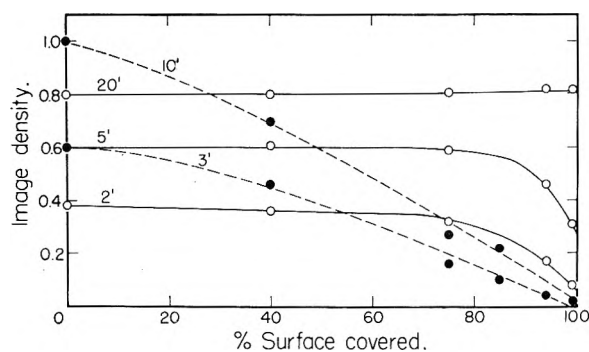


Fig. 3.—Fog-corrected developed densities for constant exposure plotted against % surface coverage by dye III; solid curves represent 2, 5 and 20 minutes' development in *s*-dimethyl-*p*-phenylenediamine; broken curves represent 3 and 10 minutes' development in hydroxylamine.

(13) S. E. Sheppard and G. Meyer, *J. Am. Chem. Soc.*, **42**, 689 (1920).

(14) T. H. James, *J. Chem. Phys.*, **14**, 536 (1946); L. J. Fortmiller and T. H. James, *PSA Journal (Phot. Sci. and Technique)*, **17B**, 102 (1951).

(15) G. I. P. Levenson, *J. Phot. Sci.*, **1**, 117 (1953).

(16) T. H. James and W. Vanselow, *J. Am. Chem. Soc.*, **74**, 2374 (1952).

(17) T. H. James, *ibid.*, **62**, 536 (1940).

The 40-Å. thickness is in good agreement with that found for monolayer formation on silver bromide.^{2,3}

Adsorbed sensitizing dyes might be expected to compete with the developer for adsorption sites, and hence retard development. The degree of retardation should depend upon the strength of adsorption of both dye and developing agent. An example which can be interpreted in this way is illustrated in Fig. 3. A photographic emulsion was divided into several samples before coating, and amounts of dye III were added to form an emulsion series in which the grain surface was covered to different degrees by the dye. These emulsions were coated on film base, exposed to blue light to which the dye does not sensitize, and developed.

In Fig. 3, the fog-corrected developed densities for one exposure step are plotted against the percentage of the grain surface covered by dye. The solid curves represent development by *s*-dimethyl-*p*-phenylenediamine (0.01 *M* developing agent, 0.10 *M* sodium sulfite, 0.025 *M* borax and 0.001 *M* KBr) for the times marked on the curves. The broken curves represent development by hydroxylamine (0.04 *M* developing agent, 0.001 *M* KBr, and *pH* 13). A depression in density of the dyed emulsion might represent either an effect upon development or a desensitization of latent-image formation. However, when the *p*-phenylenediamine is used as developer, the depression is significant only when more than 75% of the grain surface is covered, and the retarding action of the dye is completely overcome in 20 minutes' development time. Hence, the depression is primarily a development effect. When hydroxylamine is used as developer, the density drops off sharply as the amount of covered surface increases, and development is entirely prevented by complete surface coverage. These results are in accord with the chromatographic evidence that hydroxylamine is much less strongly adsorbed than the *p*-phenylenediamine derivatives. Hydroxylamine evidently is unable to displace the cyanine dye used. Experiments also were carried out with the merocyanine dye VI which is less strongly adsorbed than III. This dye retards development by hydroxylamine but does not completely prevent it, even for full surface coverage. It also shows significant desensitizing action which cannot be attributed to a development effect.

Cyanine dyes I and III *accelerate* development by hydroquinone in the initial stages, and the degree of acceleration increases with increasing surface coverage. In the later stages of development, however, less density is obtained with the dyed than with the undyed emulsions. This effect is illustrated for two different exposure levels in Fig. 4. Similar results were obtained with merocyanine dye VI, but the corresponding 3-carboxymethyl derivative actually retarded development in the early stages.

The preceding experiments illustrate three ways in which an adsorbed dye can influence the rate of development of the photographic grains. The dye can retard development by an uncharged developing agent which is strongly enough adsorbed eventually to displace the dye. A strongly adsorbed dye can completely prevent development by

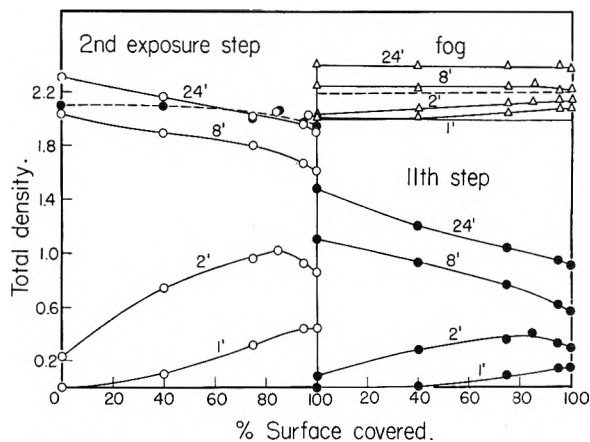


Fig. 4.—Total developed densities for second and eleventh exposure steps and fog against % surface coverage by dye III, for 1, 2, 8 and 24 minutes' development by hydroquinone (0.05 *M* hydroquinone, 0.10 *M* sodium sulfite, 0.1 *M* sodium carbonate, 0.001 *M* potassium bromide). Broken curve represents 90 minutes' development in a standard motion-picture negative M-Q developer.

a weakly adsorbed developing agent such as hydroxylamine. A positively charged dye or neutral dye which can displace bromide ion can accelerate the early stages of development by a negatively charged developing agent. The first two cases can be explained on the basis of competitive adsorption of the dye and developing agent. The third introduces another factor, the charge effect.

Lüppo-Cramer first observed that pinacyanol and pinachrome accelerate development by hydroquinone,¹⁸ and suggested that the dyes promote adsorption of the hydroquinone.¹⁹ The acceleration is similar to that produced by positively charged quaternary salts of the pyridinium type which, according to Lottermoser and Steudel,²⁰ depress the negative charge of the silver halide grain or possibly even make the charge positive, and thus permit more ready access of the negatively charged developing agent to the grain surface. The degree of acceleration increases with increasing charge of the developing agent.^{21,22} The positively charged thallos ion, which is adsorbed by silver bromide, also accelerates development by hydroquinone, as is well known. Following a suggestion by G. W. Luckey, we found that prebathing an exposed motion-picture positive emulsion in 0.01 *M* lead nitrate or acetate accelerates subsequent development by hydroquinone and hydroquinone monosulfonate. Figure 5 illustrates the relative effectiveness of lead ion, thallos ion and dodecylpyridinium ion solutions used as prebaths. Lead ion eliminates the induction period in development, just as does the quaternary ion. Chromatographic experiments show that lead ion used in 50% ethanol solution displaces dyes II and VIII from silver bromide but is less effective than dodecylpyridinium ion. This correlation between adsorption and acceleration of

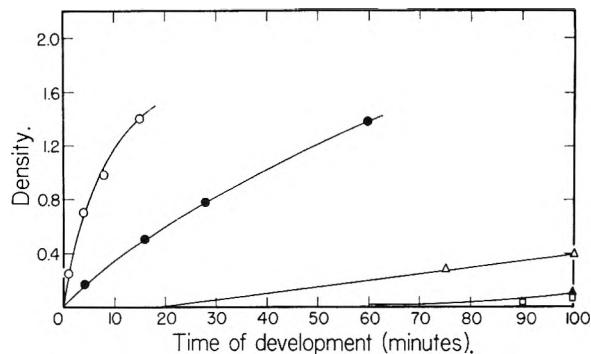


Fig. 5.—Effect of prebathing an exposed motion-picture positive film before development by hydroquinone monosulfonate. Developed densities for the log *E* = 1.90 step are plotted against time of development. Film prebathed in: ○, 0.001 *M* laurylpyridinium ion; ●, 0.01 *M* lead ion; △, 0.01 *M* thallos ion; ▲, 0.001 *M* nonylpyridinium ion; □, no addition.

development is in agreement with previous results obtained with a series of quaternary salts.²²

The acceleration of development produced by the merocyanine dye VI which has no net charge, also can be explained on the basis of the charge effect, since this dye displaces some bromide ion from the silver bromide and should decrease the negative surface charge. Both development acceleration and bromide ion displacement reach a maximum for monolayer surface coverage. The acceleration arising from reduced surface charge evidently more than offsets any retarding action which the dye might otherwise exert on the adsorption of the developing agent. When the merocyanine dye contains a carboxyl group, on the other hand, the charge effect acts in the opposite sense, since the dye itself is negatively charged in alkaline solution. This dye should increase the surface charge, and it actually retards development by hydroquinone.

The cyanine dyes likewise favor the approach of the hydroquinone to the surface, but they are not completely displaced from the surface by the developer.⁵ This poses the question of how development can occur when the surface is completely covered by dye. Possibly a reorientation of the adsorbed dye layer occurs in the presence of the oppositely charged hydroquinone, and both become strongly adsorbed. Space could be provided if the dye molecules reoriented to end-on adsorption,⁴ if the hydroquinone promoted poly-layer adsorption, or if it actually displaced the dye but held it as a secondary adsorbed layer. A further possibility is that development can occur by an electrolytic mechanism and the dye acts as an intermediate in the electron transfer.

Adsorption of Thiosulfate.—Sodium thiosulfate readily displaces neutral or negatively charged merocyanine dyes from silver bromide. Figure 6 shows the displacement curves for dye V and two thiosulfate concentrations. The thiosulfate ion, or a silver thiosulfate complex, remains adsorbed by the silver bromide. This is shown by the fact that a second portion of dye added to the column after the first has been eluted will not be adsorbed, even though the column is washed with water between the elution and the second addition of dye.

(18) H. Lüppo-Cramer, *Kolloid Z.*, **18**, 163; **19**, 17 (1916).

(19) H. Lüppo-Cramer, *Phot. Korr.*, **75**, 81 (1939).

(20) A. Lottermoser and R. Steudel, *Kolloid Z.*, **82**, 319; **83**, 37 (1938).

(21) T. H. James, *THIS JOURNAL*, **55**, 563 (1951).

(22) W. Vanselow and T. H. James, *PSA Journal (Phot. Sci. and Technique)*, **19B**, 36 (1953).

Similar results were obtained with dye VI where both dye and thiosulfate were used in 50% ethanol solution because of the low solubility of this dye in water.

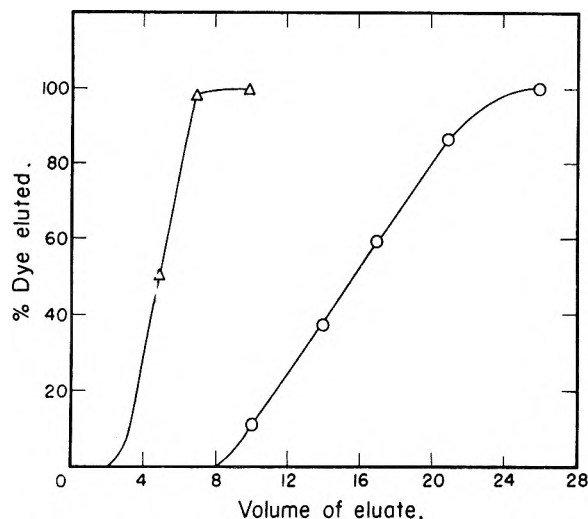
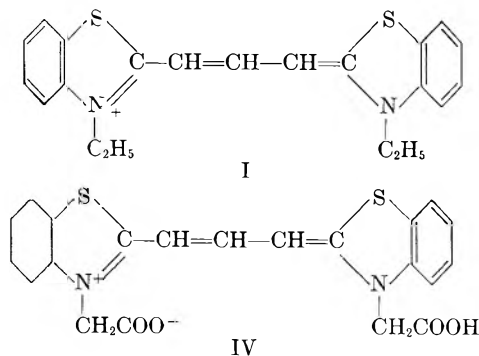


Fig. 6.—Chromatographic displacement of dye V, by sodium thiosulfate; O, 0.0001 *M*; Δ, 0.001 *M*.

The positively charged dye ions such as phenosafranin and dyes I and II are not removed by an aqueous 0.001 *M* thiosulfate solution, even though phenosafranin and dye II can be removed by water alone in sufficient volume.⁵ The thiosulfate ion evidently causes the dye ion to be more strongly held. When the thiosulfate is used in 50% ethanol solution, however, the dyes are much more readily removed by that solution than by the solvent alone. The ease of displacement is still influenced by charge. This is illustrated by a comparison of the amount of thiosulfate solution required to displace the positively charged dye I and the uncharged cyanine IV.



Displacement of 50% of these two dyes by 1.0 *M* pyridine in 50% ethanol requires 5.2 and 5.6 ml. of solution, respectively. Displacement by 0.001 *M* thiosulfate in 50% ethanol requires 19.6 and 6.2 ml., respectively. Further evidence of an effect of charge was found in experiments with several pairs of sulfonated and unsulfonated merocyanines containing a rhodanine nucleus.

Pyridine was about as effective or more effective in displacing the unsulfonated as in displacing the sulfonated dye (*e.g.*, dye VII). Thiosulfate, however, was invariably more effective in displacing the sulfonated (negatively charged) dye.

The adsorption of thiosulfate by silver bromide may be of significance in the photographic fixing process. The ion may be adsorbed as a first step, with the formation of AgS_2O_3^- as the adsorption complex. In the presence of sufficient excess thiosulfate, a second ion may then react to form $\text{Ag}(\text{S}_2\text{O}_3)_2^{2-}$ which passes into solution.

Acknowledgment.—We are indebted to Drs. B. H. Carroll, G. W. Luckey and W. West, of these Laboratories, for suggestions made during the course of this work, and to Dr. Carroll for the preparation of the special emulsion coatings used.

DISCUSSION

NORMAN HACKERMAN.—Do you have some opinions as to how the thioureas and other of the sulfur-containing compounds are bound to the halide grain? We have found very similar changes with substituted thioureas and believe that covalent bond forms.

T. H. JAMES.—Our evidence suggests covalent bond formation.

DONALD GRAHAM.—Has there been any measurement of the relative strengths of adsorption, other than the reputed displacement series?

T. H. JAMES.—Yes, some isosteric heats have been determined which are, in most cases, in line with observed displacements. These heats range from 4 to 12 kcal./mole.

DONALD GRAHAM.—The equilibrium function from adsorption data for low coverage offers a useful measure of adsorption strengths even for those cases in which the monolayer is only roughly defined.

L. F. GLEYSTEN.—What is the effect of these adsorbed ions, which accelerate development of the photographic image, on unexposed areas of the film?

T. H. JAMES.—The ions generally accelerate reaction with the unexposed areas, too, but the quantitative relations may not be equal.

BINARY LIQUID PHASE ADSORPTION

BY CARROLL L. LLOYD AND B. L. HARRIS¹*Chemical Engineering Department, Johns Hopkins University, Baltimore, Maryland**Received March 5, 1954*

Selective adsorption data for the binary liquid phase system toluene-isoöctane are presented which are believed to be the most accurate reported for any system. The curves indicate specificity of active carbon and silica gel for toluene. The aromatic index was correlated with nitrogen area for a series of samples of carbon and clay. An accuracy approaching 1% in estimating nitrogen area in the linear portion of the curve can be accomplished by this precise and rapid method. Structural changes in the adsorbent surface can also be observed as a function of activation temperature. The refractive index-composition curve of the toluene-isoöctane system was determined very completely. The linearity of the refractive index-volume per cent. curve indicated nearly ideal solution behavior. Isotherms of the adsorption of each of the two components were derived from the assumption of mutually competing adsorption without interaction. These isotherms appear reasonable and agree with pure component vapor isotherms in the region of high concentration of each component.

Introduction

The mechanism of adsorption from a binary liquid mixture onto a solid adsorbent has been studied by many investigators. Rapid progress has not been made in this field because of inherent difficulties not encountered in gas phase adsorption. The usual experimental procedure involves contacting the adsorbent with a binary solution and noting the composition of the bulk mixture before and after adsorption. A material balance is then set up.

$$W(C_a)_0 - (W - W_a - W_b)(C_a)_t = W_a$$

where

- W = total wt. of binary mixture introduced, g.
 W_a = wt. of component A adsorbed, g.
 W_b = wt. of component B adsorbed, g.
 $(C_a)_0$ = concn. of component A in original mixture, wt. %
 $(C_a)_t$ = concn. of component A in equilibrium mixture, wt. %

It is obvious that to solve this equation it would be necessary to know the weight of the mixture adsorbed by the solid. Failing measuring this directly, various indirect means have been used. Chief among these is the use of isotherm data from gaseous adsorption of the pure components of the binary mixture.

Various authors, among them Innes and Rowley,² Kipling and Tester,³ and Lewis, Gilliland, *et al.*,⁴ have studied binary vapor phase adsorption and have related it to the adsorption of the components. They found that the results could be explained by equations which assumed that the area occupied by each molecular species was independent of that occupied by the other. One expression of this equation is

$$\sum_1^n \frac{N_1}{N'_1} = 1$$

where N_1 is the number of moles of one component adsorbed from the mixture while N'_1 is the number of moles of the pure component comprising a monolayer.

It can readily be shown that for binary liquid phase adsorption the Lewis-Gilliland equation can be derived based upon simple assumptions. These are that (1) the liquid phase adsorption is unimolec-

ular (or the second and succeeding layers differ insignificantly from the bulk liquid composition), (2) any liquid condensed in the pore spaces has this same concentration, (3) no interpacking or interaction occurs between molecules, and (4) the packing factor is the same for the binary liquid and vapor phase adsorption.

Correlations of nitrogen surface areas of cracking catalysts and the "aromatic index," a measure of binary liquid adsorption of a toluene-isoöctane mixture, has been demonstrated by Scheumann and Rescorla⁵ and by Pratt.⁶ These findings are of practical interest to those needing rapid surface area data and so it would be of interest to extend such correlations to other adsorbents.

Accordingly, the authors undertook to study the adsorption of toluene-isoöctane mixtures on series of adsorbents utilizing a differential refractometer, the data to be obtained accurately enough to allow calculation according to the Lewis-Gilliland equation to test the reasonableness of that equation for exploring liquid phase studies.

Apparatus and Technique

The Differential Refractometer.—This instrument was used to determine the change in composition that occurred in the bulk liquid as a result of the adsorption process. Since the limit of accuracy of this equipment was 0.000003 refractive index unit, it was admirably suited for the application. The apparatus was manufactured by the Phoenix Precision Scientific Instrument Co. of Philadelphia. The principle of operation consisted primarily of producing, reflecting and recording the deviation of a light beam. A mercury arc lamp as the source of the radiation and suitable filters allowed the operator a choice of frequencies. In this work the green line at 5460 Å. was chosen. The radiation passed through a vertical slit which could be adjusted to any desired width. Next, the light entered the cell which contained the two liquid samples separated by a quartz barrier inclined at an angle to the axis of the beam. Thus the final direction of the light beam depended upon the refractions which occurred in both liquid samples. The cell was mounted on a swivel which rotated through 180° so that the beam could be deflected on the opposite side of the optical axis. This procedure increased the reading obtained and eliminated the necessity for a zero setting upon each occasion. After traversing the cell, the beam entered an optical train which focused it upon a scale. Readings were taken at cell positions of 0° and 180° and the difference (Δd) was recorded. A calibration factor allowed the operator to determine the refractive index difference directly from the formula

$$\Delta n = K\Delta d$$

For this apparatus the value of K was 0.000988.

(1) Box 88, Glenarm, Maryland.

(2) W. B. Innes and H. H. Rowley, *THIS JOURNAL*, **51**, 1154, 1172 (1947).

(3) J. J. Kipling and D. A. Tester, *J. Chem. Soc.*, 792, 4123 (1952).

(4) W. K. Lewis, E. R. Gilliland, B. Chertow and W. P. Cadogan, *Ind. Eng. Chem.*, **42**, 1319 (1950).

(5) W. W. Scheumann and A. R. Rescorla, *Proc. Am. Petroleum Inst.*, **27** (III), 34 (1947).

(6) T. Pratt, *ibid.*, **27** (III), 38 (1947).

A differential refractometer does not require the extreme control of temperature needed in an absolute refractometer. If the temperature changes slightly, the refractive indices of both solutions change simultaneously. An error is introduced if the temperature coefficients of the two solutions are appreciably different. In this differential refractometer the cell was surrounded by air which was maintained at constant temperature by water flowing through an outer casing. The temperature of the cell was $25.0 \pm 0.1^\circ$ in this work.

The Immersion Refractometer.—This instrument was used to determine the refractive index of toluene-isoöctane solutions as a function of composition. It was manufactured by Bausch and Lomb and possessed an accuracy of approximately 0.00005 refractive index unit. However, the best line through a large number of determinations of different composition is accurate to about 0.00002 refractive index unit. The temperature control is very important and was maintained at $25.0 \pm 0.05^\circ$. Special precautions were taken to ensure that no loss of the volatile constituents occurred.

The Vapor Phase Apparatus.—The equipment consisted of a section for producing and measuring the vacuum and another section in which adsorption occurred. A mechanical and a mercury diffusion pump combined to produce a vacuum of 10^{-6} mm. of mercury. The magnitude of the vacuum could be checked on a McLeod gage. The adsorption section consisted essentially of an adsorbent container connected to an adsorbate container. The adsorbent container was maintained at $25.0 \pm 0.05^\circ$ by a constant temperature bath with its associated equipment. The adsorbate container was surrounded by a Dewar flask in which other temperatures were accurately maintained by melting pure compounds. Adsorbate condensation did not occur in the connecting glass tubing since the environmental temperature exceeded 25.0° at all times.

Silica Gel.—This was a sample of Davidson Chemical Corp. 69514-200 gel from K1 Lot X581 having an activation temperature of 525°F . No screening was performed before use. However, the bottle was thoroughly shaken before the gel was removed to ensure random sampling. Nitrogen adsorption studies on this material showed a surface area of 793 square meters per gram when the data were evaluated by the method of Joyner, Weinberger and Montgomery.

Activated Carbon.—This adsorbent was furnished by the West Virginia Pulp and Paper Co. All of the samples were very finely divided except sample 1 which contained many small lumps of carbon. The nitrogen isotherms were intermediate in shape between Types I and II isotherms. The Joyner, Weinberger and Montgomery method was used in evaluating the nitrogen surface areas: carbon 1, 584 square meters/gram; 2, 547; 3, 755; 4, 991; 5, 1065; 6, 1050; 7, 1264.

Attapulgus Clay.—The clay was obtained from the Attapulgus Clay Company of Philadelphia, Pa. All the samples were extruded material from the same stock of raw clay and possessed a size distribution between 30 and 60 mesh. The nitrogen surface areas were determined by the conventional Brunauer, Emmett and Teller method in the laboratory at the company.

Clay	m. ² /g.	Calcination temp., °F.
A	64	1500
B	118	1400
C	127	300
D	138	400
F	134	900

Toluene.—The toluene used in the surface area correlation work was Merck and Co., reagent grade material. This chemical complied with A.C.S. specifications and possessed a boiling range of 1° including 110.6° . This toluene was sufficiently pure for this application since absolute values of toluene adsorption were not required. However, in determining selective adsorption curves and isotherms, a purer reagent was necessary. For this application a very good grade of toluene was obtained from the Eastman Kodak Co. in Rochester, New York. It was derived from sulfonic acid and possessed a boiling range of 110.2 – 110.4° . Since the degree of purity was so high, no further purification was attempted.

Isoöctane (2,2,4-Trimethylpentane).—The isoöctane used in this study was a portion of Batch 3 prepared May 4, 1950, by the Enjay Company, Inc., of New York, N. Y.

It had passed A.S.T.M. specifications for isoöctane used as primary reference fuel for knock characteristics of Motor Fuels and Aviation Fuels. The boiling point was 99.22° which was within the specification of $99.25 \pm 0.05^\circ$. The material was used without additional purification.

Stopcock Grease.—A special fluorinated lubricant was needed to withstand the attacks of organic vapors. Therefore, several samples of perfluorolube oil and perfluoro grease were obtained from the Jackson Laboratories of E. I. du Pont de Nemours and Co., Inc. The perfluoro grease was finally used in this work. Sample FCD-441 proved very effective as a stopcock lubricant and it successfully resisted both toluene and isoöctane vapor. Sample FCX-441 was only partially satisfactory because the material easily striated in the stopcock and caused leakage.

Aromatic Index Measurements.—The aromatic index is defined as the refractive index change during the adsorption of a toluene-isoöctane solution of a standard composition. This refractive index change is multiplied by 10^4 for convenience in using the numbers. In order to obtain maximum sensitivity of the aromatic index, it was necessary to evaluate several factors. First, the selective adsorption curve must be determined in order to find the optimum toluene concentration for maximum concentration change. Also the ratio of liquid to adsorbent must be kept as low as possible to obtain maximum readings. However, this ratio must be large enough so that a sufficient sample of supernatant liquid can be obtained for analysis. One other restricting factor in these experiments was the fact that the limit of the instrument was 0.0100 refractive index unit difference. Thus, the final liquid to adsorbent ratio was a compromise, and values of 12, 5 and 4 milliliters per gram were chosen for the carbon, clay and silica gel, respectively. The toluene concentration for maximum sensitivity was approximately 20 volume per cent. in each case, and this composition of binary solution was adopted.

The adsorbents were first evacuated at a pressure of 10^{-5} mm. and 100 – 110° in a test-tube to remove all volatile impurities. Then the samples were transferred under dry nitrogen into 35-ml. adsorption bottles having ground glass tops. Dry nitrogen was present in the bottles throughout the run. The standard volume of stock binary solution was pipetted into the bottle. As the adsorption proceeded liquid molecules replaced gas molecules in the adsorbent as bubbles of air were seen evolving from the solid sample. However, no escape of vapor occurred since the weight of the bottle remained constant. No mechanical shaking was provided since this operation would probably result in wetting the ground glass tops and subsequent loss of liquid by evaporation. Instead a vigorous shaking by hand every 15 minutes was substituted. Equilibrium was reached in 3–4 hours depending upon the nature of the adsorbent. The attainment of equilibrium was determined by noting refractive index change as a function of time for several samples. Very close checks within the experimental error were obtained in these runs. During the first part of the run the bottles were allowed to stand at room temperature (23 – 27°). However, for the last one-half hour they were partially immersed in a constant temperature bath maintained at $25.0 \pm 0.05^\circ$. Samples in a constant temperature bath maintained at $25.0 \pm 0.05^\circ$. Samples of the supernatant equilibrium mixture were then removed with a hypodermic syringe. The refractive index change was determined by comparing the original and equilibrium solutions in the differential refractometer.

Binary Adsorption vs. Composition.—The solution of this problem required the completion of three different sets of experiments. The refractive index change in liquid phase adsorption was compiled over the entire composition range. Secondly, the refractive index-composition curve was determined so that the refractive index change could be converted directly to composition change. Then vapor phase adsorption data were obtained for use in the Lewis-Gilliland equation. The following discussion describes the experimental method.

The experimental determination of liquid phase adsorption was accomplished by the same methods that were described above. The attainment of equilibrium was checked by the constancy of concentration change as a function of time and also by the very close agreement obtained using different samples of adsorbent. The amount of solution added to the adsorbent was determined by weight in these experiments so that increased accuracy was obtained.

The binary solutions were prepared by volume and checked by weight on an analytical balance. The error was further reduced by preparing a large volume (100 cc.) of binary mixture. The range of composition was covered with samples every five volume per cent. The solutions were kept in brown bottles with screw-type lids, using aluminum foil gasket to prevent evaporation. This method of storage proved very satisfactory since no change in refractive index of the solutions was noted over the entire period of experimentation. The refractometer was immersed in about 15 ml. of binary solution contained in a small, enclosed cup, maintained at a temperature of $25.0 \pm 0.05^\circ$. Temperature equilibrium was attained in about 15 minutes. About 10 readings were taken on the refractometer and averaged to give the final results. Each prism of the refractometer was calibrated before the determinations were made.

A gravimetric method was used to determine the adsorption of vapors on the two adsorbents. A special adsorption bottle containing a weighed amount of degassed adsorbent was maintained at a temperature of $25.0 \pm 0.05^\circ$. Thus the value of the saturation pressure of P_0 for the adsorbate was established at this temperature. The adsorbate liquid was kept at a series of lower temperatures so that different values of relative pressure could be obtained. Constant temperature for the adsorbate container was obtained by using surrounding baths at the freezing points of benzene, water, aniline and diethylene glycol. After constant temperature had been established for both adsorbent and adsorbate containers, the system was evacuated to 10^{-6} mm. and then the vapor was allowed to contact the sample. The attainment of equilibrium was determined by subsequent constant weights of the adsorbent. A correction was made for the weight of vapor contained in the sample flask and not actually adsorbed. If the air temperature at the balance varied appreciably during a run a correction was made for the difference in buoyancy between the brass weights and the sample containers. The time required for equilibrium was approximately 2 hours for carbon and 4 hours for silica gel. The absolute accuracy of this work was about ± 0.001 g./g. of adsorbent, the error being smaller when larger samples of solid were used.

The vapor pressure data were obtained from work by Stull.⁷ The data plotted as a straight line on a Clausius-Clapeyron plot over the short range of temperature involved in this work.

Results and Discussion

The aromatic indices of the various carbon and clay samples for which nitrogen areas were quoted above were found to be as

Carbon	Aromatic index	Clay	Aromatic index
1	11.50	A	2.22
2	11.72	B	4.20
3	13.72	C	10.10
4	14.96	D	9.67
5	15.42	F	5.50
6	15.24		
7	16.47		

These data are plotted in Figs. 1 and 2, respectively. In the case of carbon (Fig. 1) a reasonably good straight line was obtained in the region from 755 to 1264 square meters per gram. However, below this range a break occurred which was probably due to a structure change in the material. Possibly the activation process in this region eliminated a large number of pores which were not available for adsorption.

The correlation for clay (Fig. 2) resulted in a straight line region for samples of low surface area although the paucity of data did not establish this unequivocally. The variation of nitrogen area with activation temperature for this material has been explained in a paper by McCarter, Krieger

(7) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

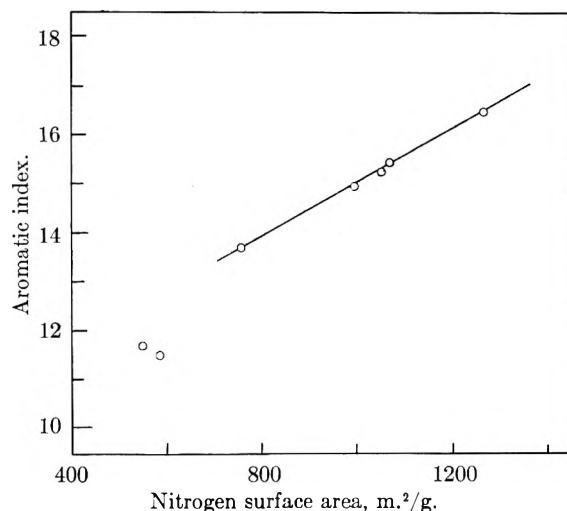


Fig. 1.—Correlation of nitrogen surface area with aromatic index for carbon; solid-liquid ratio, 1 g./12 ml.

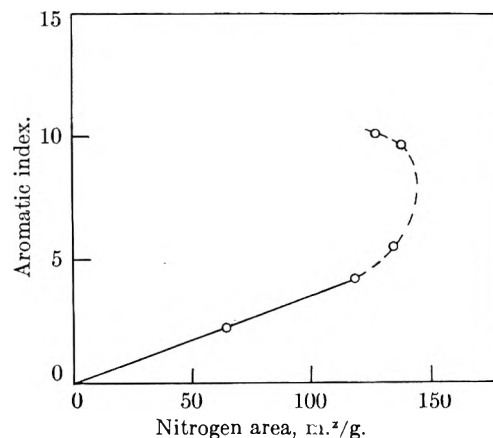


Fig. 2.—Correlating of nitrogen surface area with aromatic index for clay; solid-liquid ratio, 1 g./5 ml.; activation temperatures of samples preceding up the curve: A, 1500°F .; B, 1400° ; F, 900° ; D, 400° ; C, 300°

and Heineman.⁸ The initial increase in area up to 400°F . was attributed to the cleaning of the smaller pores. As the calcination temperature is increased, a partial breakdown of the structure occurs, but the surface area remains fairly constant since the areas now exposed on external faces were already accessible through larger pores running through the clay. The final rapid decrease in area is caused by collapse of the pores. This behavior in the case of nitrogen adsorption was not duplicated by toluene. The adsorption of this larger molecule declined continually as it was steadily excluded from the pores.

The reproducibility of these liquid phase determinations was quite good. The average deviation of all results was only ± 0.000005 refractive index unit. This deviation was practically independent of the surface area of the adsorbent. Thus the nitrogen areas of these samples of carbon and clay can be determined with an accuracy of approximately 1% where a linear relationship exists between nitrogen area and aromatic index. This improvement in experimental technique should

(8) W. S. W. McCarter, K. A. Krieger and H. Heinemann, *ibid.*, **42**, 529 (1950).

result in an increased use of this method in surface area measurements.

Complete binary adsorption data over the entire composition range were obtained for carbon 6 and for silica gel only. These data are plotted in Figs. 3 and 4. These data show selective adsorption of toluene over the entire range for both carbon and silica gel. This behavior is true even in the region where the concentration of toluene is high showing that the specificity of the surface is much greater for toluene than for isoöctane in the liquid phase. The selective adsorption curve is a straight line for both adsorbents in the range from 50–100 volume per cent. initial toluene concentration.

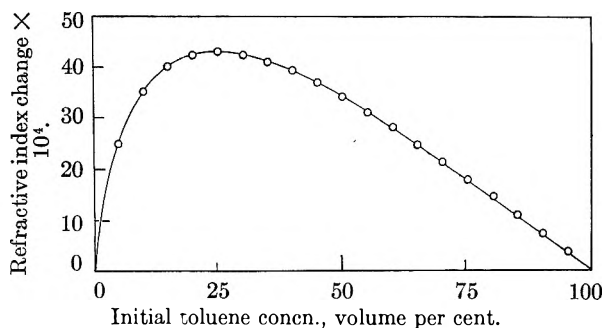


Fig. 3.—Binary adsorption data; toluene-isoöctane on silica gel A; solid-liquid ratio, 1 g./4 ml.

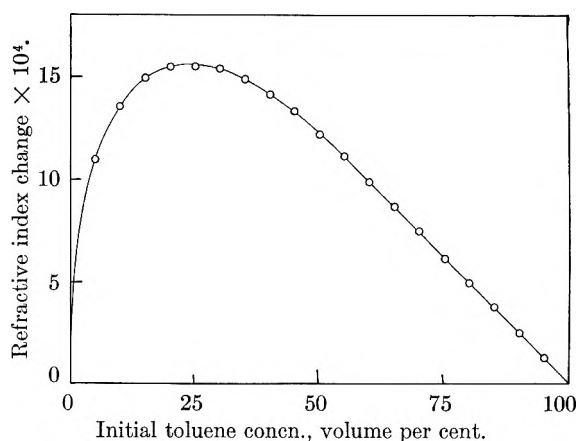


Fig. 4.—Binary adsorption data; toluene-isoöctane on carbon 6; solid-liquid ratio 0.5 g./6 ml.

The refractive index-composition curve data were plotted and found to be very nearly a straight line over the entire range of volume. Thus, the liquid mixture exhibits ideal behavior insofar as this test can be used as a criterion. The refractive index-weight per cent. plot was a shallow, smooth curve. For a range of 5–10 weight per cent. over any portion of the plot, the tangent to the curve was practically identical with the curve itself. This fact permitted the accurate calculation of composition change in liquid phase adsorption directly from refractive index change. Since the concentration change was always less than five weight per cent., the error involved was negligible.

The vapor phase adsorption runs resulted in isotherms (Figs. 5 and 6) which approach a limiting value for a relative pressure about 0.4. In each case the experimental data were represented very well as straight lines when plotted according to the

Langmuir equation. The nitrogen isotherms for both of these adsorbents had been determined in this laboratory. Silica gel A exhibited a Type I or Langmuir isotherm for nitrogen adsorption. The nitrogen isotherm for carbon 6 was intermediate between Types I and II and could be represented by the Joyner, Weinberger and Montgomery equation with an n value of 2.3. The close agreement of the data to the Langmuir equation is sufficient to show that the adsorption of toluene and isoöctane on these adsorbents from the vapor phase is unimolecular.

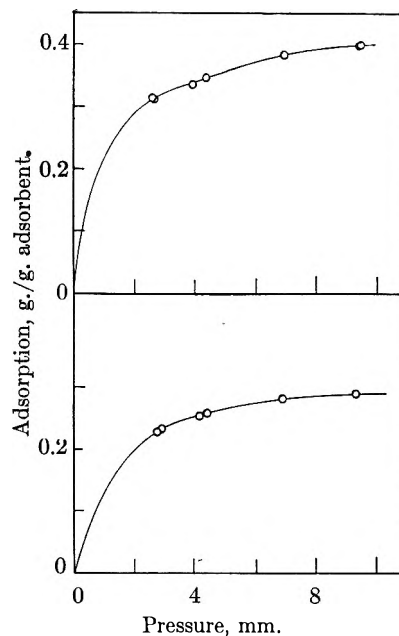


Fig. 5.—Toluene vapor isotherms: upper curve, carbon 6; lower curve, silica gel A.

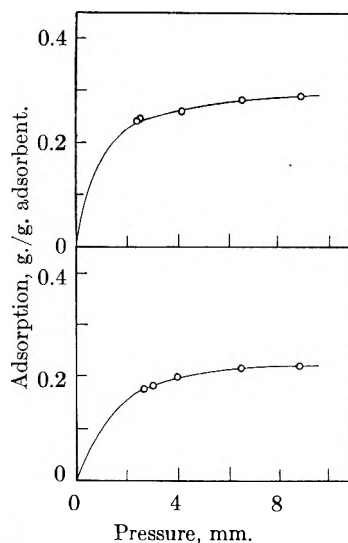


Fig. 6.—Isoöctane vapor isotherms: upper curve, carbon 6; lower curve, silica gel A.

The surface area of both adsorbents was calculated from the Langmuir plots using molecular areas calculated assuming liquid packing. Using densities at 25° of 0.8622 and 0.6879, the molecular areas of toluene and isoöctane were calculated to be 34.5

and 46.2 square ångström units, respectively. The areas were as follows.

	Gel A	Carbon 6
Nitrogen surface area, m. ² /g.	792.8	1050
Toluene surface area, m. ² /g.	735.1	991.7
Isoöctane surface area, m. ² /g.	614.9	752.7
Ratio of toluene to nitrogen area	0.927	0.945
Ratio of isoöctane to nitrogen area	0.775	0.717

The ratio of surface area as determined by an organic molecule to nitrogen surface area is usually about 0.5 to 0.7. However, the ratios obtained in this work were higher, especially in the case of toluene. This fact suggests that the organic molecules were not being excluded from the pores. Thus the adsorbents were mainly composed of pores of moderately large size which presented easy access to these molecules. This result is a further substantiation for the adoption of the assumption equating the composition of the pore liquid and the bulk liquid.

The binary adsorption data were used to calculate isotherms of toluene on the adsorbents according to the frequently used assumption that no isoöctane was adsorbed. The adsorption so calculated was much lower than the vapor phase adsorption and decreased in the region of high toluene concentration in the case of the silica gel. These facts suggest that such an assumption is erroneous and that the adsorption of toluene is low due to simultaneous adsorption of isoöctane.

The isotherms of Figs. 7 and 8 represent the application of the Lewis-Gilliland equation to the experimental data. These curves successfully show the high specificity of each adsorbent for toluene. In addition they show identical adsorption of the pure component in both the liquid and vapor phase case. Since liquid phase adsorption can often be expressed by application of the Freundlich equation, the data were checked and found to follow this equation very well over a large range of concentration for toluene on carbon and isoöctane on both carbon and silica gel. However, the data for the adsorption of toluene on silica gel could not be satisfactorily expressed in this way.

Although the discussion presented in this work requires unimolecularity in liquid phase adsorption, the data were plotted according to the Joyner, Weinberger and Montgomery equation as a matter of interest. The resulting graphs were good straight lines up to 60 mole per cent. if mole fraction

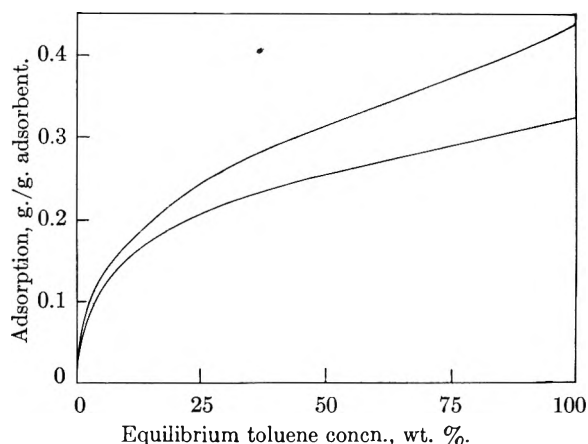


Fig. 7.—Calculated liquid phase adsorption of toluene from binary solution assuming Lewis-Gilliland equation: upper curve, carbon 6; lower curve, silica gel A.

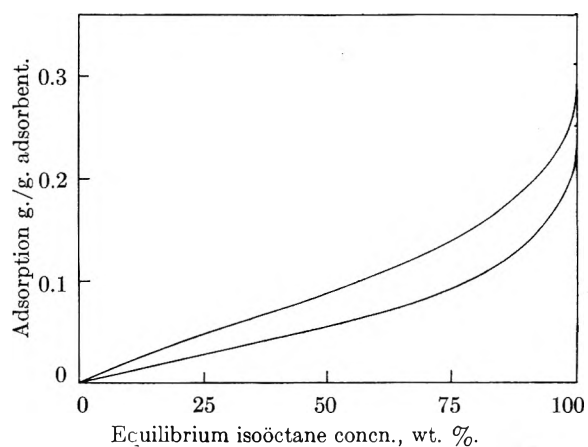


Fig. 8.—Calculated liquid phase adsorption of isoöctane from binary solution assuming Lewis-Gilliland equation: upper curve, carbon 6; lower curve, silica gel A.

was employed as a parameter comparable to relative pressure. The following values of n were obtained.

	n
Toluene on silica gel A	2.3
Isoöctane on silica gel A	3.8
Toluene on carbon 6	2.9
Isoöctane on carbon 6	3.8

Attempts were made to apply the Langmuir mixed adsorption equation to calculation of the liquid phase data from the constants of the pure component vapor phase fit of the Langmuir plots of those data, but without success.

THE ADSORPTION OF SULFATE IONS FROM AQUEOUS SOLUTIONS BY IRON SURFACES

BY NORMAN HACKERMAN AND SARAH JANE STEPHENS¹

Department of Chemistry, University of Texas, Austin, Texas

Received March 5, 1954

The quantity of sulfate ions sorbed by iron surfaces was determined directly with $S^{35}O_4^{--}$ in an air-free system at room temperature. It was studied as a function of time, sulfate ion concentration, surface preparation and pH. Uptake was determined also from mixed solutions of sulfate and chloride, and sulfate and chromate. Isotherms of firmly held sulfate on iron showed that adsorption approached a limiting value equivalent to about 0.35 monolayer. The presence of chromate ions in solution reduced the amount of sulfate adsorbed, as did large concentrations of chloride ion. Small concentrations of the latter increased the sulfate pick-up. Up to pH 10 hydroxyl ions showed no noticeable effect on the sulfate isotherm but above that the quantity of sulfate adsorbed declined appreciably. There was removal of hydroxyl ion at all pH values studied, *i.e.*, from 7 to 12.

Introduction

Ionic adsorption on metals has been detected indirectly by the effect on the electrocapillary curve.² Radiotracers were used by Paneth³ who determined the specific surface area of lead with thorium B. This isotope was also used by von Hevesy,^{4,5} to show that exchange occurs between a metal and its ions in solution; about 1000 atomic layers were said to be involved. Exchange between silver and radiosilver in solution was demonstrated by Rollin⁶ and by Coffin and Tingley.⁷ These studies also showed that gold and platinum acquired activity in this solution. There was no proof that this was exchange rather than adsorption, but exchange with non-common ions is possible.

Radiosodium ions have been sorbed from aqueous solution onto glass, aluminum, steel, silver and platinum.⁸ Exchange of cobalt tracer from solution with a number of metals both in the absence and in the presence of air was reported by Simnad and Ruder.⁹ They concluded that the amount of radioactivity acquired was the result of electrodeposition by local cell action. Adsorption isotherms have been obtained for radiocobalt on hydrous ferric oxide, and the effects of pH, ion concentration and quantity of sorbate also were determined.¹⁰

The work cited so far deals solely with cations in solution and metals or metal oxides. Attempts to study the adsorption of chloride ion on chromium were made by Marshall¹¹ using $NaCl^{36}$. The results were equivocal because of the low activity of the tracer and because of contamination by sulfur-35. A more successful study involved the uptake of tagged chromate on chromium¹² and on

steel.¹³ A portion of the chromate ions which became attached under a variety of conditions were firmly sorbed. Because of the possibility of reduction of the chromate it was not proved conclusively that this was a true sorption process. For instance, with steel at high enough chromate concentration to cause passivation a definite, reproducible amount of chromate was picked up and was uniformly spread over the surface. At lower concentration corrosion occurred and some chromate reduction must have occurred. In the latter cases, however, the pick-up was much greater, although less reproducible. Radioautographs showed that the uncorroded areas (cathodes) acquired more activity and also that a considerably greater amount was associated with the reaction products at the local anodes.

Sulfur-35 in sulfate offered a means of determining anion sorption on iron. The activity acquired by the sorbate should be that due to adsorption alone, since the possibility of reduction of the sulfate ion under the conditions used was small. The potential differences between local anodes and cathodes are too small to give electrochemical reduction, and the possibility of direct reaction in the essentially neutral sodium sulfate solutions is nil. The radiotracer has a sufficiently high activity and a long enough half life to make it convenient to handle and measure. Competitive effects between this and other anions were studied by noting the effect of the "cold" foreign anion on the sorption of sulfate.

It was necessary to work in an air-free system because iron corrodes to a noticeable extent in these salt solutions in the presence of air. Even if the last traces of oxygen were not removed the procedure described below reduced it to a point such that the iron did not corrode in the solutions even on long standing.

Preparation of Materials

Radioactive Sulfate Solutions.—Carrier-free sulfate containing 87.1 day half-life sulfur-35 was obtained from the United States Atomic Energy Commission at Oak Ridge. It came in 0.2 ml. of approximately 0.1 N HCl and had a total activity of 10 millicuries. The solution was diluted to 2 ml. and chloride was removed by electrolysis. This was done first between platinum electrodes until oxygen evolution started, and was completed using a silver anode. A low current density was used in order to convert silver to the

- (1) du Pont Fellow, University of Texas, 1951-1952.
- (2) N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, London, 1941, pp. 340-342.
- (3) F. Paneth, *Z. Elektrochem.*, **28**, 113 (1922).
- (4) G. von Hevesy, *Physik. Z.*, **16**, 52 (1915).
- (5) G. von Hevesy and B. Blitz, *Z. physik. Chem.*, **B3**, 271 (1929).
- (6) B. V. Rollin, *J. Am. Chem. Soc.*, **62**, 86 (1940).
- (7) C. C. Coffin and I. I. Tingley, *J. Chem. Phys.*, **17**, 502 (1949).
- (8) J. W. Hensley, A. O. Long and J. E. Willard, *J. Am. Chem. Soc.*, **70**, 3146 (1948).
- (9) M. T. Simnad and R. T. Ruder, *J. Electrochem. Soc.*, **98**, 301 (1951).
- (10) M. H. Kurbatov, G. B. Wood and J. D. Kurbatov, *THIS JOURNAL*, **55**, 1170 (1951).
- (11) D. I. Marshall, Ph.D. Dissertation, University of Texas, 1946.
- (12) N. Hackerman and R. A. Powers, *THIS JOURNAL*, **57**, 139 (1953).

- (13) R. A. Powers and N. Hackerman, *J. Electrochem. Soc.*, **100**, 314 (1953).

chloride directly on the electrode. The final chloride concentration was less than $1 \times 10^{-6} M$.

Solutions were prepared with doubly distilled water and J. T. Baker Analyzed Chemicals. A small volume of the active solution was then added as required for the particular experiment. Generally, 15 μ l. of active solution was added to 50 ml. of solution of appropriate concentration. Each solution was checked before and after use by evaporating a small aliquot and counting the activity of the residue. In no case was there enough sulfate removed from the solution to cause an appreciable change in concentration.

Iron Coupons.—These were cut in circular form from 1.6 mm. thick sheets of Armco iron and finished to 1.9 cm. diameter. The iron analysis¹⁴ was: C, 0.010; Mn, 0.010; P, 0.005; S, 0.012; Si, 0.002; Cu, 0.040; rest Fe. Unless otherwise noted the surfaces were treated as follows: washed several times in fresh, thiophene-free benzene, abraded with no. 2 emery paper, carefully wiped free of all abrasive with clean cloth, washed twice in fresh, hot benzene, and stored in a desiccator until used. The coupons were prepared just prior to each set of experiments but several hours always elapsed before they were actually exposed to the solutions. The coupons were handled only with clean cotton gloves or with carefully cleaned tongs. Metal surfaces prepared as described were always found to be completely wet by water.

The specific surface area was determined by adsorption of krypton at 78°K., and the metal was found to have a roughness factor of 3.¹⁵

Method

Apparatus.—The adsorption experiments were carried out in a dry-box, using air-free solutions in a nitrogen atmosphere. The dry-box, 18 × 18 × 12 in. high, was made of 1/4 in. lucite and was sealed onto a bottom glass plate for each series of experiments. All plastic to plastic joints were reinforced with paraffin. The neoprene gloves were joined to the box with rubber cement, and glass tube inlets and outlets were attached to the box with suitable cement.

The counting was done with conventional scalars and thin mica window Geiger-Müller tubes. The voltage plateau was determined for each tube and all operations were carried out in the central region of the plateau, usually at about 1300 volts. The coupons were all counted in the same manner, the counts were corrected for background which was checked at frequent intervals, and all counting data were corrected for decay of the radioisotope.

Procedure.—All materials needed for the experiments were placed in the box which was then sealed and flushed thoroughly with a stream of rapidly flowing nitrogen. The nitrogen passed through a train consisting of two bottles of acidified vanadyl sulfate,¹⁶ concentrated NaOH and water before entering the dry-box. The gas left the box *via* a water bubbler to prevent back flow of air. After the flushing treatment the nitrogen was led through the solutions also, but at a reduced rate, to displace dissolved air. With the gas flowing slowly so as to minimize vaporization losses the coupons were placed in the solutions. The gas flow was continued for several minutes after which the container with the solution-metal system was closed. After exposure the coupons were removed with tongs and washed by dipping numerous times, *e.g.*, 20, in each of three beakers containing about 75 ml. of distilled water. The coupons were then dried with filter paper, removed from the dry-box, and the remaining activity was counted.

At the end of each run, the solutions were acidified with HCl and analyzed for iron colorimetrically using isonitrosodimethylidihydroresorcinol.¹⁷ Considerably less than 0.5 p.p.m. of iron was found in all cases, and in some none was detected.

Sorption of Sulfate

Rate.—At all concentrations there was an increase in activity picked up during the early exposure period. The uptake went through a maxi-

mum with time and then fell off, first quite rapidly and then more slowly to a relatively constant value. The curves were reproducible as to form but were not reproducible quantitatively. The values obtained for exposures of less than 12 hours were quite erratic, but those which fell on the descending portion of the curves were much steadier. Figure 1 shows typical rate curves at two solution concentrations, 1×10^{-4} and $1 \times 10^{-6} M$ Na₂SO₄. The pH in each case was adjusted to 7; each point is the average of counts from four different coupons.

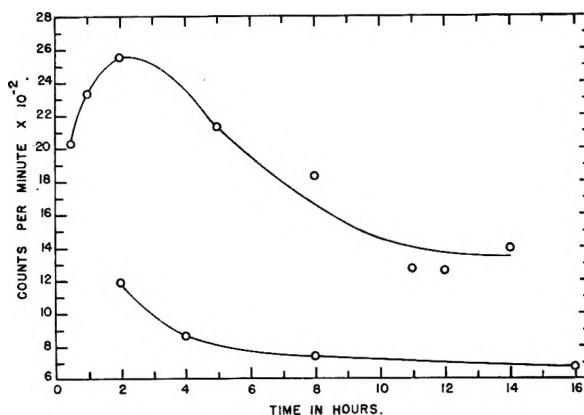


Fig. 1.—Adsorption of sulfate ion on iron as a function of time, at room temperature and initial pH 7: upper curve for $1.0 \times 10^{-4} M$ Na₂SO₄; lower curve for $1.0 \times 10^{-6} M$ Na₂SO₄.

It was found that a larger portion of the activity acquired by the surface on long exposure was firmly held than was the case with that picked up in the shorter exposures. In the latter case as much as 50% of the activity was removable by rinsing with water, whereas in the former not more than 10% could be so removed. In fact, the activity acquired on short exposure could all be removed with enough rinsings, whereas with longer exposures essentially all sulfate which could desorb came off on the first washing. In order to remove the activity entirely in the latter cases it was necessary to strip the surface by etching or polishing. The exposure periods for all experiments reported below were always 16 hours or more.

Surface Treatment.—Isotherms were obtained over the range 1×10^{-6} to $5 \times 10^{-4} M$ Na₂SO₄ with a set of coupons finished with #2 emery paper and with another set finished with #4/0 emery paper. The latter group consistently picked up more activity than did the former, acquiring from 4 to 7 times as much and averaging about 5 times as much. The individual variations are not significant but the consistently greater values with surfaces finished with the finer grit must be considered to be real.

Adsorption Isotherm.—The uptake of sulfate as a function of solution concentration is shown in Fig. 2. All solutions were initially at pH 7, the temperature was $32 \pm 2^\circ$, the exposure time was 16 hours, and the counts were corrected for decay. Each point represents the average of values from eight separate coupons. The coverage was calculated using the roughness factor of 3 for the metal, an area of 23.3 Å.² for the sulfate ion as

(14) As supplied by Armco Steel Corp., Youngstown, Ohio.

(15) The procedure used is described in detail by M. J. Joncich, Ph.D. Dissertation, The University of Texas, 1953.

(16) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(17) S. C. Shome, *ibid.*, **20**, 1205 (1948).

calculated from crystallographic data,¹⁸ and assuming undistorted, close packing. On the plateau of the curve the activity indicates enough sulfate ions to form 0.35 of a monolayer.

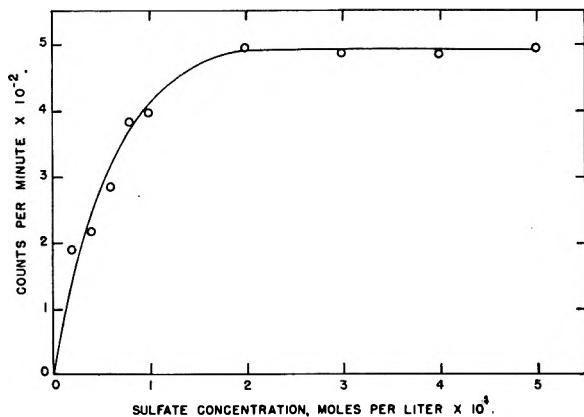


Fig. 2.—Adsorption isotherm for sulfate ion on iron coupons at room temperature and initial pH 7.

Effect of Other Anions.—The experiments were repeated identically in all details except that a constant ratio of chloride ion concentration to sulfate ion concentration of 2.64 was maintained throughout. This isotherm is shown in Fig. 3. The activity taken up was greater at all concentrations of sulfate (note change in scale of ordinate) and a constant value was not obtained in this case even at the highest concentrations. In experiments in which the chloride ion concentration was held constant at $1 \times 10^{-3} M$ and sulfate ion concentration was varied, the second effect is shown even more strikingly (Fig. 4). There was some decrease in sulfate uptake up to about $4 \times 10^{-4} M$ Na_2SO_4 but a very sharp increase occurred thereafter. In a solution containing $1 M$ NaCl and $1 \times 10^{-4} M$ Na_2SO_4 the amount of sulfate ion adsorbed was negligible.

With all details of the experiment with sulfate alone the same but in the presence of $0.002 M$ Na_2CrO_4 in all cases, the activity picked up was as follows: $0.00005 M$ Na_2SO_4 , 27 counts/min.; 0.0001 , 59; 0.0002 , 92; 0.0003 , 83. This should be compared to approximately 500 c./min. as obtained from the plateau of the curve in Fig. 2. Thus the chromate ion reduces sulfate adsorption to 15 or 20% of the original value when it is present in a ratio of about 10/1 or better.

An increase in hydroxyl ion concentration also reduces the uptake of sulfate ion. The effect of this ion was first observed in the change in pH of the solutions from which the isotherm data of Fig. 2 were obtained. The final pH was rather uniformly 5.6. On the other hand in the experiments using both sulfate and chloride at constant ratio the pH change was hardly significant, rising by a small amount. At constant chloride concentration (Fig. 4) the pH dropped to 6.0 and 6.3 for the two lowest concentrations but otherwise showed no significant change. Again with chromate in the solution there was no change in pH in excess of 0.1 to 0.2 of a pH unit.

An isotherm was run with all conditions as for the

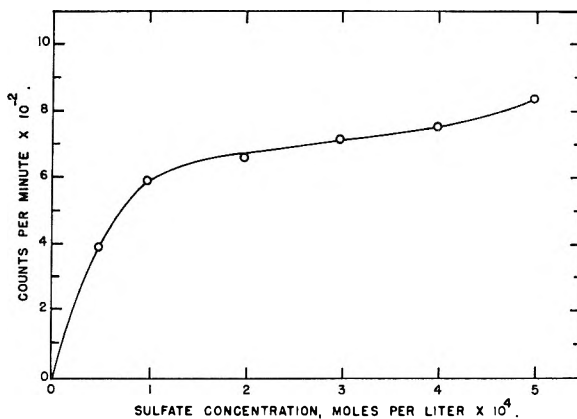


Fig. 3.—Adsorption of sulfate ion in the presence of chloride ion; chloride ion concentration 2.64 times sulfate ion concentration throughout, room temperature, initial pH 7.

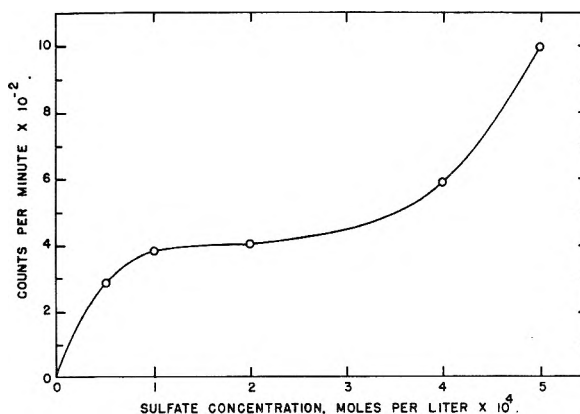


Fig. 4.—Adsorption of sulfate ion in the presence of chloride ion; chloride ion concentration $1.0 \times 10^{-3} M$ throughout, room temperature, initial pH 7.

experiment giving the curve of Fig. 2 except that the pH was adjusted to 11. The following data on comparison with Fig. 2 show no particular effect on sulfate pick-up but a considerable, constant decrease in pH occurred.

Concn. Na_2SO_4 , M	c./min.	pH at equilibrium
0.00002	93	8.5
.00004	125	8.5
.00006	287	8.4
.00008	305	8.4
.00010	319	8.4
.00015	286	8.5

With sulfate ion held constant at $0.0001 M$ over a pH range of 7 to 12 and using 100 ml. of solution there was no change in pH but the amount of activity sorbed decreased markedly at the higher alkalities.

pH	7	8	9	10	11	12
c./min.	490	524	478	450	38	4

This larger volume prevented pH change by depletion. For example, using 10 ml. of solution the value changed from an original pH of 7 to 6.4 and from an original 10 to 7.7. Using the usual 50-ml. portion adjusted to pH 12.5 virtually no activity was found on the surface, in keeping with the data listed just above.

(18) W. H. Zachariasen and G. E. Ziegler, *Z. Krist.*, **81**, 92 (1932).

Discussion

The experimental evidence suggests that sulfate ions are chemisorbed on the surface presented by the iron coupon. The probability of reduction of the sulfate and incorporation of the radioisotope in some other oxidation state is small. Although local galvanic cells do exist on a single piece of metal¹⁹ the potentials at the local electrodes are insufficient to reduce the sulfate to sulfur or sulfide, or to convert it to persulfate. Direct reduction of sulfate by iron at pH 7, or above, which was the case in these experiments, may also be ruled out. This means that the sulfur would not be chemically incorporated into any reaction product.

There remains the possibility that corrosion of the iron provided small amounts of fairly high specific surface area hydrous oxides which adsorbed the sulfate. In this case the activity counted would have only incidentally been held on the coupon surface. The results of the experiments designed to show anion competition may be used as evidence of this view. For instance, at high pH the sulfate pick-up was materially reduced, and this can be ascribed to the fact that under these conditions the corrosion rate is negligible. However, in view of the fact that little or no iron was found in solution, this possibility becomes less likely.

The sulfate remaining on the surface after washing is considered to be chemisorbed because the procedure for removal of the activity was quite vigorous. Indeed at room temperature the activity could be removed only by methods which literally destroyed the original surface. The firmly held material was present always in less than monolayer amount. Autoradiographs showed it to be evenly distributed over the surface.

The activity acquired by coupons polished with #4/0 emery was consistently higher than that with #2 emery. The difference in roughness factor, namely 2.6 as compared to 3.0, is not sufficient to account for this effect. It may be that this must be explained on the basis of an oxide film. Polishing undoubtedly caused high surface temperatures. With the finer grit a longer polishing time was required and the extended period of high temperature would produce a thicker oxide. It is consistent with properties of surface layers to assume that the thicker oxide was more easily penetrated by the solution. Thus sorption would occur in this case through a larger amount of a relatively porous mass whereas in the other case most of the pick-up would obtain on the external surface. This is supported by the fact that reproducibility of data taken with the coupons polished with #2 emery was a good deal better than was that obtained with the other coupons.

The uptake rate (Fig. 1) was sufficiently reproducible to show that the phenomenon was real. It is not related to change in pH since this was the same over-all regardless of the length of exposure. The only explanation offered at this time is that it is an orientation effect such as has been postulated

for polar organic molecules on steel.²⁰ It is possible that initially the sorbing species congregates rapidly at the sorbent surface in a random manner and in so doing blocks some portion of the sites on which the particle could become firmly attached. If firm attachment requires formation of a true bond²¹ then it becomes necessary to provide proper orientation of the bond-forming portion of the particle relative to the appropriate site. Loose aggregation might readily occur though in the close confines of the interface, and would account for the excessive uptake in the earlier periods. The more concentrated the solution the more pronounced this should be, as was the case. However, such a tangled mass would not be likely to be held very firmly and should be readily reversible, as indeed it was. In addition, because some sites giving rise to chemisorption would necessarily be blocked the amount chemisorbed would be less than that found at equilibrium. With time, of course, rearrangement must occur and attachment of properly oriented particles to appropriate points can take place.

Regardless of the actual surface on which the activity appears, the data show clearly that there is anion competition for surface. The chromate ion in equal or greater concentration than sulfate considerably decreased the pick-up of sulfate by the iron coupon. The case for the reverse system using chromium metal as the sorbate has already been demonstrated.¹² These two ions are rather alike structurally, *e.g.*, size, geometry and polarizability, and it is reasonable to presume that they compete directly for the same sites.

The effect of pH suggests strongly that hydroxyl and sulfate compete²² in this system also. A similar competition was shown between chromate and hydroxyl previously.^{12,13} Contact potential measurements in those cases indicated that the hydroxyl ion was fixed with the oxygen facing out. Since this leaves the hydrogen as the bonding agent it appears that this anion requires an oxide surface for adsorption.

At pH 7 the number of hydroxyl ions removed from solution is enough to provide 0.01 of a monolayer. At higher pH the extent of pH change is greater hence the number of OH⁻ removed by the solid increases, reaching a value equivalent to many monolayers. It is at this stage that it interferes seriously with sulfate uptake. It is possible that the hydroxyl ion in the more alkaline solutions peptizes the oxide already in place, thereby increasing the area available for sorption. However, this is not amenable with the fact that while OH⁻ depletion at pH 10 is great, the amount of sulfate retained by the solid is just about the same as at lower pH values. The removal of such large amounts of hydroxyl ion at higher pH could be

(20) N. Hackerman and E. E. Glenn, Jr., *THIS JOURNAL*, **54**, 497 (1950).

(21) See, for example, N. Hackerman and A. C. Makrides, *Ind. Eng. Chem.* (in press) and references therein.

(22) An interesting parallel appears in the competition between sulfate and hydroxyl, and sulfate and chloride as gegenions for monolayers of long chain surface active agents on water. (See C. M. Judson, A. A. Lerew, J. K. Dixon and D. J. Salley, *THIS JOURNAL*, **57**, 916 (1953), for example.) The systems differ in that there the metal is more specific.

(19) U. R. Evans, "An Introduction to Metallic Corrosion," Edward Arnold & Co., London, 1948, p. 35.

attributed to reaction except that there was no visual evidence that any occurred.

The increase in sulfate sorption in the presence of chloride ion is probably caused by a change in the surface. The efficiency of chloride ion in destroying passivity is attributed by some to its ability to penetrate the oxide covering.²³ Analogous changes in this system provide the means wherein fresh and increased surface could become available to the sulfate ion. One facet in the chloride effect not yet properly explored is the fact of chloride as a complexing agent for iron ions in solution and the possibility of it being the same for the metal ion in the lattice (metal or oxide). The puzzling fact about this anion pair is that at high enough $\text{Cl}^-/\text{SO}_4^{=}$ ratio the chloride apparently adsorbs as shown by the decreased sulfate ion in the left hand portion of Fig. 4. This sorption competition was

(23) U. R. Evans, "Metallic Corrosion, Passivity and Protection," 2nd edition, Edward Arnold & Co., London, 1946, p. 21.

shown also by Marshall,¹¹ but neither of these instances are enough on which to base firm conclusions.

In summary, it appears that sulfate ion does chemisorb on iron coupons prepared as described, but it is more likely than not that it sorbs on oxide. It competes with other anions, specifically, chromate, hydroxyl and chloride, for such surface as it adheres to. The firmly held portion corresponds to less than a monolayer and microscopically, *i.e.*, by radioautograph, covers the surface uniformly even though only fractionally.

Acknowledgment.—The authors are happy to take this opportunity to note that this research was supported in part by the Office of Naval Research under Contract Nonr 375 (02). They are also pleased to acknowledge the aid of Nicos Komodromos, of this Laboratory, who made the surface area determinations on the metal coupons.

THE APPARENT ADSORPTION OF SOME ALIPHATIC COMPOUNDS FROM AQUEOUS SOLUTIONS AS INFERRED FROM HYDROGEN OVERVOLTAGE MEASUREMENTS¹

BY ROBERT S. HANSEN AND BERT H. CLAMPITT

Contribution No. 310 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa.

Received March 5, 1954

Apparent isotherms for the adsorption of a number of organic compounds from aqueous solution by silver and copper have been measured by double layer capacitance and steady state current-overvoltage techniques. Apparent surface coverages inferred from double layer capacitance changes and from overvoltage changes at several currents were found to be in reasonably good agreement. Results for slightly soluble adsorbates appear reasonable in order of magnitude, but may be slightly low due to coreduction of, or hydrogen discharge through, the adsorbed layer. In the case of highly soluble adsorbates, care must be taken to correct for change in reversible cell potential.

Introduction

The development of methods especially suited to the study of adsorption at interfaces of comparatively small area appears almost essential to adequate studies of adsorption on metals and to such related phenomena as heterogeneous catalysis and corrosion inhibition. Hydrogen overvoltage measurements offer considerable promise for solution adsorption aspects of this problem, and it is the object of this paper to present preliminary results and reservations based on experience in this Laboratory on the inference of isotherms for adsorption of organic compounds from aqueous solutions by metals from such measurements.

Although Tafel² recognized the area dependence of current-overvoltage curves in 1905, Bowden and Rideal³ applied the proportionality between double layer capacitance and interfacial area to the measurement of surface area in 1928, and Proskurnin and Frumkin⁴ warned in 1935 of the marked effect of adsorbable contaminants on double layer

capacitances, the earliest work recognizing a quantitative relation between alteration in double layer capacitance and adsorption appears to be due to Barclay and Butler⁵ in 1940, and the earliest published quantitative inference of adsorption from steady state current-overvoltage measurements appears to be that of Ch'iao and Mann⁶ in 1947.

Basically, inferences of adsorption from solution either from double layer capacitance or steady state current-overvoltage measurements have depended on the assumption (doubtless not always valid) that adsorbed material acts only as an inert blanket on the electrode surface, so that if A denotes the original electrode surface area and θ the fractional coverage by adsorbed material, then an area $A(1 - \theta)$ remains to contribute to double layer capacitance and to the steady state rate of hydrogen evolution. The double layer capacitance is measured by the initial rate of increase of potential with current, thus

$$C = \frac{dQ}{dE} = i \frac{dE}{dt} \quad (1)$$

Since this capacitance is assumed proportional to the area of surface free from adsorbate there follows immediately

$$\theta = 1 - C/C_{0-0} \quad (2)$$

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

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

(3) F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc. (London)*, **120A**, 59 (1928).

(4) M. Proskurnin and A. Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935).

(5) I. M. Barclay and J. A. V. Butler, *ibid.*, **36**, 128 (1940).

(6) S. Ch'iao and C. A. Mann, *Ind. Eng. Chem.*, **39**, 910 (1947).

The steady state dependence of overvoltage on current is given by the Tafel equation

$$\eta = a + b \log j \quad (3)$$

in which η is the overvoltage; j , the current density; and a and b , constants. A given overvoltage implies a fixed current density; assuming that the accessible area is $A(1 - \theta)$ there results

$$\theta = 1 - \frac{i}{i_{\theta=0}} \quad (\eta \text{ fixed}) \quad (4)$$

the currents being measured at the same overvoltage. Measurements at several overvoltages then permit a check for self-consistency. Alternatively

$$\theta = 1 - e^{\Delta\eta/b} \quad (i \text{ fixed}) \quad (5)$$

the overvoltages being measured at constant current, and $\Delta\eta$ representing the difference in overvoltage due to introduction of adsorbate. Measurements at several currents then permit a check for self-consistency.

Precautions necessary for reliable results will at least include those necessary for reliable overvoltage results in general; these are extensive and have been well summarized by Bockris and co-workers.⁷⁻⁹

Experimental

The apparatus employed was similar to that of Bockris and co-workers.⁷⁻⁹ Overvoltages were measured against a silver-silver chloride electrode in 0.1 *N* perchloric acid solutions containing 0.001 *N* potassium chloride and the organic compounds indicated. Preparations for measurement were as follows: The cathode, suitably prepared, was placed in the reaction compartment, and perchloric acid in a still compartment of the apparatus. The apparatus was evacuated, then filled with hydrogen. Distilled water was allowed to flow through a reducing ion exchange column¹⁰ designed to remove dissolved oxygen and thence into a water still compartment.

The system was re-evacuated and perchloric acid and water were distilled into a pre-electrolysis chamber, where the resulting solution was pre-electrolyzed for 12 hours at 10⁻³ ampere. Anode and cathode compartments of the pre-electrolysis chamber were separated by porous plugs and a U tube containing the solution which was frozen at about -10° during the process.

The solution was now allowed to enter the reaction chamber. The adsorbate and KCl were added to the reaction chamber as pure substance or concentrated solution by means of a hypodermic syringe through a small rubber diaphragm, covered with a mercury seal, located on top of the reaction chamber. The only stopcock used in the system was one connecting to the vacuum line; all other transfers were made through glass U tubes which could then be frozen to prevent flow.

The cathodes were approximately 4 cm.² in geometric area. The silver cathode, prior to inclusion in the apparatus, was heated to 700° in air, cooled in nitrogen, and immediately placed in the apparatus. Cathodes prepared by vacuum sputtering, and by outgassing *in vacuo* at 700°, in both cases breaking bulbs containing them under the solution to avoid all contact with air, gave the same results within experimental error as those prepared by the simpler technique. The copper cathode was cleaned with 1:1 nitric acid to free dissolution and washed thoroughly with water.

Hydrogen was purified by passage over copper turnings at 600°, followed by passage through charcoal at 77°K.

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

(8) A. M. Azzam, J. O'M. Bockris, B. E. Conway and H. Rosenberg, *Trans. Faraday Soc.*, **46**, 918 (1950).

(9) E. C. Potter, Thesis, University of London, 1950.

(10) G. F. Mills and B. N. Dickinson, *Ind. Eng. Chem.*, **41**, 2842 (1949).

The organic compounds were central fractions obtained from distillation of Eastman best grade chemicals (except for *n*-caproic acid and *n*-heptaldehyde which were Eastman practical grade) through a 30-plate Oldershaw column at 10-1 reflux ratio (in the case of *n*-octanoic acid this distillation was under reduced pressure).

Current was supplied from a 250-volt source with suitable resistances in series, so that variations in current due to opposing polarization and variation in resistance of solution were negligible. Double layer capacitances were determined from potential-time sweeps photographed on a Dumont 304-H oscillograph. Steady state overvoltage measurements were obtained by means of a Leeds and Northrup No. 7552 potentiometer. During all measurements, a reasonably efficient stirring was obtained and concentration polarization thereby reduced by bubbling purified hydrogen vigorously through the solution in the neighborhood of the electrode surface.

In measurements of double layer capacitance, a 30-minute electrolysis at the current subsequently used for measurement was carried out for the purpose of reducing any oxides on the cathode surface, and the overpotential allowed to decay to zero (within experimental error). (This required from 30 minutes to one hour.) The current of either 10⁻⁶ or 10⁻⁴ amp. and the oscillograph sweep were then triggered with a simultaneous switch. A measured amount of adsorbent was added and the process repeated. The initial portions of the potential-time sweeps were quite linear, and little difficulty was encountered in computing capacitances. Steady state overvoltages corresponding to a specified current were obtained by switching on the polarizing current and measuring the overvoltage periodically until the change in overvoltage was less than 2 millivolts in 30 minutes (about three hours). This appears to be common practice in overvoltage measurements^{7,11}; it is admittedly unsatisfactory, and results from the fact that the overvoltage actually increases steadily, although in small amount, over a period of days and it is uncertain whether this increase is attributable to the basic electrode process. A measured quantity of adsorbate was then added and the overvoltage again followed until constant in the same sense (about one hour). The process was repeated at all concentrations desired; overvoltage-concentration series were established at polarizing currents of 10⁻⁶ and 10⁻⁴ amp. Using the aqueous 0.1 *N* HClO₄, 0.001 *N* KCl electrolyte previously described, the following cathode-adsorbate systems were investigated: silver cathode, acetic, *n*-caproic, *n*-heptylic and *n*-octanoic acids; copper cathode, *n*-heptylic and *n*-octanoic acids, heptanol-1 and *n*-heptaldehyde.

Results

Apparent fractional surface coverages were obtained from double layer capacitance measurements in the systems silver-*n*-heptylic acid and silver-*n*-octanoic acid by means of eq. 2, and from steady state current-overvoltage measurements in all systems by means of eq. 5. The constant b was taken as 0.051 = (0.118/2.303).⁷

Results are presented graphically in Figs. 1-5. Figure 1 presents a comparison of apparent isotherms for the adsorption of *n*-octanoic acid on silver as determined from double-layer capacitance measurements and steady state current-overvoltage measurements at two currents. Deviations between results obtained by the different methods are within limits of reproducibility. Steady state current-overvoltage measurements at three different current to geometric area ratios are shown in Fig. 2; parallelism of lines generated again indicates self-consistency of data. Figures 3 and 4 present apparent adsorption isotherms for fatty acids on silver and copper, respectively. Abscissas are reduced concentration (concentration divided by saturated concentration) in all cases.

(11) See, for example, A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, **36**, 1226 (1940).

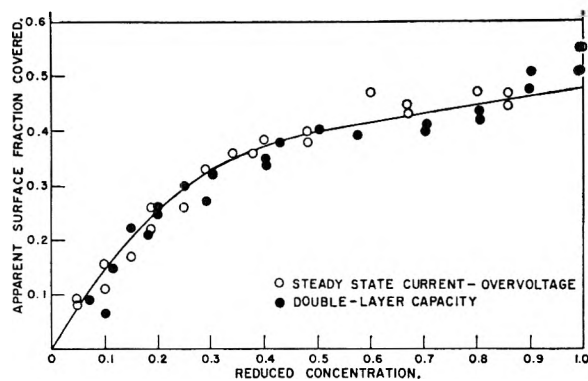


Fig. 1.—Adsorption of octanoic acid on silver as determined by double layer capacitance and steady state current-overvoltage measurements.

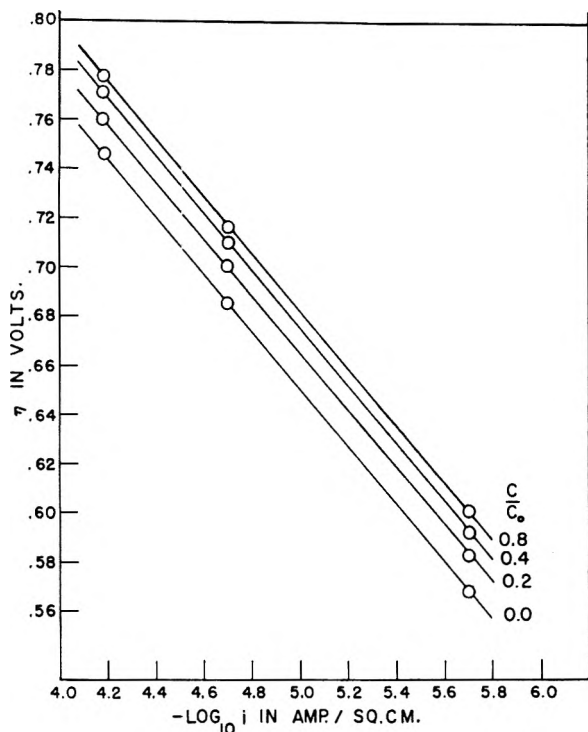


Fig. 2.—Steady state current-overvoltage values at various current densities for the system silver-octanoic acid.

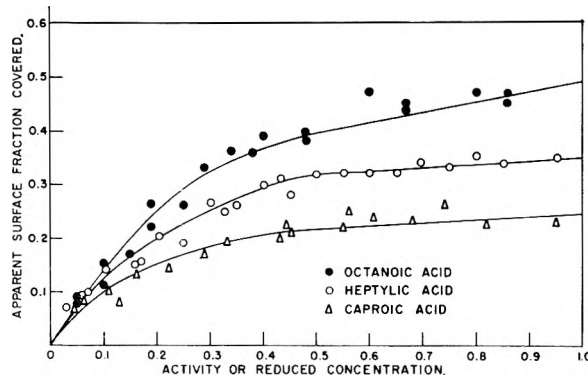


Fig. 3.—Adsorption of normal aliphatic acids on silver.

Figure 5 presents a comparison of the apparent isotherms for the adsorption of *n*-heptylic acid, *n*-heptaldehyde and heptanol-1 on copper.

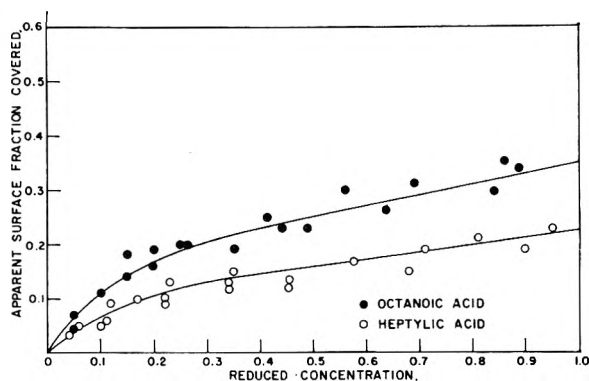


Fig. 4.—Adsorption of normal aliphatic acids on copper.

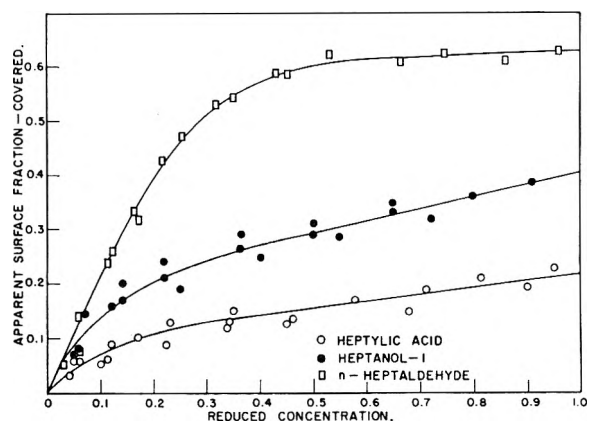


Fig. 5.—Adsorption of normal C₇ compounds on copper.

Discussion

The comparative adsorption of fatty acids on metals indicated in Fig. 3 and Fig. 4 is in general reasonable. The results would indicate that with increasing chain length a somewhat larger number of molecules will be adsorbed at a given activity (*i.e.*, that energy of adsorption increases with chain length); surface coverage would be increased *a fortiori* since the larger molecules would also have larger molecular cross-sections.

No apparent adsorption of acetic acid, within limits of experimental error, was observed up to concentrations of 2.5 molar (activity 0.11), in conflict with the observations of Wetterholm.¹² An increase in cell potential was observed, but was compensated within limits of experimental error by a corresponding increase in reversible potential. It would appear from Wetterholm's discussion that he did not correct for this effect; it should be noted that this correction will be important whenever the adsorbate concentration is sufficient to alter the dielectric properties of the solution appreciably. The change in reversible potential was found to be negligible in the systems involving slightly soluble adsorbates investigated. In addition to the change in reversible potential, Bockris¹³ found that the actual overvoltages on copper and lead were lowered by acetic acid; the lowering in the case of copper was (estimated from figure given

(12) A. Wetterholm, *Trans. Faraday Soc.*, **45**, 861 (1949).

(13) J. O'M. Bockris, *Discs. Faraday Soc.*, **1**, 95 (1947).

by Bockris) about 7 millivolts per per cent. increase in acetic acid concentration. This reflects a lowering of the Tafel "a" constant, contrary to assumptions used in deriving eq. 4 and 5.

Two results offer cause for some concern. First, in no fatty acid-water system was an apparent coverage greater than 50% observed. A similar observation was made by Bockris and Conway.¹⁴

Secondly, the marked progression, heptaldehyde > heptyl alcohol > *n*-heptanoic acid, at any given activity is also rather difficult to interpret in terms of plausible adsorption mechanisms. Both of the above results suggest that the assumption of inertness of adsorbed layer be made with reservations, since any current carried by reduction of adsorbed materials would lead to an apparent surface coverage less than the actual coverage. The possibility of fatty acids especially, and perhaps alcohols and aldehydes, forming proton-containing complexes in the adsorbed layer and thereby furnishing an alternate hydrogen discharge path must be recognized. At least in the case of fatty acids this possibility would appear consistent with polarographic behavior at dropping mercury electrodes. The coreduction of aldehyde must also be con-

(14) J. O'M. Bockris and B. E. Conway, *THIS JOURNAL*, **53**, 527 (1949).

sidered possible but probably not extensive at the high acidities employed.¹⁵

Notwithstanding the reservations listed, it is concluded that reasonable adsorption results can be obtained both from double layer capacitance and steady state current overvoltage measurements if the adsorbate is of limited solubility. Work aimed at establishing procedures for correcting for coreduction of, and hydrogen discharge through, the adsorbed layer is in progress.

DISCUSSION

J. J. BIKERMAN.—I hope Dr. Hansen will continue this study which bears on a most fascinating problem. A recent contribution by Antropov (*Zhur. Fiz. Khim.*, **25**, 1494 (1951)) may be of use in this work. It is known from the electrocapillary curves of mercury in electrolyte solutions that mercury adsorbs preferentially neutral molecules near the zero-charge potential φ_0 of the metal, anions when the metal is considerably more positive than at φ_0 , and cations when the metal is considerably more negative than at φ_0 . The same rules apply to solid metals. Thus, if adsorption by polarized electrodes is investigated, the first question to be answered is whether the electrode potential (for the given reaction!) is near the potential of the zero charge, is more positive, or more negative. In the first instance, uncharged molecules; in the second, anions; and in the third, cations, will be preferentially absorbed.

(15) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, pp. 656, 708.

DETERMINATION OF THE FORMULA OF AN OXIDE OF POLONIUM¹

By A. W. MARTIN

Mound Laboratory, Monsanto Chemical Company, Miamisburg, Ohio²

Received February 18, 1954

The procedures and apparatus used in establishing the stoichiometric relationship of polonium to oxygen as PoO_2 are described. The results of three separate determinations are given. The purification of polonium by fractional volatilization is described. The amount of dry oxygen gas reacting was ascertained by measuring the pressure decrease of a known volume of gas in contact with a known amount of polonium at definite temperatures (room and 25°). A Bourdon gage of Pyrex glass was used to observe the pressure difference accompanying the reaction. X-Ray diffraction data on both polonium dioxide prepared in these experiments and polonium dioxide formed in the decomposition of the nitrate of polonium gave additional evidence of the existence of quadrivalent polonium, Po^{+4} . It is concluded that the yellow dioxide, PoO_2 , is formed when dry oxygen gas is allowed to react with polonium. The reaction is slow at room temperature but the reaction rate increases with temperature and is rapid at 300°.

In preparing samples of polonium metal for X-ray diffraction studies, it was found that exposure to air caused a change in the appearance of the metal sample. It was suspected that certain of the X-ray diffraction patterns of what was thought to be polonium metal were actually patterns of a polonium oxide.³ A survey of the literature on polonium and its compounds suggested formulas of the oxides and oxidation states of polonium.⁴⁻⁷ Based on periodic clas-

sification analogies, the formulas PoO , PoO_2 , Po_2O_3 , or even higher oxides such as PoO_3 might represent the stable oxide under the preparation conditions described. It was important to know something of the stoichiometric relationships between polonium and oxygen in order to interpret the X-ray powder patterns of polonium metal and of the suspected polonium oxide.

This work was done to determine the formula of the oxide and an oxidation state of polonium. Quantitative weight analysis did not appear to be as effective a method for this purpose as the measurement of pressure changes accompanying the reaction of oxygen gas with polonium. The number of micromoles of oxygen gas reacting was calculated from the change in pressure of a measured volume of the gas. The quantity of polonium was determined by calorimetric measurement of the oxide, and these data were used to calculate the formula of the oxide of polonium formed under the conditions of the experiment.

(1) Presented before Kansas City Meeting of Physical and Inorganic Chemistry Division, American Chemical Society, Paper No. 52. Summary of Mound Laboratory Report MLM-855, July 7, 1953.

(2) Mound Laboratory is operated by Monsanto Chemical Company for the United States Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

(3) T. LaChapelle, "Oxidation States of Polonium and Preparation of Some of its Compounds," Mound Laboratory Report MLM-M529, May, 1, 1946.

(4) C. H. D. Clark, *Trans. Faraday Soc.*, **33**, 1390 (1937).

(5) M. A. Rollier, *Atti Congr. intern. chim. 10th Cong. Rome, 1938*, **2**, 770 (Pub. 1939).

(6) R. A. Staniforth, Progress Report, Feb. 1, 1946, Mound Laboratory Report MLM-M446, 8 (1946)

(7) G. V. Hevesy and F. Paneth, *Monatsh.*, **36**, 45 (1915).

Apparatus.—An all-glass apparatus was fabricated for making pressure measurements. This apparatus consisted of a chamber containing a small Bourdon tube to the outer free end of which was attached a pointer. The outer end of the pointer was positioned near an indicator so that movement of the pointer was easily observed. A microscope lamp was placed so as to project a beam of light through a lens onto the pointer and thereby throw a shadow of the pointer on a wall of the room so that small movements of the pointer were magnified.

The interior of the Bourdon tube was connected to a reaction tube approximately 14 mm. in diameter, having a 2 mm. capillary section interposed between the Bourdon tube and the open end of the tube, the wall of which was thickened near the open end so that it could be sealed after introduction of a sample of purified polonium.

A short tube was attached to the capillary section of the reaction tube whereby the reaction tube could be connected to a source of vacuum. An oxygen tube was sealed to the capillary section of the reaction tube adjacent the vacuum connection and was provided with a frangible partition which could be broken when desired by means of a breaker operated by a magnet on the outside of the tube. The outer end of the oxygen tube was connected to a source of oxygen and the tube was thickened near this end so that it could be sealed after introduction of oxygen. The oxygen tube was filled with water and the weight of water required to fill the oxygen space was determined before the tube was attached to the apparatus. The volume of oxygen was calculated from these data.

A volatilization tube was fabricated from quartz and consisted of a straight tube approximately 14 mm. in outside diameter having one end drawn down to an outside diameter of about 4 mm. The outer end of the smaller section of the tube was sealed and the opposite end of the larger section was fitted with a joint suitable for connection to a source of vacuum. The wall of the tube adjacent this joint was thickened so that it could be sealed when desired.

Experimental

Purification of Polonium.—A metallic deposit of polonium as free from impurities as possible was required for the oxide determination. Preliminary volatilization in a quartz volatilization tube was used as a means of purifying the polonium.

Approximately 10 micromoles of polonium on a platinum foil was placed in the larger section of the volatilization tube near point of attachment of the smaller section. The volatilization tube containing polonium was placed on the vacuum line and evacuated for several hours. The polonium was volatilized from the platinum foil onto the walls of the tube at a temperature slightly above 1000° by means of an oxygen flame applied to the quartz tube. This heating and volatilization was done with the vacuum pumps in operation so as to outgas the quartz tube and to remove any oxygen which might be produced by decomposition of polonium oxide.

The volatilization tube was sealed at the thickened section and the sealed portion was placed in an electrically-heated tube furnace with about four inches of the smaller section extending outside the furnace. Polonium was volatilized into the small section by maintaining a temperature of from 550 to 600° in the furnace for a period of one hour. The small section, containing the polonium, was sealed at the point of attachment to the larger section and the larger section was separated from the smaller section.

The small section was placed in an electrically-heated furnace with about one inch extending outside of the furnace. Polonium was volatilized into this one-inch section by maintaining a temperature of from 500 to 550° in the furnace for one hour.

Polonium was deposited on the walls of the tube immediately outside of the furnace, but a small dull-black deposit appeared on the outermost end of the tube. Apparently, this was some impurity which was more volatile than polonium. The tube was turned end-for-end in the furnace and heated at a temperature from 280 to 300° for one hour, causing the impurity to deposit in the end of the tube opposite the polonium. The tube was sealed between these two deposits and the end containing the purified polonium was transferred to the pressure-measuring apparatus.

First Determination.—The end of the quartz tube containing the purified polonium was broken in a helium-filled

dry-box. The two pieces of this quartz tube were inserted into the reaction tube connected to the open end of the Bourdon gage. The open end of the reaction tube was sealed immediately after the insertion of the two pieces of quartz tube containing the polonium. The apparatus was connected to the vacuum line through a vacuum connection. After evacuation for several hours at approximately 10^{-6} mm. of mercury pressure an electrically-heated tube furnace was placed around the section of the reaction tube containing the polonium and the metal was volatilized from the pieces of quartz tube onto the walls of the reaction tube. The tube was sealed between the volatilized polonium and that portion of the tube containing the two pieces of quartz tube. Material not volatilized from the quartz pieces was retained in the sealed-off portion. The vacuum pump was turned off, and purified dry helium gas was admitted to the evacuated system through the vacuum connection. The helium was purified by passing it over heated copper turnings and anhydrous phosphorus pentoxide and through a liquid-air trap. The pressure of helium gas was adjusted to 747.0 mm. of mercury at a room temperature of 23°.

The helium remained in the system and in contact with the polonium for 17 hours. The thin edge of the deposit of polonium changed from a metallic appearance to a light yellow color.

The seal between the oxygen tube and the reaction tube was broken and the oxygen was allowed to diffuse into the system for two days at room temperature. It was observed that the deposit of polonium had changed from a shiny, metallic appearance to a light yellow color. However, considerable of the metallic appearance remained, especially in that portion where the deposit was thickest.

An electrically-heated tube furnace was placed around the end of the reaction tube containing polonium and with heating at 200 to 250° for a period of one hour, the rate of reaction between oxygen and polonium increased as shown by readings of the Bourdon gage.

A second and a third heating of the reaction end of the apparatus gave no noticeable change in Bourdon gage readings. It was concluded, from the absence of an observable decrease in gas pressure as well as from the appearance of the deposit, that the reaction was complete. The deposit was yellow to orange in color, although not uniform in appearance.

The section of reaction tube containing the polonium dioxide was removed and was enclosed in a glass capsule for a calorimetric determination of the amount of polonium. The calorimetric value was 11.17 micromoles, which, when corrected to the time of sealing off, gave a value of 11.28 micromoles. A half life of polonium of 138.3 days was used.⁸

Summary of the Data for the First Oxide Determination. Helium gas (5.167 cc.) at a pressure of 747.0 mm. of mercury pressure and a temperature of 23.0° was in contact with the metallic polonium mirror for 17 hours before the addition of dry purified oxygen gas (1.042 cc.) at a pressure of 747.0 mm. of mercury pressure and 23.0°. With both helium and oxygen in contact with the polonium metal at room reference temperature for a period of 49.5 hours there was a decrease of 3.7 micromoles of gas. With heating to 200 to 255° for one hour and cooling to 23.0° a decrease of 20.4 mm. of mercury pressure was observed, corresponding to a calculated total decrease of 6.9 micromoles of gas. A second heating to 200 to 240° for 4.5 hours with cooling to 23.0° produced a total decrease of 10.7 micromoles of gas. A third and final heating to 200° to 233° for two hours followed by cooling to 23.0° produced no change in the number of micromoles of gas reacting with polonium metal. The combination of 10.7 micromoles of oxygen with 11.28 micromoles of polonium gives a ratio of 1.90 atoms of oxygen per atom of polonium. Allowing for an error of 0.1% in volume measurements, 1.6% for pressure measurements, and 0.2% for calorimetric measurements the total accuracy for the measurements in this first oxide determination is about $\pm 5.2\%$.

Second and Third Determination.—The apparatus described for the first oxide determination was modified by elimination of all stopcocks within the system where oxygen might react with stopcock grease. By making a small frangible seal on the end of the volatilization tube, the section

(8) J. F. Eichelberger, Progress Report, June 16-30, 1947, Mound Laboratory Report MLM-M171.

containing the sample of purified polonium was introduced into the apparatus without exposing the sample to contact of air. The Bourdon gage was used as a null instrument, and thereby measuring a greater total pressure difference. The apparatus could be immersed in a water-bath and maintained at a constant temperature. The volume of the reaction tube was determined before the polonium was introduced, using the density and weight of water required to fill it.

Volatilization of the polonium was done in a manner similar to that described above.

The quartz tube, after the final volatilization and sealing, was inserted into the open end of the reaction tube. The open end of the tube was sealed, and the apparatus was connected to the vacuum line and evacuated for 24 hours or longer under a pressure of 1×10^{-6} mm. of mercury. After thorough evacuation, oxygen, dried over phosphorus pentoxide, was admitted slowly through a Dry Ice trap until the pressure of the system was about 1 cm. below atmospheric pressure.

Observations of pressure changes were made for several hours with the apparatus at room temperature, or, in the third determination, at a temperature of 25°. The end of the tube containing the purified polonium was broken by striking it against the sealed end of the reaction tube. Observations of pressure changes were made over a period of several days at room temperature or at a maintained temperature of 25°.

The reaction end of the apparatus was heated as previously described to increase the rate of reaction. Pressure readings were made after the system had cooled and had been maintained at room temperature, or 25°, a sufficient time for the temperature to reach equilibrium.

It was concluded that equilibrium had been reached when there was no change in pressure upon successive heating and cooling. The reaction tube was carefully broken, the quartz tube containing the oxide was transferred to a Pyrex tube, the Pyrex tube was sealed, and the amount of polonium was determined by calorimetric measurement. Some polonium oxide on the walls of the reaction end of the apparatus was removed by washing several times with concentrated nitric acid, rinsing thoroughly with distilled water, and collecting the acid and washings in a volumetric flask. An assay of the amount of polonium in the washings was made.

Summary of Data for Second and Third Oxide Determinations.—In the second oxide determination 5.684 cc. of purified and dried oxygen gas at a pressure of 616.9 mm. of mercury and a reference temperature of 21.5° was placed in contact with metallic polonium. No measurable decrease in pressure was observed after 24 hours of contact of the gas with the metal. Upon heating 400 to 425° for one hour and cooling to a reference temperature of 22.0° a calculated decrease of 3.5 micromoles of gas was obtained. A second heating 423 to 432° for one hour with cooling to a reference temperature of 20.0° produced an additional decrease of 0.7 micromole of gas. A third and final heating 400 to 418° for one hour and cooling to 21.5° indicated complete reaction with a total of 4.6 micromoles of oxygen combining with 4.496 micromoles of polonium metal. The number of atoms of oxygen per atom of polonium for the second determination was 2.04.

For the third oxide determination 5.186 cc. of purified oxygen gas at 679.7 mm. of mercury pressure and a refer-

ence temperature of 25.0° was placed in contact with polonium metal. After contact for 43 hours at the reference temperature of 25.0° there was a decrease of 2.6 micromoles of oxygen. Upon heating 300 to 310° for six hours with cooling to 25.0° a total decrease in the amount of oxygen gas was calculated from the pressure measurements as 9.4 micromoles. A second heating 300 to 310° for three hours and cooling to 25.0° gave no observable decrease of pressure on the contained gas. A total of 9.4 micromoles of oxygen combining with 9.335 micromoles of polonium represents 2.02 atoms of oxygen per atom of polonium. The accuracy of measurements for the second and third determinations was about $\pm 5\%$.

Polonium dioxide prepared by the oxidation of elemental polonium and by the decomposition of polonium nitrate was placed in thin-walled X-ray capillary tubes, and X-ray diffraction analyses were made.⁹ In both cases, it was found that the oxide exists successively in different solid phases. The first phase, which lasts only a few days after the compound is prepared, has a tetragonal structure. The second phase has a fluorite (CaF_2) type of crystal structure with the lattice parameter $a_0 = 5.59$. This compound has a theoretical density of 9.18 and the radius of the Po^{+4} ion is 1.02 Å. It is interesting to note that the radii ratio,¹⁰ r/x , of this compound is 0.73, which is the lower limit of stability for the cubic coordination. This probably explains why both the tetragonal and the cubic structures are found. Thorium dioxide and polonium dioxide possess almost identical crystal structures with the lattice parameters differing by less than 0.5%.

When polonium decays, helium and lead are formed, one helium atom for each lead atom. The effect of alpha bombardment on conditions in the reaction tube is not definitely known. Calculations of the amount of oxygen which would be used up in the formation of the oxides of lead and of the volume of helium formed in the decay of polonium corresponded to an effective increase of from 0.02 to 0.025 micromole of gas. Since this value is small and the accuracy of measurements ($\pm 5\%$) does not warrant correcting for the changes, no correction was made.

Polonium dioxide has a light yellow color, and the deposit appeared to be quite uniform when viewed through a microscope with the light focused on the end of the containing tube.

Conclusions.—It may be concluded that the yellow dioxide, PoO_2 , is formed when dry oxygen gas reacts with polonium. The reaction is slow at room temperature but the rate increases with temperature and becomes rapid at 300°.

Powder patterns of polonium dioxide, prepared both by oxidation of the elemental polonium and by the decomposition of polonium nitrate, possess identical crystalline structures which may be attributed to quadrivalent polonium.

(9) R. E. Brocklehurst, "Crystal Structure of Some Compounds of Polonium," MLM-205, September 30, 1948.

(10) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1945, p. 570.

STUDIES ON SILICIC ACID GELS. XVIII. THE ACTION OF SODIUM HYDROXIDE ON THE GEL

BY CHARLES B. HURD AND STEPHEN H. LANING

*Chemical Laboratory, Union College, Schenectady, New York**Received February 24, 1964*

A study of the attack of sodium hydroxide on thin films of silicic acid gel is reported. The clear film of gel turns milky-white about one second after the 1 *M* NaOH attacks it. This is followed by the appearance of a network of cracks all over the surface. These grow larger and deepen with time. Some shrinkage of the film occurs between the cracks. The film disappears eventually. A series of photographs illustrates the phenomena. The time required for the NaOH to develop visible cracks on the surface of the film is approximately proportional to the age of the gel when the NaOH is applied. We are undoubtedly here observing a reversal of the normal condensation reactions in simple silicic acid, which result in the formation of silicic acid gels.

Introduction

Although it has been known for many years that solutions of strong alkalis will dissolve silicic acid gel, *cf.*, Monier,¹ the actual process has attracted little attention. Silicic acid gels result when solutions of sodium silicate and acids are mixed, providing the concentration of SiO₂ is high enough and providing the *pH* of the mixture is less than 11. Another way of decreasing the *pH* has been employed by Treadwell and his co-workers,²⁻⁴ who removed the NaOH from a solution of sodium silicate by electrolysis in a special cell. As the *pH* decreased, the solution formed a gel.

The action of NaOH in dissolving a silicic acid gel evidently reverses the process involved in gel formation. Chance observations in this Laboratory of the appearance of the gel surface when under attack by strong alkali led to the investigation reported here.

Experimental

Silicic acid gel mixtures were prepared by mixing solutions of sodium silicate and acetic acid. The method has been reported many times.⁵ The silicate was prepared by diluting "E" brand silicate, made by the Philadelphia Quartz Company. The gels prepared contained about 0.6 g. mole SiO₂ per liter, although the amount may be varied consid-

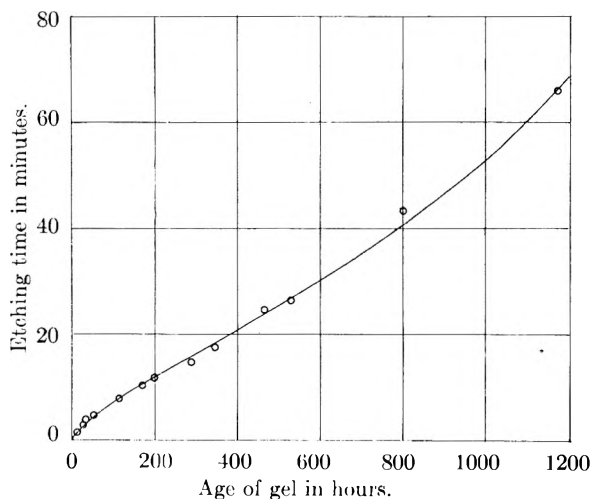


Fig. 1.—Etching time for sodium hydroxide on silicic acid gel as a function of age of the gel.

- (1) E. Monier, *Comp. rend.*, **85**, 1053 (1877).
- (2) W. D. Treadwell, *Trans. Faraday Soc.*, **31**, 297 (1935).
- (3) W. D. Treadwell and W. König, *Helv. Chim. Acta*, **16**, 54 (1933).
- (4) W. D. Treadwell and W. Wieland, *ibid.*, **13**, 842 (1930).
- (5) C. B. Hurd and P. S. Miller, *THIS JOURNAL*, **36**, 2194 (1932), and other papers of this series.

erably. They were acid gels, containing excess acetic acid. The *pH* and concentrations were not critical, although all *pH* values were below 7.

A few drops of the mixture were placed immediately on several microscope slides, which were placed flat in a desiccator containing water in the bottom. The gels set in from 10 to 15 minutes at room temperature, 21 to 23°. The temperature was not critical. The age of the gel film was noted when 1 *M* NaOH solution was placed on it. This age, namely, the time elapsed between time of set of the gel film and the start of the attack by 1 *M* NaOH, was important.

The action of the NaOH was followed visually and by photographs, with illumination from above. The main gel mixture was also kept and the amount of syneresis determined as a function of the age of the gel.

Results

The gel films were clear, were from 0.1 to 0.4 mm. thick and appeared black in the photograph, before attack by the NaOH solution. No cracks were visible. The 1 *M* NaOH when applied caused the film to turn white, both to the eye and in the photograph. About 1 second was required for a fresh gel.

The second phenomenon was the appearance of a maze of fine cracks on the gel surface. The time required for these cracks to appear depended on the age of the gel when the NaOH was applied. The cracks spread rapidly and the gel dissolved away from the edges, appearing to shrink and disappear.

Results on a number of specimens showed the same relation, namely, that the time required for the NaOH to show the first cracks in the gel surface is practically proportional to the age of the gel when the NaOH is applied. This is shown in Fig. 1. This gel set in 12 minutes. The curve shown is practically linear.

Figure 2 shows three series of photographs to illustrate the behavior of the gel film under attack by 1 *M* NaOH. The magnification in the photograph is between 1× and 2×. The first series is for a gel film 3 hours old when the NaOH was applied. The photographs were taken 55, 60, 65 and 70 seconds after the NaOH was applied. The second series is for a gel film 7 days old when the NaOH was applied. The photographs were taken 510, 550, 590 and 750 seconds after NaOH was applied. The third series is for a gel film 20 days old when the NaOH was applied. The photographs were taken 1860, 1920, 2010 and 2370 seconds after NaOH was applied.

Discussion

The films of silicic acid gel, having been kept in a desiccator over water, could not have undergone

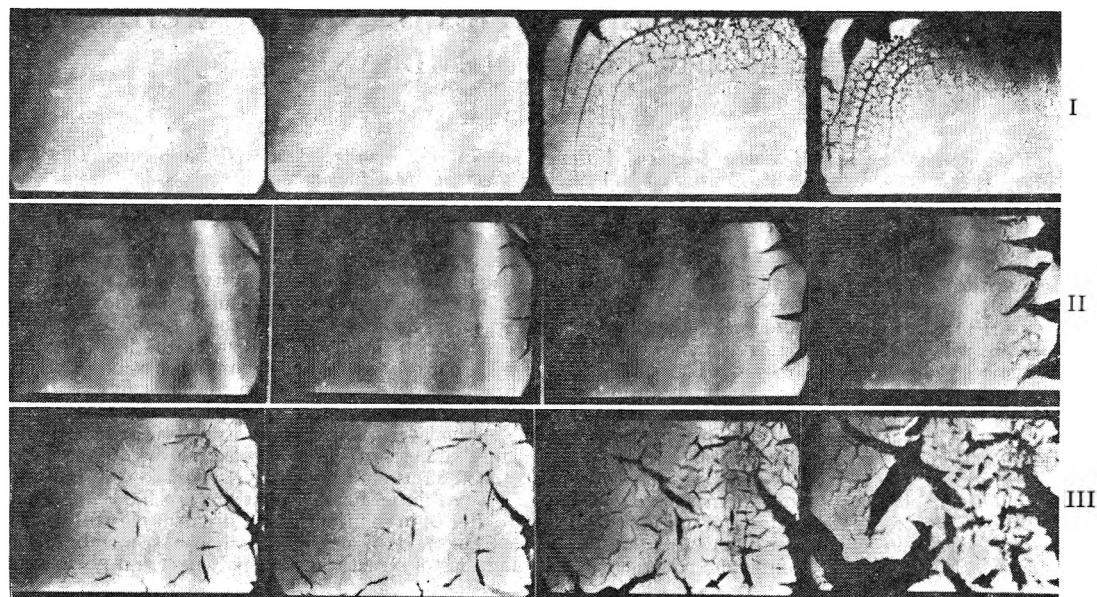


Fig. 2.—Films of silicic acid gel under attack by solutions of sodium hydroxide.

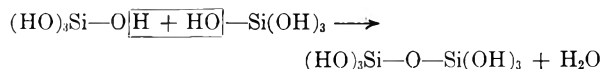
any drying by evaporation, since they were in an atmosphere saturated with water vapor. They were transparent before the NaOH was applied. The NaOH caused the films to become white, almost at once. Because of the very short time required, one or two seconds, this must be a surface effect.

Further attack by NaOH resulted in the appearance of cracks. The time required for the first recognizable cracks to appear is approximately proportional to the age of the gel when the NaOH is applied (Fig. 1). This must mean that the gel becomes harder with age. The cracks would appear to be due to strains set up in the gel due to shrinkage. This gradual shrinkage also results in syneresis and is probably due to continued condensation of the silicic acids.

Attack by NaOH also causes additional shrinkage as shown by the latest photographs in each series, especially series 2 and 3. The honeycomb or cell-like structure shown in the photographs may have been present in the gel before attack, but it is probably the result of strains either in the gel or developed by the NaOH. This honeycomb structure can certainly not be taken as any proof of the Honeycomb Theory of Gel Structure proposed by

Bütschli,⁶ since the dimensions of the sections shown between the cracks are surely of a much larger order of magnitude than suggested by Bütschli.

We are dealing here with a reversal of the reactions of condensation normally occurring in the formation of silicic acid gels, namely



to illustrate only the first step in a long series of condensations. The NaOH neutralizes the simpler silicic acids, which are stronger acids than are the polysilicic acids. This neutralization, by removing the simplest species, upsets the equilibria present in a gel and causes the more complex condensation products to hydrate and form the simpler acids. This causes solution of the gel.

A more complete discussion of this equilibrium has appeared recently⁷ in connection with a discussion of experiments on extended dialyses of silicic acid sols and gels.

(6) O. Bütschli, "Untersuchungen über Strukturen," Leipzig, 1898.

(7) C. B. Hurd, M. D. Smith, F. Witzel and A. C. Glamm, Jr., *THIS JOURNAL*, **57**, 678 (1953).

THE PREPARATION AND PROPERTIES OF STRONG ACID TYPE COLLODION-BASE MEMBRANES¹

BY REX NEIHOF

National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Public Health Service, Department of Health, Education, and Welfare, Bethesda 14, Maryland

Received March 25, 1954

Electronegative strong acid type, collodion-base membranes of extreme electrochemical activity were prepared by casting membranes of any desired porosity from collodion solutions containing dissolved sulfonated polystyrene, or by the adsorption of sulfonated polystyrene from aqueous solutions on preformed highly porous collodion membranes whose porosity can subsequently be reduced to the desired degree by drying. The charge density on the walls of the pores of these membranes can be adjusted at will. The membranes combine strong-acid character with the mechanical strength, flexibility and thinness characteristic of collodion membranes. The membranes of high porosity show high anomalous osmotic activities in solutions of acids as well as in neutral electrolyte solutions. The most useful permselective membranes give rise to concentration potentials which agree with the calculated thermodynamic maximum potential in solutions of potassium chloride and hydrochloric acid up to 0.1 *N* within the meaningfulness of the method. At higher concentrations the measured potential becomes gradually less than the theoretical value. The ohmic resistances of the permselective membranes of highest selectivity (as measured in 0.1 *N* KCl) may be adjusted from about 30 ohms cm.² upward. In solutions of uni-univalent electrolytes the more highly selective membranes have preferential permeabilities for cations which are 1000–2000 times that for anions at 0.1 *N*; in more dilute solutions of uni-univalent electrolytes or in solutions of uni-divalent electrolytes the relative permeability for cations may be many times greater. The general methods of making collodion-base membranes may be applied to the preparation of membranes from a variety of combinations of structural high polymers and polyelectrolytes.

Introduction

The collodion and collodion-base membranes of highest electrochemical activity developed over the last several years in this Laboratory have been extremely useful in the systematic study of the properties and functions of membranes of high electrochemical activity.^{2–5} Membranes of high porosity have been used in studies of anomalous osmosis.^{3,4,6–8} Dried type, permselective membranes with extreme ionic selectivity have made possible the study of certain types of Donnan equilibria involving only the ions of strong inorganic electrolytes^{2,3,9}; they were used successfully as membrane electrodes for the determination of numerous cations and anions for many of which other suitable electrodes do not exist^{10,11}; and they have also been used in the study of mosaic membranes.^{12–14}

The electronegative oxidized collodion membranes which were used heretofore in this work have, however, certain shortcomings arising from the weak-acid character of the dissociable groups which are fixed on their pore walls.^{2,15} They lose a considerable part of their characteristic electrochemical properties in acidic solutions and in the presence of the bivalent cations Ca⁺⁺, Sr⁺⁺ and Ba⁺⁺. In addition it has become clear in the course of the last few years that permselective membranes with an even higher selectivity than that of the oxidized collodion membranes are required for studies of Donnan equilibria (including membrane hydrolysis) over wide concentration

ranges¹⁶; for the determination of ion activities in solutions of mixed electrolytes¹⁷; for the investigation of the effect of water transport, membrane hydrolysis and related effects on the membrane potential^{2,18,19}; and in the construction of certain complex membrane model systems of biological interest.

An obvious approach to the problem of preparing improved types of electronegative membranes lies in the utilization of materials which carry dissociable groups of strong-acid character, such as sulfonic acid groups, and, in addition, have sufficiently low equivalent weights so that there will be a considerable surface density of charged groups on the pore walls of the membrane.

Membranes of strong-acid type have been prepared repeatedly by impregnating cellulose derivative membranes with dyestuffs carrying sulfonic acid groups.^{20,21} This approach has apparently never been pursued very far, probably because ordinary dyestuffs are rather readily washed out of the membranes.

In recent years ion-exchange resins of the commercial type have been utilized in various ways for the preparation of permselective type membranes; no effort has apparently been made to use these materials for the preparation of strong acid membranes of high porosity. Wyllie and Patnode have produced sulfonic acid type membranes in the form of rigid disks from one-half to several millimeters in thickness by molding under pressure an intimate mixture of powdered cation exchanger and an inert thermoplastic resin.²² These membranes give very high ionic concentration potentials even in nearly saturated solutions of sodium chloride; they have, however, low permeabilities and, correspondingly, slow rates of equilibration with electrolyte solu-

(1) Presented before the Division of Colloid Chemistry, American Chemical Society, Chicago, Ill., September 8, 1953.

(2) K. Sollner, *J. Electrochem. Soc.*, **97**, 139C (1950).

(3) K. Sollner, *Ann. N. Y. Acad. Sci.*, **57**, 177 (1953).

(4) K. Sollner, *THIS JOURNAL*, **49**, 47 (1945).

(5) K. Sollner, *ibid.*, **49**, 171, 265 (1945).

(6) K. Sollner and I. Abrams, *J. Gen. Physiol.*, **24**, 1 (1940).

(7) I. Abrams and K. Sollner, *ibid.*, **26**, 369 (1943).

(8) E. D. Grim, Ph.D. Thesis, University of Minnesota, 1950.

(9) K. Sollner and H. P. Gregor, *J. Am. Chem. Soc.*, **67**, 346 (1945).

(10) K. Sollner, *ibid.*, **65**, 2260 (1943).

(11) H. P. Gregor and K. Sollner, *THIS JOURNAL*, **58**, 409 (1954).

(12) R. Neihof, Ph.D. Thesis, University of Minnesota, 1950.

(13) R. Neihof and K. Sollner, *THIS JOURNAL*, **54**, 157 (1950).

(14) R. Neihof and K. Sollner, in preparation.

(15) K. Sollner and H. P. Gregor, *J. Colloid Sci.*, **6**, 557 (1951).

(16) R. Tamamushi and K. Sollner, unpublished data.

(17) K. Sollner, *J. Am. Chem. Soc.*, **68**, 156 (1946).

(18) A. J. Staverman, *Trans. Faraday Soc.*, **48**, 176 (1952).

(19) G. Scatchard, *J. Am. Chem. Soc.*, **75**, 2883 (1953).

(20) K. H. Meyer and J. H. Sievers, *Helv. Chim. Acta*, **19**, 665 (1936).

(21) K. H. Meyer and P. Bernfeld, *ibid.*, **28**, 972 (1945).

(22) M. R. J. Wyllie and H. W. Patnode, *THIS JOURNAL*, **54**, 204 (1950).

tions. Other strong-acid membranes have been prepared by Juda and McRae,²³ Kressman,²⁴ Bonhoeffer and Schindewolf,²⁵ Manecke,²⁶ and Winger, Bodamer and Kunin.²⁷ The membranes developed by all these investigators have low resistances but none appear to have selectivities as high as those of Wyllie and Patnode.

In this Laboratory the possibility of utilizing cellulose derivatives in the preparation of membranes of the strong acid type with high charge densities which combine high selectivity and low resistance was taken up and more thoroughly explored several years ago.^{12,28} The use of cellulose derivatives, particularly of collodion, as the structural materials of the membrane offers several practical advantages, such as ease in preparing thin sturdy membranes either of high porosity or of molecular sieve character in the form of flat sheets or of bags.

The methods which were considered for the possible preparation of collodion membranes of the strong-acid type are: (1) the introduction of strong-acid groups, *e.g.*, of semi-esterified sulfate groups, into bulk collodion or into the formed membranes, in analogy to the oxidative method of activation used in the preparation of carboxylic (weak-acid type) membranes²⁹⁻³¹; (2) the casting of membranes from collodion solutions which contain dissolved materials carrying strong-acid groups (dissolution method); and (3) the adsorption on precast membranes of materials carrying strong acid groups (adsorption method). The latter two methods seemed most promising.

The dissolution method, with dyestuffs as activating materials, has been used in the past with only moderate success. The dyestuff-containing membranes lacked stability, particularly if they were of high porosity, because of the inadequate retention of the relatively low molecular weight dyestuffs within the membranes. Such membranes are not suitable for exact studies, particularly those of long duration. The successful application of the dissolution method obviously requires the selection of an activating material which, besides being soluble in collodion solutions and carrying an adequate number of strong acid groups, also has a sufficiently high molecular weight to be permanently retained in the membrane.³²

(23) W. Juda and W. A. McRae, *J. Am. Chem. Soc.*, **72**, 1044 (1950); U. S. Patent 2,636,851.

(24) T. R. E. Kressman, *Nature*, **165**, 568 (1950).

(25) K. F. Bonhoeffer and U. Schindewolf, *Z. physik. Chem.*, **198**, 281 (1951).

(26) G. Manecke, *ibid.*, **201**, 193 (1952).

(27) A. G. Winger, G. W. Bodamer and R. Kunin, *J. Electrochem. Soc.*, **100**, 178 (1953).

(28) K. Sollner and R. Neihof, *Arch. Biochem. Biophys.*, **33**, 166 (1951).

(29) K. Sollner, I. Abrams and C. W. Carr, *J. Gen. Physiol.*, **25**, 7 (1941).

(30) C. W. Carr and K. Sollner, *ibid.*, **28**, 119 (1944).

(31) H. P. Gregor and K. Sollner, *THIS JOURNAL*, **50**, 53 (1946).

(32) With membranes prepared by the dissolution method the mechanism of retention of activating material may be visualized as follows. After casting the membrane the collodion solution containing the dissolved activating material soon sets to a gel as the solvents evaporate. The gel is then either precipitated in water in the case of membranes of high porosity or dried completely in the case of permselective membranes. The molecules of activating material are entangled or embedded in the nitrocellulose as the membrane sets and hardens. Embedding will be increasingly effective as the molecular weight and especially the chain length of the activating molecules is increased.

Although the adsorption method has been used successfully with materials not carrying strong-acid groups,^{7,33-35} it has not led to membranes of satisfactory stability when strong-acid dyestuffs were used. Evidence that the adsorption method is useful, however, has been provided by work on permselective membranes of Dr. E. D. Grim in this Laboratory (unpublished) who used as activating materials the chemotherapeutic drugs, Trypan Red, Trypan Blue and Suramin (Baeyer 205). These materials have molecular weights of around 1000 and carry several sulfonic acid groups per molecule. It is apparent that a suitable activating material for preparing strong-acid type membranes by the adsorption method must strike a balance between having a sufficiently low equivalent weight, a sufficiently high molecular weight and suitable chemical constitution for strong adsorption and having a molecular size small enough to enter the pores of the membrane.³⁶

As already indicated in a preliminary note, synthetic, strong-acid polyelectrolytes were found to be valuable activating materials for collodion membranes.²⁸ Of the various types of polyelectrolytes tested as activating materials for collodion membranes, the most advantageous was polystyrenesul-

fonic acid $(-\text{CH}_2-\overset{|}{\text{CH}}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_n$. Sulfonated polystyrene (SPS) has an acid strength comparable to that of the strong inorganic monobasic acids. SPS is soluble in ether-alcohol in the free acid form, and in water as the alkali salt or as the free acid; it is, therefore, suitable for use with either the adsorption or the dissolution method of activation.²⁸ SPS has the additional advantage of being a monofunctional compound. It is easily prepared from polystyrene resins which are commercially available in various molecular weights.

This paper describes in some detail the preparation of sulfonated polystyrene collodion-base membranes and presents a systematic survey of their properties.

The Preparation of Sulfonated Polystyrene Collodion-base Membranes

For the preparation of sulfonated polystyrene (SPS), commercial polystyrene resins were used which had average molecular weights, as given by the manufacturers, in the range from 6,000 to 70,000.

The resin (ground to 40-mesh or finer) was sulfonated by mixing it with 5 to 10 times its weight of concentrated sulfuric acid and 1% of its weight of silver sulfate as catalyst, and heating the mixture to about 100° with continuous stirring.³⁷ The higher ratios of sulfuric acid were used with the high molecular weight resins in order to prevent the reaction mixture from becoming too viscous. As soon as a drop of the mixture dissolved completely when stirred with water, the reaction was stopped, ordinarily after 1-3 hr.

(33) J. Loeb, *J. Gen. Physiol.*, **2**, 255, 577 (1920).

(34) C. W. Carr, H. P. Gregor and K. Sollner, *ibid.*, **28**, 179 (1945).

(35) H. P. Gregor and K. Sollner, *THIS JOURNAL*, **50**, 88 (1946).

(36) There is, aside from adsorption an additional mechanism which, in the case of dried type, permselective membranes, is of importance in retaining activating material. During immersion of the membranes of high porosity in the aqueous solution of activating material, some of the latter is adsorbed on the pore walls and varying amounts, depending on the thoroughness of the subsequent washing, are also present in the water which fills the pores. When the membrane is dried it shrinks to a denser structure; the activating material becomes entrapped.

(37) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, 3299 (1949).

In general, the longer periods of heating were necessary for higher molecular weight or less finely ground resins.³⁸

The degree of sulfonation was determined by titrating weighed samples of the purified, dried, sulfonated resins in the free acid form (see below). The acid values were in the range of 5.20 to 5.47 meq./g. as compared with a theoretical value of 5.43 meq./g. calculated for a linear polymer having one sulfonic acid group on each benzene ring.

For use with the dissolution method, the free acid form of the sulfonated polystyrene (H-SPS) was used. The latter was conveniently separated from the excess sulfuric acid used in the sulfonation process by dialyzing an aqueous solution of the crude sulfonation mixture using a cellophane membrane, or by electrodialysis, or by passing the solution through a column of an anion-exchange resin in the hydroxide form. The sulfuric acid-free solution was evaporated to dryness on a steam-bath. The resulting rather hygroscopic material was yellow or brown in color. It was dried in an oven at 110–120° for about 4 hr. or until constant weight was reached. In this form the H-SPS has been stored for more than two years without detectable deterioration.

For the preparation of membranes by the adsorption method, a stock solution of the sodium salt of sulfonated polystyrene (Na-SPS) was prepared by slowly stirring the reaction mixture, maintained at room temperature, into about ten volumes of water and neutralizing to a pH of about 2 by the addition of 3 *M* NaOH solution. This stock solution seems to be stable indefinitely. For the actual adsorption process it was further diluted.

The preparation of membranes of high porosity by the dissolution method consists of casting membranes from collodion solutions containing 1–2 g./l. H-SPS. H-SPS collodion solutions can be conveniently prepared by adding the H-SPS in the form of an 8–15% alcoholic solution.³⁹

The incorporation of H-SPS in collodion solutions increases their viscosity. With the lower molecular weight SPS preparations this effect can be disregarded; the alcoholic solutions of H-SPS may be added to 3.5% solutions of Collodion Cotton, U.S.P., in 50:50 ether-alcohol. (Other collodion preparations may require higher alcohol ratios.) With the higher molecular weight SPS preparations 3.5% collodion solutions may be too viscous to permit casting membranes of uniform thickness; the use of more dilute solutions is then indicated (see below).

Numerous factors influence the porosity of the membranes. The composition of the collodion solution has some effect: a high collodion concentration and a high molecular weight collodion both make for more viscous solutions which, *ceteris paribus*, lead to more porous membranes; high alcohol-ether solvent ratios and the presence of non-volatile substances such as water or glycerol also make for increased porosity.⁴⁰ The conditions of casting are of considerable influence; short drying times, low air temperature, and, particularly, a high atmospheric humidity make for increased porosity.⁴¹

For uniformity and convenience most of the membranes were cast by pouring the H-SPS-collodion solution over a 25 × 100 mm. test-tube rotating in a horizontal position according to a previously described procedure.^{30,31} Two-layer membranes were found satisfactory for most purposes. Depending on the porosity desired and the atmospheric humidity at the time of casting, the first layer was dried 3 or 4 min. and the second 4 to 20 min. The membranes, after being washed in water for an hour, were slipped off their casting tubes and reimmersed in water for a day. Tied to glass rings they were ready for use. Such membranes have been stored in potassium chloride solution for more than six months without change in their electrochemical properties as measured by anomalous osmosis.

(38) K. W. Pepper, *J. Appl. Chem.*, **1**, 124 (1951).

(39) It is possible to prepare satisfactory membranes from collodion solutions to which have been added appropriate amounts of the raw sulfonation mixture which still contains excess free sulfuric acid. If this is done the membranes should be cast immediately since the nitrocellulose is degraded by the sulfuric acid.

(40) W. J. Elford, *Trans. Faraday Soc.*, **33**, 1094 (1937).

(41) Due to condensation brought about by the cooling effect of the evaporating solvent and to its hygroscopicity, atmospheric moisture collects in the membrane while it is being cast; this moisture exerts a similar precipitating effect on the collodion as does water added intentionally to the collodion solution used for casting.⁴⁰

The preparation of dried type, permselective membranes by the dissolution method was carried out by casting membranes from collodion solutions containing 0.3 to 3 g./l. H-SPS (depending on the properties desired) and drying them completely on their casting tubes. The final properties of these membranes depend primarily on the H-SPS content of the collodion solutions from which they are prepared. The atmospheric conditions are of only minor significance; in this respect the dissolution method has a distinct advantage over the adsorption method (see below).

The routine procedure was to cast one layer of the H-SPS collodion solution on the outside of test-tubes according to the methods described above for membranes of high porosity; 3 or 4 min. later a second layer was added, and the membrane allowed to dry for 24 hr. Next they were placed in water for a few hours, removed from their casting tubes and secured to glass rings with linen thread. Thereafter, the membranes were dried in air for 12 hr. at room temperature or, preferably, in an oven at 60–70° for one hour. They should not be heated for prolonged periods or at higher temperatures since, aside from the danger of explosive decomposition, the collodion suffers a gradual decomposition which decreases their mechanical strength. The oven drying reduces the possibility that the membranes will undergo further changes if they are subsequently exposed to air of low humidity. Before use the membranes were stored in water or electrolyte solution for about three days.

The thickness of these membranes was about 30–35 μ . (Thinner membranes can be obtained by using more dilute collodion solutions; casting three or more layers of collodion yields thicker membranes.) They were smooth and of test-tube shape; they were transparent and glass-clear or, in the case of those with high SPS content, slightly brown in color. Such permselective membranes have been stored in the dry state in the potassium form, and in dilute potassium chloride solutions (to which a preservative such as thymol was added for protection against mold growth) for periods up to a year with no changes in their electrochemical properties aside from small changes in ohmic resistance. Analytical data showed that no significant amount of SPS was removed from the membranes during ten months storage in water. It should be mentioned that the membranes should not be kept for long periods in the acidic form in the dry state, since the collodion undergoes a gradual decomposition under such conditions.

For the preparation of membranes of high porosity by the adsorption method collodion membranes of suitable porosity prepared in any convenient manner were washed in water and immersed for 2–3 days in an aqueous solution of about 0.5% of Na-SPS at pH 3. After being washed overnight in water the membranes reached a state of relative stability which, though adequate for certain experiments, was considerably inferior to that of membranes prepared by the dissolution method. For this reason the membranes prepared by the adsorption method were not investigated in detail.

The first step in the preparation of dried type, permselective membranes by the adsorption method is the casting of collodion membranes of high porosity which are suitable for the adsorption of Na-SPS from aqueous solution. The properties of the dried membranes ultimately obtained are determined by the amount of Na-SPS which is taken up during the adsorption process by the membranes in the highly porous state.

The greater the porosity of the membranes of high porosity the greater is the uptake of Na-SPS. The factors affecting porosity which were already discussed in connection with membranes of high porosity prepared by the dissolution method apply also here. With membranes of a given porosity the amount of Na-SPS taken up becomes greater as the molecular weight of the SPS is decreased, apparently because more pores become accessible to it. The amount of Na-SPS of a given molecular weight which is taken up increases with the concentration of the Na-SPS solution. With a given concentration of any particular Na-SPS preparation, the amount taken up increases with decreasing pH of the solution and with increasing concentration of inorganic electrolyte (either of the sodium sulfate resulting from the neutralization of the excess sulfuric acid or of a deliberately added electrolyte). No systematic attempt was made to explore fully the effect of all these variables.

The routine procedure used in preparing permselective membranes was as follows: Membranes of high porosity

were cast from a 3.6% solution of Baker Collodion Cotton, U.S.P., dissolved in equal volumes of absolute alcohol and anhydrous ether, by the methods already described. At normal room temperatures and average relative humidities (35–55%) a second layer of collodion was added 3 min. after pouring the first; 5 min. later the membranes were immersed in water which was changed several times during a period of several hours. At low relative humidities (less than 30–35%) 2% water was added to the collodion solution before casting in order to ensure adequate porosity. The membranes at this stage have a water content of 80–90% by weight and an average thickness between 190 and 220 μ .

The membranes, still on their casting tubes, were activated by immersing them for two days at room temperature in 0.04 to 2.0% aqueous solutions of Na-SPS at pH 3. The adsorption time can be shortened if the membranes are slipped off their casting tubes after the first few hours' immersion so that adsorption can take place from both sides of the membranes.

Following the adsorption process the membranes were removed from their casting tubes, if this had not been done before, and washed for one hour to remove inorganic salts which otherwise might later crystallize in them during drying. More prolonged washing removes appreciable quantities of SPS which results in a decrease in conductance of the final membranes. Next, the membranes were replaced on their respective casting tubes and dried in air for 24 hr. For greater reproducibility this may be done in a humidistat, *e.g.*, over a saturated solution of CaCl_2 at about 31% relative humidity.³¹ The membranes were then placed in water for about 2 hr. and removed from their casting tubes.⁴² Glass rings were slipped into the open ends of the membranes and secured with linen thread. Thereafter, the membranes were dried again, this time without support, preferably in an oven at 60–70° for an hour (the previously stated precautions being observed). The appearance, thickness and stability of these membranes are similar to those of membranes prepared by the dissolution method.

The Properties of Sulfonated Polystyrene Collodion-base Membranes of High Porosity

The electrochemical activity of SPS collodion-base membranes of high porosity is conveniently determined by the measurement of anomalous osmosis across them.

"Anomalous osmosis" is the liquid mass movement across porous (non-swelling) membranes separating solutions of different concentrations of an electrolyte which, according to their rate or the pressures obtained, are not explained on the basis of the laws of normal osmosis.^{6,43}

The extent of anomalous osmosis is a function of the dynamic membrane potential across the membrane and of its electrokinetic potential.^{43,44} The extent of anomalous osmosis under standard conditions can serve as a sensitive indicator of the relative electrochemical activity of various membranes provided they have approximately the same porosity.²⁹

To measure anomalous osmosis, the membrane, tied to a glass ring, was filled with electrolyte solution of known concentration. A rubber stopper holding a capillary tube (1.25 mm. inside diameter) and a siphon tube provided with a stopcock was then firmly inserted in the glass ring, and the membrane placed in a beaker filled with distilled water. The meniscus in the manometer tube was adjusted to a position corresponding to the capillary rise above the outside

water level. The rise of the meniscus during the next 20 min. was taken as the measure of the extent of anomalous osmosis. The experiment was repeated until successive 20-min. readings agreed within 5%.

In testing the influence of different modes of activation of membranes by means of anomalous osmosis it is a prerequisite that the membranes to be compared have about the same thickness and similar porosities. As measures of the functional porosity the filtration rate and the "sucrose value" were employed. The sucrose value is the osmotic rise in mm. in the capillary manometer 20 min. after the membrane, filled with 0.25 *M* sucrose solution, is placed in water.²⁹ Filtration rates are calculated from the rates of passage of a 1 *M* KCl solution through a membrane under a standard head.²⁹

Anomalous osmosis across a series of membranes prepared by the dissolution method and appropriately dried so as to have closely similar sucrose values and filtration rates was determined with a solution of 0.002 *M* K_2SO_4 .²⁸ With H-SPS concentrations in the collodion of 0.2, 0.7, 1.2, 1.8 and 3.0 g./l. the anomalous osmotic rises after 20 min. were 215, 480, 660, 700 and 680 mm., respectively. With H-SPS concentrations of more than about 3.0 g./l. the mechanical strength of the membranes becomes too low to support the pressures which arise.

The less stable membranes prepared by the adsorption method showed analogous increases in anomalous osmotic activity with increasing concentrations of Na-SPS in which they were immersed for activation.

Anomalous osmosis across a typical SPS collodion-base membrane of high porosity prepared by the dissolution method was determined with several electrolytes over a wide range of concentrations and compared with the behavior of a typical oxidized collodion membrane under the same conditions.

The SPS collodion-base membrane was a two-layer membrane cast from a collodion solution containing 1.8 g./l. H-SPS. It had an accessible area of about 50 cm.², a sucrose value of 220 mm. and a filtration rate of 4.1 ml./hr./100 cm.²/10 cm. pressure head. The oxidized collodion membrane was activated by 15-min. immersion in 0.5 *M* NaOH; its thickness, surface area, sucrose value and filtration rate were closely similar to those of the SPS collodion membrane. The solid line curves in Fig. 1 denote the pressure rises obtained with the SPS collodion-base membrane, the dotted curves the results for the oxidized collodion membrane.

From Fig. 1a it is evident that in neutral electrolyte solutions both types of membranes show similar anomalous osmotic behavior. The curves for the SPS collodion-base membrane lie slightly to the right of those for the oxidized collodion membrane. This is probably due to the higher charge density of the former.

Figure 1b demonstrates that the anomalous osmotic rises with the strong-acid type membrane are considerably greater in acid solutions than those of the oxidized collodion membrane. This is due to the fact that the active groups of the SPS collodion membrane are completely dissociated even in considerable concentrations of acids and thus in the same state as in neutral solutions while the dissociation of the active groups of the oxidized collodion membrane is repressed in the presence of acids.

Strong-acid type membranes of high porosity are

(42) If this operation proves difficult it may be facilitated by first loosening the membrane over the hole at the bottom of the casting tube by working it with the thumb. The tube is then filled with water and a tight fitting stopper pushed into the open end, thus forcing a film of water between the membrane and the tube; the water acts as a lubricant and facilitates the removal of the membrane.

(43) K. Sollner, *Z. Elektrochem.*, **36**, 36, 234 (1930); K. Sollner and A. Grollman, *ibid.*, **38**, 274 (1932); A. Grollman and K. Sollner, *Trans. Electrochem. Soc.*, **61**, 477, 487 (1932).

(44) J. Loeb, *J. Gen. Physiol.*, **4**, 213 (1921); **4**, 463 (1922).

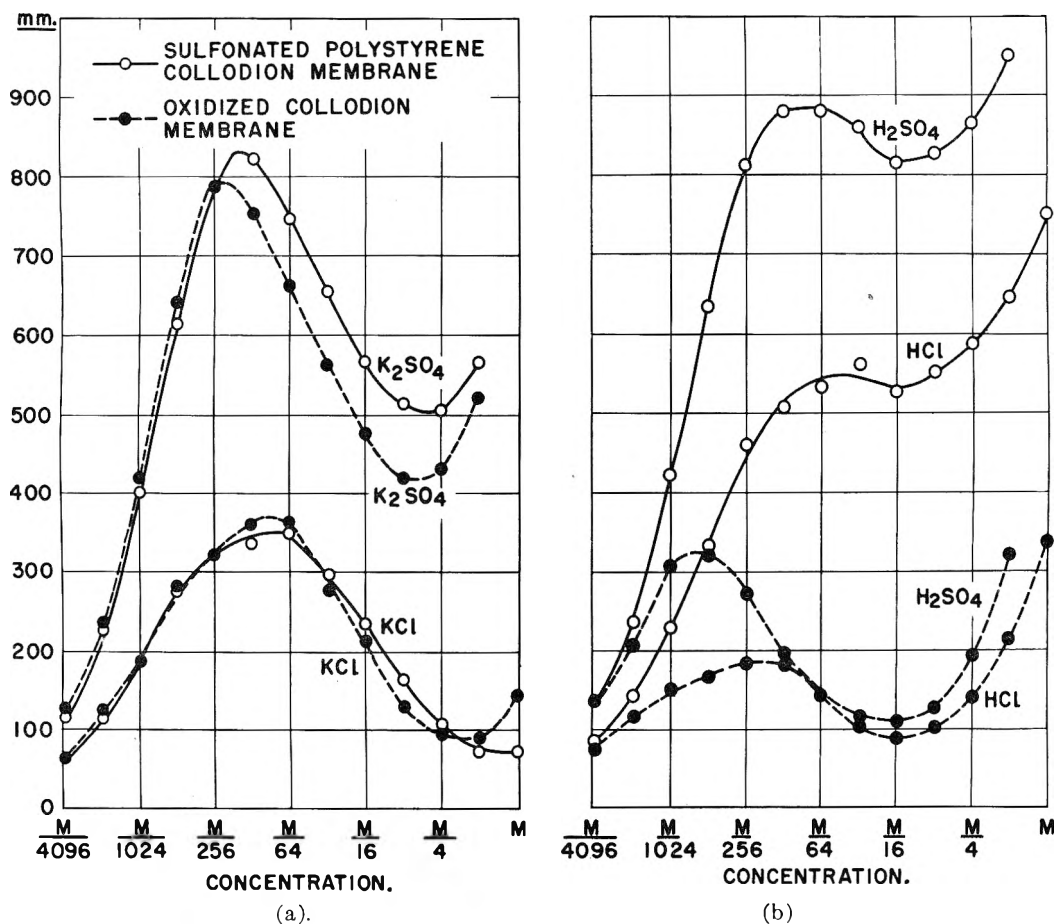


Fig. 1.—Comparison of anomalous osmosis across a sulfonated polystyrene collodion-base membrane and an oxidized collodion membrane: a, in solutions of neutral electrolytes; b, in solutions of acids.

of potential usefulness in studies on dialysis, electrodialysis and electro-osmosis; such applications have yet to be investigated.

The Properties of Permselective Sulfonated Polystyrene Collodion-base Membranes

A variety of permselective, SPS collodion-base membranes were prepared by both the dissolution and adsorption methods and characterized by: (a) thickness, (b) cation-exchange capacity, (c) SPS content, (d) water content, (e) the rate of osmotic water movement, (f) the ohmic resistance in contact with 0.1 *N* KCl solution and, (g) the concentration potential in the chain 0.4 *N* KCl/membrane/0.2 *N* KCl. Following this survey a few membrane specimens of the types found most useful for physicochemical investigations were studied for their electromotive properties in concentration chains over a wide range of electrolyte concentrations, and for the rates of movement of critical ions (cations) and of non-critical ions (anions) across them.

The membranes prepared by the dissolution method were cast from collodion solutions containing from 0.30 to 2.5 g./l. ($\pm 5\%$) of H-SPS (nominal mol. wt. in the sulfonated state, 125,000). For H-SPS concentrations of 0.30, 0.50 and 0.70 g./l., the H-SPS was added to 3.5% collodion solutions. For higher concentrations of H-SPS more dilute collodion solutions were used in order to obtain approximately the same final membrane thickness (see above), 3.0, 2.5 and 1.5% solutions of collodion being used with H-SPS concentrations of 1.0, 1.4 and 2.5 g./l., respectively. Twelve two-

layer membranes were prepared under the same conditions from each of these six different H-SPS collodion solutions.

The membranes prepared by the adsorption method were two-layer membranes cast at 20° and 33% relative humidity from a 3.6% collodion solution containing 2% water. Sets of twelve membranes each were immersed in six different aqueous Na-SPS (nominal mol. wt., 18,000) solutions with concentrations from 0.04 to 2.0%. After 24 hr. the membranes were removed from their casting tubes and reimmersed in the same solutions for another 24 hr. to permit the Na-SPS solution to be in contact with both sides of the membranes. They were washed and dried under the same conditions, as described above.

The thickness of the membranes was measured in the water-wet state with a thickness gage which had a reproducibility of $\pm 2 \mu$. It was measured at several points over the surface of two to four membranes randomly selected from each of the twelve sets. The fluctuations in thickness over each membrane were never more than $\pm 5 \mu$ except in the case of the membranes prepared by the dissolution method from collodion solutions containing 2.5 g./l. H-SPS; the thickness of these membranes varied as much as $\pm 10 \mu$ because of the relatively high viscosity of the collodion solution. There were no significant differences in the average thicknesses among the membranes of a given set.

The cation-exchange capacity of the membranes was determined with four membranes selected at random from each of the twelve sets. The membranes were slit open lengthwise, and 5.0 \times 7.0 cm. rectangles from the flat portion were cut into strips and placed in Pyrex bottles. In order to bring this material into a state in which all of the accessible fixed charged groups were compensated by ammonium ions, 0.1 *M* NH₄Cl solution was added and changed several times during a period of three days. Thereafter, the membranes were repeatedly washed with double distilled water for several days until a portion of the wash water no longer gave a positive test for ammonium ion with Nessler.

reagent. The ammonium ion in the membranes was then displaced by adding 40.0 ml. of 0.5 *M* KCl solution to the wet material. After standing for three days with occasional stirring the KCl solution was analyzed for ammonium ion content. Addition of a fresh portion of KCl solution showed that the ion exchange was complete in the first treatment. From the concentration of ammonium ion found after the first exchange with KCl the cation-exchange capacity of the membranes in meq./cm.² was calculated. The material used in the base-exchange measurements was subsequently washed and its dry weight used to calculate the cation-exchange capacity per gram of dry membrane in the hydrogen form. The error in the base-exchange capacity is estimated to be not more than 5% for the membranes with the lowest SPS content; it is less for the membranes with higher SPS content.

The SPS content of the membranes was determined with an error of 1-5%, depending on the SPS content of the membranes, by an analysis of the total sulfur in the same membrane material used for the base-exchange measurements. It is expressed as meq./g. of dry membrane in the hydrogen form.

The water content was determined on four membranes of each set which had been converted to the hydrogen form. The membranes were slit lengthwise and their upper rims and half-spherical bottoms removed. The resulting flat parts of the membranes were then blotted dry with filter paper, placed immediately in a tared weighing bottle, and their weight in the wet state determined. Then they were dried over phosphorus pentoxide *in vacuo* until constant weight was reached. The difference in weight gives the water content. The reproducibility of these measurements was about ± 0.5 when the results are expressed as g. water/100 g. wet membrane.

The rate of osmotic water movement across the membranes was determined using a 0.2 *M* solution of sucrose, a solute for which the membranes are virtually impermeable. The membrane was filled with this solution, fitted with a rubber stopper carrying a graduated, capillary manometer tube and placed in a beaker of water in a thermostat at $25.00 \pm 0.05^\circ$.

After thermal equilibrium was reached the meniscus level was observed at various times and the average rate of water transport computed. The reproducibility in the rate of water movement was about $\pm 10\%$. Measurements with 0.4 and 0.8 *M* sucrose solution indicated that the rate of water transport is proportional to the difference in the activity of the water on the two sides of the membrane.

The ohmic resistance of the membranes in 0.1 *N* KCl solution was determined after they had been immersed in this solution for a time more than sufficient to permit equilibration. The cell used in measuring the resistance was similar to that described by Gregor and Sollner,³¹ the only difference being that the larger of the two test-tube shaped platinized platinum electrodes between which the membrane was held was made from perforated platinum sheet in order to make its area approximately equal to that of the smaller inside electrode. The ohmic resistance of the cell filled with 0.1 *N* KCl solution was determined at $25.00 \pm 0.05^\circ$ in the presence and in the absence of the membrane using the Kohlrausch method with a frequency of 1000 cycles. The difference between the two values multiplied by the area in cm.² of the membrane was taken as the standard membrane resistance, ρ^* . The reproducibility of the membrane resistance from day to day was about $\pm 3\%$.

A variable condenser was used in parallel with the known resistance arm of the bridge in order to obtain a sharp balance. The capacitance necessary to obtain a balance of the bridge with SPS collodion-base membranes varied from 0.06 to 0.6 $\mu\text{f.}/50\text{ cm.}^2$ membrane area. There was no definite correlation of capacitance with the other membrane properties measured although larger capacitances were generally required with membranes having a high SPS content and concomitant low resistance. No attempt has been made to correct the resistance values for the capacitance. The full significance of the capacitance effects in terms of the permeability of these membranes has yet to be investigated.⁴⁵

The concentration potential of the membranes in the series of survey experiments was measured with 0.4 *N* KCl inside and 0.2 *N* KCl outside after they had been kept overnight in contact with these solutions.³¹ These concentra-

tions of potassium chloride were used instead of the customary 0.1 and 0.01 *N* solutions because the small differences in selectivity between the different groups of membranes prepared in the course of this work were more readily apparent at the higher concentration levels. All measurements were made in a thermostat at $25.00 \pm 0.05^\circ$ using saturated calomel half-cells equipped with saturated potassium chloride-agar bridges. Test measurements with membranes of various resistances showed no detectable difference in the concentration potential when the position of the two solutions was reversed. The measurements were made repeatedly with each membrane immediately after the addition of fresh solutions until a steady value was obtained. With membranes having a resistance of less than about 30 $\Omega\text{ cm.}^2$ in 0.1 *N* KCl it was necessary to stir the solutions in order to obtain a steady, reproducible potential. Because of the asymmetry of the liquid junction potential at the tips of the potassium chloride bridges, the potential values measured by the outlined procedure are too high by 0.33 mv.¹⁶ The concentration potentials reported in this paper are reduced accordingly. The reproducibility of the potential measurements was ± 0.05 mv. or better with membranes whose resistance was more than about 30 $\Omega\text{ cm.}^2$. With membranes having a lower resistance the reproducibility was in no instance lower than ± 0.15 mv.

The measurements of the electromotive properties of the selected membranes were carried out with potassium chloride and hydrochloric acid at ten concentration levels between 0.001 and 2.0 *N*, the concentration ratio being 2:1. The procedure just described was followed except that instead of calomel electrodes, silver-silver chloride electrodes prepared by the method of Rule and La Mer¹⁶ were used. The reproducibility of these potential measurements was about ± 0.05 mv. except for the 1.0:0.5 and 2.0:1.0 concentration ratios of hydrochloric acid where it was about ± 0.3 mv. The membrane potential was computed from the measured potential of the chain by subtracting the potential difference of the silver-silver chloride electrodes. The latter value was calculated assuming the activity of the chloride ions in the two solutions to be equal to the mean activity of the electrolyte.

The rates of movement of cations and of leak of anions across the membranes were measured in order to describe their permeability and selectivity more completely and accurately.³¹ Radioactive tracers would be most suitable for such experiments⁴⁷; however, meaningful results can also be obtained if two different electrolytes are selected which have cations that give only a small bi-ionic potential.⁴⁸ The uni-univalent electrolyte system, $\text{KNO}_3/\text{NH}_4\text{Cl}$, and the uni-bivalent system, $\text{K}_2\text{SO}_4/(\text{NH}_4)_2\text{C}_2\text{O}_4$ were used. The bi-ionic potential with ammonium and potassium as cations at 0.1 *N* concentration was not more than about 3 mv. for the membrane of highest resistance used ($\rho^* = 420\ \Omega\text{ cm.}^2$) and was practically zero for the membranes of low resistance.

The membranes were filled with 25 ml. of one electrolyte solution (usually the potassium salt) and placed in a tube containing 25 ml. of a solution of the other electrolyte at the same concentration in a position which brought the inside and outside solutions to the same level. Both solutions were stirred by streams of air bubbles. The effective membrane area in contact with the solutions was about 48 cm.². Since a period of time is required before a reproducible state of diffusion across the membrane is set up, the solutions were withdrawn after an appropriate time and immediately replaced by fresh 25-ml. portions of the original solutions, the moment of this replacement being taken as zero time of the experiment proper. After a measured interval the experiment was stopped and the solution initially containing the potassium salt was analyzed by conventional semi-micro methods for ammonia and for the anion, chloride⁴⁹ or oxalate. Several such experiments were made with each membrane using suitably different time intervals. The concentrations of ammonia and of chloride or oxalate were plotted against time, and the slopes of the initial straight-line portions of these curves determined. These slopes are a direct measure of the permeability of the membrane to critical ions and of its "leak" of non-critical ions.

(46) C. K. Rule and V. K. La Mer, *J. Am. Chem. Soc.*, **58**, 2339 (1936).

(47) K. Sollner and H. P. Gregor, *THIS JOURNAL*, **51**, 299 (1947).

(48) K. Sollner, *ibid.*, **53**, 1211 (1949).

(49) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 331.

(45) K. Sollner and H. P. Gregor, *J. Colloid Sci.*, **7**, 37 (1952).

TABLE I

PROPERTIES AND FUNCTIONAL BEHAVIOR OF VARIOUS PERMELECTIVE SULFONATED POLYSTYRENE COLLODION-BASE MEMBRANES PREPARED BY THE DISSOLUTION METHOD

1	2	3	4	5	6	7
Concn. of H-SPS in collodion soln., g./l.	H-SPS content of dry membrane, meq./g.	Cation-exchange capacity, meq./g.	Water content, %	Av. rate of osmotic water movement (0.2 M sucrose), mm. ³ /hr. 100 cm. ²	Av. unit area resistance ^a in 0.1 N KCl, ρ^* ($t = 25.0^\circ$), Ω cm. ²	Av. concn. potential ^a 0.4/0.2 N KCl ($t = 25.00^\circ$), mv.
0.30	0.050	0.046	5.0	5.3	50,100 (11,000)	15.16 (0.22)
.50	.072	.070	5.6	8.4	2,030 (350)	15.45 (.10)
.70	.106	.104	5.7	13.7	435 (80)	15.48 (.02)
1.0	.203	.169	7.0	57	54.5 (10.5)	15.32 (.01)
1.4	.306	.280	10.3	190	26.3 (3.7)	15.09 (.04)
2.5	.73	.72	26.8	2000	18.5 (3.5)	13.9 (.2)

^a Figures in parentheses indicate maximum deviations from the mean value.

TABLE II

PROPERTIES AND FUNCTIONAL BEHAVIOR OF VARIOUS PERMELECTIVE SULFONATED POLYSTYRENE COLLODION-BASE MEMBRANES PREPARED BY THE ADSORPTION METHOD

1	2	3	4	5	6	7
Concn. of Na-SPS in aqueous soln., g./l.	H-SPS content of dry membrane, meq./g.	Cation-exchange capacity, meq./g.	Water content, %	Av. rate of osmotic water movement (0.2 M sucrose), mm. ³ /hr. 100 cm. ²	Av. unit area resistance ^a in 0.1 N KCl, ρ^* ($t = 25.0^\circ$), Ω cm. ²	Av. concn. potential ^a 0.4/0.2 N KCl ($t = 25.00^\circ$), mv.
0.040	0.106	0.073	5.7	8.5	32,500 (6000)	13.34 (1.10)
.050	.122	.113	5.6	8.6	7,800 (3700)	15.26 (0.11)
.060	.144	.144	6.4	21	240 (55)	15.42 (.02)
.10	.201	.190	7.7	75	38.5 (1.5)	15.30 (.03)
.20	.265	.267	8.7	154	26.6 (3.1)	15.26 (.11)
2.00	.354	.357	10.3	370	28.9 (1.1)	15.12 (.07)

^a Figures in parentheses indicate maximum deviation from the mean value.

All of the experiments with the uni-univalent electrolyte system gave satisfactory results. In the uni-bivalent electrolyte system only experiments with the most leaky membranes were carried out because of the extremely low rate of leak of bivalent anions which most types of membranes showed.

Table I summarizes the properties of the various types of membranes prepared by the dissolution method. Column 1 gives the concentration of H-SPS dissolved in the collodion solution used for casting the membranes. Column 2 shows the H-SPS content of the membranes as determined by the sulfur analyses. Column 3 gives the cation-exchange capacity expressed as meq./g. of dry membrane. Column 4 shows the water content by weight; from these data the volume per cent. water content may be calculated.^{31,50} Column 5 gives the average rate of osmotic water movement measured with two membranes of each type using 0.2 M sucrose solution; the difference between the rates for the two membranes was less than 15% in most cases. Columns 6 and 7 present the mean values of measurements made with four individual membranes selected at random from the twelve membranes of each type (see above). The figures in parentheses show the maximum deviation from the mean value and, thus, indicate the variation which is inherent in the method of preparation. Column 6 shows the average of the standard resistances of four membranes of each type, column 7 the average concentration potential of the same four membranes.

Table II shows the properties of various types of membranes prepared by the adsorption method. Column 1 indicates the per cent. Na-SPS in the aqueous solution used for adsorption; the other

columns have the same meaning as the identically numbered columns of Table I.

The average thicknesses of the membranes in Table I were 30–34 μ except for those prepared from collodion containing 2.5 g./l. of H-SPS which had an average thickness of 43 μ . All of the membranes in Table II had thicknesses of 25–28 μ .

The cation-exchange capacity expressed on an area basis was 0.19, 0.32, 0.50, 0.69, 1.14 and 3.20 meq./cm.² for the membranes of Table I and 0.26, 0.44, 0.51, 0.74, 1.05 and 1.38 meq./cm.² for those of Table II.

Table III presents the potentials obtained in concentration chains with solutions of potassium chloride and hydrochloric acid with a SPS collodion-base membrane of relatively low resistance which, as can be seen from Tables I and II, is not of the highest degree of selectivity which can be obtained by the described methods. This representative membrane was prepared by the adsorption method; it had a standard resistance, ρ^* , of 80 Ω cm.². In order to permit a comparison of the electromotive behavior of this membrane with that of a permselective oxidized collodion membrane³¹ the potentials obtained with a membrane of the latter type ($\rho^* = 300 \Omega$ cm.²) are also included in Table III.

Tables IV and V show the results of the studies on the rates of exchange of cations and of leak of anions across SPS collodion-base membranes. The last column of each table gives the ratio of the permeabilities of cations to anions.

Discussion

The data on the SPS collodion-base membranes of high porosity (Figs. 1a and 1b) need no further

TABLE III

CONCENTRATION POTENTIALS ($c_1:c_2 = 2:1$) WITH SOLUTIONS OF KCl AND HCl ACROSS A REPRESENTATIVE PERMSELECTIVE SULFONATED POLYSTYRENE COLLODION-BASE MEMBRANE AND AN OXIDIZED COLLODION MEMBRANE

($t = 25.00 \pm 0.05^\circ$)

1 Concn. of electrolyte soln., $c_1:c_2$, equiv./l.	2 — Potassium chloride — 3			4 Oxidized collodion membrane mv.	5 — Hydrochloric acid — 6 — 7		
	Theoretical max., mv.	Sulfonated polystyrene collodion membrane mv.			Theoretical maximum, mv.	Sulfonated polystyrene collodion membrane mv.	Oxidized collodion membrane mv.
0.002/0.001	17.45	17.25		17.20	17.45	17.45	17.45
.004/0.002	17.31	17.19		17.04	17.34	17.26	17.26
.01/0.005	17.10	16.97		16.95	17.15	17.08	17.02
.02/0.01	16.86	16.74		16.74	16.97	16.88	16.66
.04/0.02	16.63	16.52		16.47	16.84	...	16.04
.1/0.05	16.30	16.10		15.80	16.76	16.59	15.31
.2/0.1	16.11	15.74		15.09	16.87	...	15.33
.4/0.2	15.95	15.40		13.90	17.49	17.37	15.66
1.0/0.5	16.32	14.58		10.93	19.89	19.1	17.7
2.0/1.0	17.34	13.86		8.01	24.39	23.2	22.0

TABLE IV

THE RATES OF MOVEMENT OF CRITICAL AND NON-CRITICAL IONS ACROSS VARIOUS PERMSELECTIVE SULFONATED POLYSTYRENE COLLODION-BASE MEMBRANES IN THE SYSTEM, 0.1 N $\text{KNO}_3/0.1$ N NH_4Cl ($t = 22 \pm 2^\circ$)

1 Method of preparation	2 ρ^* , Ω cm. ²	3 Initial rate of movement of NH_4^+ , $\mu\text{eq./hr.}$ cm. ²	4 Initial rate of movement of Cl^- , $\mu\text{eq./hr.}$ cm. ²	5 Ratio of initial rates, of movement of NH_4^+ to Cl^-
Dissolution	22	93	0.167	560
Adsorption	27	156	.28	560
Adsorption	38	37	.050	740
Dissolution	75	12.0	.0076	1580
Adsorption	195	4.9	.00234	2100
Dissolution	420	1.63	.00098	1660

TABLE V

THE RATES OF MOVEMENT OF CRITICAL AND NON-CRITICAL IONS ACROSS A TYPICAL PERMSELECTIVE SULFONATED POLYSTYRENE COLLODION-BASE MEMBRANE ($\rho^* = 80 \Omega$ CM.²) AT VARIOUS CONCENTRATION LEVELS IN THE SYSTEM $\text{KNO}_3(c_1)/\text{NH}_4\text{Cl}(c_2)$, ($t = 25.0 \pm 0.1^\circ$)

1 Concn. (c_1), equiv./l.	2 Initial rate of movement of NH_4^+ , $\mu\text{eq./hr.}$ cm. ²	3 Initial rate of movement of Cl^- , $\mu\text{eq./hr.}$ cm. ²	4 Ratio of initial rates of movement of NH_4^+ to Cl^-
0.01	9.8	0.000147	67,000
.02	9.8	.00054	18,100
.05	10.2	.00223	4,600
.10	11.5	.0090	1,280
.20	12.3	.0277	440
.50	14.5	.143	101
1.00	17.0	.44	39
2.00	19.0	1.34	14.2

comment. The discussion below is confined to the permselective membranes; it takes up some selected points concerning the membranes of the survey Tables I and II and then discusses in more detail the data on the concentration potential and the rates of exchange of cations and leak of anions of Tables III to V.

A comparison of the cation-exchange capacity (col. 3, Tables I and II) with the SPS content (col. 2) shows that practically all of the sulfonic acid groups in the membranes prepared by both the dissolution

and the adsorption methods are available for ion exchange.

With respect to the unit area-exchange capacity (see above) it is pertinent to point out that in many physicochemical experiments it is desirable to have membranes with low cation-exchange capacities relative to the number of equivalents of ionic constituents in the surrounding solutions, for example, in the electrometric determination of ionic activities, and in studies of Donnan equilibria. The small unit area exchange capacities of the SPS collodion-base membranes in combination with their extreme selectivity make them particularly suitable for such studies.

The rate of osmotic water movement across the membranes (col. 5) becomes rapidly greater as the water content of the membranes increases (cf. col. 4). The water movement across the membranes which, it will be recalled occurs under a driving force corresponding to 50 m. of water pressure is decidedly low except in the case of those with the highest SPS content. The low water permeabilities are helpful in studies where it is necessary to keep solutions of different water activity separate for long periods of time.

The resistances (col. 6) of the membranes of a given type prepared under nominally identical conditions show substantial variations. Small increments in SPS content result in very large differences in the resistances. These data can serve as a guide for the preparation of membranes having resistances in the range desired for a particular purpose.

The data on the membrane resistances together with the data on the rate of osmotic water movement can be made the basis for the selection of membranes (of satisfactory ionic selectivity) which allow ionic processes to take place across them at a maximum rate with a minimum rate of simultaneous water transfer. For this purpose membranes should be selected which show a minimum in the product of the values for resistance and rate of osmotic water movement. In the case of the membranes prepared in this study this optimum occurs with membranes having standard resistances in the range of about 40–60 Ω cm.².

The degree to which the concentration potentials

(col. 7) of the membranes deviate from ideality at the 0.4/0.2 *N* KCl concentration level can be estimated by comparing them with the theoretical upper limit of the concentration potential, 15.95 mv. This latter value is calculated for the concentration chain in which it is assumed that the membrane acts electromotively like two ideal potassium electrodes connected by a metallic conductor and that the activity of the potassium ion is equal to the mean activity of potassium chloride. The activity coefficients were taken from the book of Harned and Owen⁵¹ and converted from the molality to a normality basis.

The concentration potentials across the membranes with medium SPS contents approach the maximum theoretical potential more closely than do those with very low or very high SPS contents. The lower selectivity of the membranes with low SPS contents is very probably due to a lower average density of charged groups at critical points in the pores of the membranes; with membranes of high SPS content, most conspicuously those prepared by the dissolution method, the lower selectivity can be assumed to be correlated with the increased water content (*cf.* col. 4) and the generally looser structure of the membrane.

In connection with the Teorell, Meyer-Sievers theory^{20,52,53} it is of interest to look for a correlation of the selectivities of the various types of membranes as manifested by their concentration potentials and the equivalent concentrations of acid groups in the pore water of the membranes. The latter values as derived from col. 3 and 4 assuming all of the water to be available are, in order of increasing H-SPS in the collodion solutions (Table I), 0.9, 1.2, 1.7, 2.2, 2.4 and 2.0 equiv./l. and, in order of increasing Na-SPS in the aqueous solutions used for adsorption (Table II), 1.2, 1.9, 2.1, 2.3, 2.8 and 3.1 equiv./l. These values are identical with the selectivity constants of the Teorell, Meyer-Sievers theory. The theory postulates the highest concentration potentials with the membranes having the highest equivalent concentration of active groups. The empirically found correlation does not show any consistent trend.^{5,54}

We turn now to Table III on the concentration dependence of the concentration potential across an average permselective SPS collodion membrane, and to its comparison with an oxidized collodion membrane which was chosen for its high selectivity.

The concentration potentials of the SPS collodion-base membrane in potassium chloride solutions are 0.1 to 0.2 mv. below the calculated maximum at all concentrations from the most dilute solutions up to 0.1/0.05 *N*; for more concentrated solutions the deviation becomes greater.

The SPS collodion-base membrane, in agreement with its higher charge density, shows consistently higher concentration potentials in chains with potassium chloride than does the oxidized collodion membrane, the difference being more noticeable at the higher concentrations.

With hydrochloric acid solutions the concentration potentials across the SPS collodion membrane show a smaller deviation from the calculated maximum than with potassium chloride; in the most dilute system the measured and calculated potentials coincide. The difference between the results in potassium chloride and hydrochloric acid can, for the most part, be understood on the basis of the much higher mobility of the hydrogen ion.

In chains with hydrochloric acid the concentration potential is higher than that of the oxidized collodion membrane at all but the lowest concentrations. The differences in the range of medium concentrations is to be expected not only because of the lower charge density of the oxidized collodion membrane but also because of the incomplete dissociation of its weak acid groups.

In passing, an additional property of the SPS collodion-base membranes should be mentioned which may be attributed to their strong acid character. They yield reproducible concentration potentials of the expected magnitude in chains with solutions of the bi-univalent alkaline earth metal salts.^{55,56} Thus these membranes may be used as membrane electrodes for the determination of the activities of these bivalent cations.⁵⁵

In evaluating the ionic selectivity of membranes from concentration potentials, it is usually assumed that a leak of non-critical ions across the membranes is the only factor which causes the measured potential to be less than the calculated theoretical maximum.^{30,57} However, there are other complicating factors which may become significant under certain conditions. If the membranes are not ideally selective and if the solutions are very dilute, the electrolyte concentrations in the non-stirred, adhering water layers of the membrane may be significantly different from those in the bulk solutions.⁵⁸ The measured potential would thus be lower than that which would arise if the concentrations in the adhering water layers and bulk solution were the same; expressed in another way, the true ionic selectivity of the membrane would be higher than that calculated in a straightforward manner from the concentration potential. Membrane hydrolysis¹⁹ may lower the measured potential in dilute solutions of neutral electrolytes (but not in solutions of acids). Water movement across the membrane may also be expected to reduce the measured potentials,^{2,18,19} *e.g.*, as result of the unavoidable transport against a water activity gradient of water of hydration of electromotively active ions or as a result of an opposing electrokinetic potential produced by osmotic movement of water. It must also be kept in mind that a non-thermodynamic assumption is made in the calculation of the theoretical maximum potential and in assigning a part of the measured potential of a concentration chain to the membrane concentration potential.

For all these reasons it becomes inadvisable to equate without reservation an apparent deficit in membrane concentration potential with a lack of

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

(52) T. Teorell, *Froc. Soc. Exptl. Biol. Med.*, **33**, 282 (1935).

(53) K. H. Meyer and J. F. Sievers, *Helv. Chim. Acta*, **19**, 649 (1936).

(54) K. Sollner and C. W. Carr, *J. Gen. Physiol.*, **28**, 1 (1944).

(55) C. W. Carr, *Arch. Biochem. Biophys.*, **43**, 147 (1953).

(56) R. Neihof, unpublished.

(57) L. Michaelis, *Bull. Natl. Research Council*, No. 69, 119 (1929).

(58) A. Noyes and W. Whitney, *Z. physik. Chem.*, **23**, 689 (1897); W. Nernst, *ibid.*, **47**, 52 (1904); E. Brunner, *ibid.*, **47**, 56 (1904).

ionic selectivity. The degree of ionic selectivity of a membrane might better be established by a direct determination of its relative permeabilities to critical and non-critical ions⁴⁷ (Tables IV and V).

The data of Table IV on the **rates of movement of cations and of anions** across several SPS collodion-base membranes provide a direct description of their ionic permeabilities in 0.1 *N* solutions. The initial rate of movement of cations (col. 3) across the various membranes shows a rough inverse proportionality to their standard resistances (col. 2) except for the second membrane listed which falls out of line for some unknown reason.⁵⁹ The initial rate of movement of the anions (col. 4) shows a similar but considerably steeper inverse relationship with the membrane resistance.

The ratio of the initial rates of movement of the cations to that of the anions (col. 5) represents a direct measure of the degree of preferential permeability of the membrane for the critical ions over the non-critical ions; the reciprocal of this ratio is the measure of the relative "leak" of the membranes under the conditions of the experiment.

With the electrolyte system 0.1 *N* K₂SO₄/0.1 *N* (NH₄)₂C₂O₄ the leak of anions was so small that even after 30 days it could be assayed only in the case of the two membranes of lowest selectivity listed first in Table IV. The leak of oxalate ions with these membranes was found to be approximately 1/1000 that of the leak of chloride ions. The leak of non-critical ions across these membranes in the uni-bivalent, 0.1 *N* electrolyte system is, therefore, of the order of one part in 500,000; the leaks of the more highly selective membranes would be expected to be even lower.

The **rates of exchange of critical ions** (col. 2, Table V) across a membrane of medium resistance change by a factor of two for a 200-fold change in concentration. The **rate of movement of anions** (col. 3), however, changes by a factor of more than 9000 over this concentration range. The **selectivities** (col. 4) show a striking rise from rather low values at high concentrations to 1280 to one at 0.1 *N*, and to 67,000 to one at 0.01 *N*. These data are of value in circumscribing the conditions under which membranes can be used in uni-univalent electrolytes without significant disturbances due to leak.

It is of interest to observe that both the high values of the selectivity and the considerable change in selectivity with concentration which are

(59) Calculated values of the rates of self-diffusion of cations to be expected from the standard resistances of the membranes in Table IV according to the Nernst-Einstein diffusion relation as used recently by Schlögl (*Z. Elektrochem.*, **57**, 195 (1953)) and K. S. Spiegler and C. D. Coryell (*THIS JOURNAL*, **57**, 687 (1953)) agree fairly well with the initial rates of movement of cations.

observed in the range of the more dilute solutions in Table V could not have been predicted from concentration potential data. The differences between the calculated maxima and experimental concentration potentials indicate lower and practically constant selectivities in this range (see Table I).

This discussion might be concluded with some remarks concerning the application of the methods described in this paper to the preparation of membranes from other structural materials and with different activating agents.

The use of high polymer materials having greater rigidity and less inherent capacity to swell in water than collodion can be anticipated to result in membranes of higher selectivity than those described here. A suggestive indication in this direction can be seen in the fact that the plastic bonded, ion-exchange resin membranes of Wyllie and Patnode²² have much higher selectivities than ion-exchange resin membranes which can swell with no restraint other than that of their own cross linking. Preliminary experiments indicate that various plastics can be substituted for collodion which are not only more rigid but also have higher chemical stability particularly in alkaline solutions.

There is a large variety of possible activation agents which might be used. For example, weak-acid type collodion-base membranes have been prepared by using polyacrylic acid as the activating polyelectrolyte. These membranes have higher charge densities and greater mechanical strength than oxidized collodion membranes. Strongly basic, electropositive membranes are currently being prepared in this Laboratory by impregnating collodion membranes with polyelectrolytes carrying quaternary ammonium base groups.⁶⁰ Activating materials such as amphoteric polyelectrolytes,⁶¹ polymers having pronounced ionic specificities, particularly chelating materials,⁶² electron-exchange polymers,⁶³ and materials of biological origin or of specific biological activity might be used in preparing membranes of special interest.

Acknowledgment.—The author wishes to express appreciation to Dr. Karl Sollner for many helpful suggestions and criticisms in the course of this work particularly during the preparation of the manuscript. The author is also grateful to Dr. William C. Alford for the sulfur analyses, and to the Dow Chemical Company and the Monsanto Chemical Company for various samples of polystyrene.

(60) M. H. Gottlieb, R. Neihof and K. Sollner, in preparation.

(61) T. Alfrey and H. Morawetz, *J. Am. Chem. Soc.*, **74**, 436 (1952); T. Alfrey, R. M. Fuoss, H. Morawetz and H. Pinner, *ibid.*, **74**, 438 (1952).

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

(63) H. G. Cassidy, *Proc. Natl. Acad. Sci.*, **38**, 934 (1952).

α -RADIOACTIVITY OF SOME ROCKS AND COMMON MATERIALS

By JOHN B. OCKERMAN AND FARRINGTON DANIELS

*Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin**Received April 23, 1954*

The α -ray activity of nearly three hundred samples of material are reported here. They include granites, limestones, bentonites, building materials, well water residues and plant litter. Measurements were made with a scintillometer and range from 0.05 to 12 α -counts per hour per sq. cm. from a powder layer of infinite thickness.

During the course of an extended study of the geochemistry of uranium, approximately two thousand determinations of relative α -activity were carried out on specimens collected from many localities in North America. Scintillation counters were employed for these measurements on thick sources of pulverized sample. The greatest amount of study was devoted to granite, limestone, bentonite, water residues, plant ashes and various types of building brick and tile. This paper summarizes the data accumulated by presenting the average α -activity (counts per hour per sq. cm.—c.p.h./cm.²) found for each class of material together with the range of variation encountered.

Apparatus.—Scintillation counters were selected for measurement of α -radioactivity because of low background and high efficiency of counting. The type of instrument employed has been described by Reed.¹ Two such counters were purchased from the R-C Scientific Instrument Co. and a third was built from components consisting of a photomultiplier tube (RCA 5819), a mounting and light-tight housing for the tube, phosphor screen and sample holder, and a Nuclear Instrument and Chemical Co. Model 162 scaler which also served as the high voltage supply.

The detector unit of each counter was a 5819 photomultiplier tube and a phosphor screen 2.25 in. in diameter below which was placed a tray to hold the sample in a reproducible position directly below the screen. The screen was prepared by stretching acetate-base Scotch tape, 3 inches wide, across the hole in an aluminum screen frame and sprinkling silver-activated zinc sulfide phosphor over the sticky surface. A uniform, reproducible layer is obtained when the excess phosphor is removed by inverting the frame and tapping lightly. This technique is described by Reed.¹ The Type D ZnS-Ag phosphor was obtained from E. I. du Pont de Nemours Co., Photo Products Department, Towanda, Pa. The screen was replaced between the powdered sample and the photomultiplier tube with the phosphor side down and only 4 mm. above the powder. When the α -particles were ejected from the sample, they hit the phosphor and emitted a bright light which was transmitted through the transparent tape and into the photomultiplier tube where it was counted. The sample tray was an aluminum plate having a circular depression in the center in which a 2 in. diameter lucite sample dish was placed. An amplifier and scaler unit with a stabilized high voltage supply and register made up the balance of the counter. The voltage of the a.c. power input to each counter was regulated by a constant-voltage transformer.

Calibration and Technique.—At a fixed amplifier and discriminator setting and with a monoenergetic source of α -particles, the scintillation counters used in this study may exhibit a long plateau (100–200 volts) in the counting-rate vs. voltage curve between 800 and 1000 volts. The amount of amplification and the discriminator adjustment, which fixes the minimum pulse voltage required to produce a count in the scaling circuit, will affect the nature of the plateau as will the use of a source emitting α -particles of mixed energy such as a thick source of uranium ore. In the calibration, curves of counting-rate were plotted against voltage for several amplifier and discriminator settings using a polonium source. The best plateau thus obtained was further investigated by making counts of a standard pitchblende sample at voltages along the lower two-thirds of the plateau until the previously determined counting rate of

the standard sample was consistently reproduced by the counter. It then remained to check the background counting rate at the voltage setting thus established. It was usually advisable to prepare a new phosphor screen before measuring this background rate to avoid the effects of contamination. Contamination with radon required frequent replacement. The background should not exceed 0.1 to 0.2 count per hour per sq. cm. for these instruments when the sample tray is inserted with the depression empty, or filled with mineral oil.

The counters were calibrated in this way in order to have confidence in the relative comparisons of many samples. Standard pitchblende samples were used as an aid in interpreting counting rates in terms of uranium content when certain types of materials were studied but generally the possible presence of members of the thorium family and the uncertainty regarding radioactive equilibrium makes such estimation of a specific emitter very doubtful.

Samples for counting were prepared by grinding to pass 100 mesh and then were stored 2 to 4 weeks to allow gaseous disintegration products to approach equilibrium. For counting, the sample was packed lightly and leveled off in a clean lucite dish 2 in. in diameter and 1.5 mm. deep. Such sources have been tested and found to be infinitely thick, *i.e.*, any natural α -particle directed upward from the bottom of the sample will be absorbed before reaching the top surface of the sample.

The samples on which this article is based were counted to a statistical precision of $\pm 20\%$ at the 90% confidence level which required the accumulation of at least 70 counts above background. Duplicate counts were made on many samples. Background counts were ordinarily made overnight and the screen replaced when background exceeded 0.2 to 0.25 counts per hour per sq. cm.

Results²

1. **Standard Ore Samples.**—Tabulated below are the counting rates of standard samples which were the basis of calibration of the counters. The rates given were established when the standards became available by making several counts of each sample in one of the counters. The other instruments were then referred to these counts for calibration. The variation encountered in the original determinations is shown as a percentage of the average rate. Secular equilibrium was assumed to exist in these samples in which short-lived daughter products are in equilibrium with a parent of long life and are decaying at the same rate as the parent.

A. Pitchblende standards, Department of Mines and Technical Surveys, Canada		c.p.h./cm. ²
R-T-1-1	220 p.p.m. U	70 \pm 8%
R-T-1-3	2540 p.p.m. U	763 \pm 2%
B. Thorium ore standards, U.S. National Bureau of Standards		
A	10 p.p.m. Th + 0.4 p.p.m. U	1.7 \pm 12%
B	100 p.p.m. Th + 4.0 p.p.m. U	9.1 \pm 12%
C	200 p.p.m. Th + 8.0 p.p.m. U	17.8 \pm 13%
D	500 p.p.m. Th + 20.0 p.p.m. U	45.4 \pm 10%
E	1000 p.p.m. Th + 40.0 p.p.m. U	82.0 \pm 6%

These infinitely thick pitchblende samples indi-

(2) More detailed descriptions of these samples may be obtained from the American Documentation Institute or from the authors.

(1) C. W. Reed, *Nucleonics*, **7**, no. 6, 56 (1950).

cate that 1 part per million of uranium in equilibrium gives roughly 0.31 c.p.h./cm.². This ratio was found in a large number of materials containing uranium in radioactive equilibrium.

2. α -Activity of Rocks, Water Residues, Plant Ashes and Miscellaneous Building Materials.—

The following results are reported first as the average counting rate of all the samples tested together with the maximum and minimum values obtained. In addition, the individual results in each series are tabulated in order of increasing activity. All values are given in c.p.h./cm.².

a. Granite—40 samples

Av. activity, 3.2

Max. activity, 9.6

Min. activity, 0.2

Individual measurements: 0.2, 0.4, 0.4, 0.6, 0.6, 0.7, 0.8, 0.8, 1.0, 1.0, 1.1, 1.2, 1.3, 1.4, 1.6, 1.7, 1.7, 1.7, 1.8, 2.0, 2.4, 2.5, 3.3, 3.4, 3.5, 3.6, 3.8, 4.1, 4.4, 4.6, 5.1, 5.3, 5.7, 6.1, 6.4, 6.6, 8.1, 8.2, 8.6, 9.6

b. Limestone—82 samples

Av. activity, 0.4

Max. activity, 1.7

Min. activity, 0.05

Individual measurements: 0.05, 0.05, 0.06, 0.06, 0.06, 0.08, 0.08, 0.09, 0.10, 0.12, 0.12, 0.13, 0.13, 0.13, 0.15, 0.15, 0.15, 0.18, 0.18, 0.20, 0.20, 0.20, 0.20, 0.20, 0.25, 0.25, 0.25, 0.25, 0.25, 0.25, 0.25, 0.30, 0.30, 0.30, 0.30, 0.30, 0.30, 0.30, 0.33, 0.36, 0.36, 0.36, 0.36, 0.37, 0.38, 0.41, 0.43, 0.43, 0.43, 0.43, 0.46, 0.51, 0.51, 0.51, 0.51, 0.51, 0.51, 0.55, 0.56, 0.56, 0.61, 0.61, 0.61, 0.66, 0.66, 0.66, 0.71, 0.71, 0.71, 0.76, 0.82, 0.86, 0.87, 0.97, 1.02, 1.07, 1.12, 1.73

c. Bentonite (Ordovician)—36 samples

Av. activity, 4.1

Max. activity, 10.3

Min. activity, 1.0

Individual measurements: 1.0, 1.2, 1.8, 2.1, 2.4, 2.4, 2.6, 2.6, 2.6, 3.0, 3.0, 3.2, 3.4, 3.5, 3.5, 3.6, 3.9, 4.0, 4.0, 4.1, 4.3, 4.3, 4.3, 4.6, 4.7, 4.7, 4.7, 4.8, 4.8, 5.2, 5.4, 6.1, 6.6, 6.7, 6.9, 10.3

d. Wisconsin well water residues—41 samples

These results were obtained by making counts on the solid material remaining after evaporation of the water samples.

Av. activity, 3.7

Max. activity, 11.7

Min. activity, 0.1

Individual measurements: 0.1, 0.2, 0.2, 0.3, 0.3, 0.4, 0.4, 0.4, 0.5, 0.5, 0.6, 0.7, 1.0, 1.1, 1.5, 1.8, 2.1, 2.1, 2.4, 2.5, 3.0, 3.3, 3.3, 4.0, 4.0, 4.5, 5.5, 5.5, 5.6, 6.1, 6.5, 6.6, 7.1, 7.1, 7.6, 7.6, 7.8, 8.6, 9.2, 9.8, 11.7

e. Ashes from plant litter

The α -activity of plant material ash collected throughout Wisconsin is presented below. Litter from several types of trees is included as well as that from

prairies. With each litter sample an additional sample was collected from the soil just below.

Plant Litter—34 samples

Av. activity, 3.6

Max. activity, 10.2

Min. activity, 1.0

Individual measurements: 1.0, 1.6, 1.7, 2.1, 2.2, 2.3, 2.5, 2.5, 2.7, 2.7, 2.8, 2.8, 2.9, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.4, 3.8, 3.8, 3.9, 3.9, 4.0, 4.1, 4.1, 4.2, 4.3, 4.3, 5.5, 6.3, 9.1, 10.2

Soil below plant litter—33 samples

Av. activity, 2.2

Max. activity, 6.8

Min. activity, 1.0

Individual measurements: 1.0, 1.1, 1.2, 1.5, 1.5, 1.6, 1.6, 1.6, 1.7, 1.7, 1.7, 1.7, 1.7, 1.7, 1.8, 1.8, 1.8, 1.8, 1.8, 1.8, 1.9, 2.1, 2.2, 2.3, 2.7, 2.9, 3.1, 3.4, 3.7, 4.8, 6.8

f. Miscellaneous building materials (brick and tile)—25 samples

Av. activity, 2.4

Max. activity, 3.4

Min. activity, 1.5

Individual measurements: 1.5, 1.8, 1.8, 1.9, 2.0, 2.0, 2.1, 2.1, 2.2, 2.2, 2.2, 2.2, 2.3, 2.4, 2.4, 2.6, 2.6, 2.7, 2.8, 2.8, 2.9, 2.9, 3.0, 3.3, 3.4

Conclusions

These results show that the occurrence of radioactivity is widespread. It has been generally known that granites contain traces of uranium and thorium and their decay products but the fact that other common materials also contain them has perhaps not been so well recognized. Bentonite clays with adsorbed uranium and other α -emitters are somewhat more active than granites. Clay materials used for building carry along with them traces of radioactive materials.

Most of the findings here will be described in other reports from this Laboratory. They have been made in connection with studies on the geochemistry of uranium. Emphasis has been placed on the possible role of volcanism in supplying uranium in small amounts which is then leached and concentrated. The radiation damage caused by these α -particles over geological ages, particularly in limestones, has been the object of extensive study in this Laboratory with emphasis on measurements of thermoluminescence. This investigation has been made possible by financial support from the Atomic Energy Commission, for which the authors are grateful.

The samples have been contributed by Drs. J. A. S. Adams, J. T. Curtis, Sheldon Judson, J. K. Osmond, D. F. Saunders, and E. J. Zeller. Mrs. Joyce B. Muckenfuss assisted with some of the measurements.

NOTE

THERMODYNAMIC FUNCTIONS OF HOCl AND Cl₂O

By N. W. LUFT

Received June 7, 1954

Research Department, Simon-Carves Ltd., Cheadle Heath, Stockport, England

Recently the thermodynamic functions of hypochlorous acid and chlorine monoxide, both singlet molecules in the ideal gas state at 1 atm., were calculated at this Laboratory, according to the familiar quantum-statistical methods¹ based on the as-

sumption of harmonic oscillations and rigid rotation. The molecular and spectroscopic data (cf. Table I) were taken from the recent literature^{2,3} and the products of principal moments of inertia,

($I_1 I_2 I_3$), were evaluated by Hirschfelder's⁴ determinantal method. The thermodynamic functions, viz., $S^\circ =$ entropy, $(F) = -(F^\circ - H_0^\circ)/T =$ free energy function, $C_p^\circ =$ molar heat capacity, $(H) = (H^\circ - H_0^\circ)/T =$ mean heat capacity between 0 and $T^\circ\text{K.}$, are given in Table II for the temperature range from 200 to 1500°K. Since, apart from some uncertainty about the frequency ν_2 in Cl₂O, the basic data are regarded as reliable, the calculated values should be sufficiently accurate. The possibility of

TABLE I
STRUCTURAL DATA

XOCl	Bond length (Å)		Angle (°)	Fundamentals (cm. ⁻¹)			$I_1 I_2 I_3$ (g. cm. ²) ³	Symmetry no.
	OCl	XO		ν_1	ν_2	ν_3		
HOCl	1.70	0.957	113	3626	1242	739	3.941×10^{-117}	1
ClOCl	1.701	1.701	110.8	688	320	969	1.165×10^{-114}	2

TABLE II
THERMODYNAMIC FUNCTIONS AT 1 ATM.

T, °K.	HOCl				Cl ₂ O			
	S°	(F)	C_p°	(H)	S°	(F)	C_p°	(H)
200	53.00	45.00	8.25	8.00	59.54	51.00	9.69	8.54
298.16	56.41	48.23	8.89	8.19	63.63	54.51	10.85	9.12
300	56.47	48.28	8.90	8.19	63.70	54.57	10.87	9.13
400	59.12	50.67	9.55	8.45	66.95	57.27	11.74	9.68
500	61.36	52.58	10.09	8.73	69.64	59.48	12.33	10.15
600	63.19	54.20	10.51	8.99	71.92	61.37	12.72	10.55
800	66.30	56.85	11.12	9.45	75.65	64.50	13.19	11.16
1000	68.83	59.00	11.59	9.83	78.62	67.03	13.43	11.59
1200	70.98	60.82	11.97	10.16	81.08	69.18	13.57	11.91
1400	72.85	62.41	12.28	10.44	83.18	71.03	13.66	12.15
1500	73.70	63.13	12.41	10.57	84.13	71.88	13.69	12.25

sumption of harmonic oscillations and rigid rotation. The molecular and spectroscopic data (cf. Table I) were taken from the recent literature^{2,3} and the products of principal moments of inertia,

inversion doubling has been considered, too. In agreement with the absence of splitting from the spectrum the inversion barriers, estimated by a method outlined elsewhere,⁵ turn out to be so high that splitting has no effect on the thermodynamic functions up to very high temperatures.

(1) H. S. Taylor and S. Glasstone, "Treatise on Physical Chemistry," Vol. I, Van Nostrand and Co., Inc., New York, N. Y., 1946.

(2) K. Hedberg and R. M. Badger, *J. Chem. Phys.*, **19**, 508 (1951).(3) K. Hedberg, *ibid.*, **19**, 509 (1951).(4) J. O. Hirschfelder, *ibid.*, **8**, 431 (1940).(5) N. W. Luft, *Disc. Faraday Soc.*, **14**, 114 (1953).

FIRE RETARDANT PAINTS

Number nine  of the
**ADVANCES IN
CHEMISTRY
SERIES**

A collection of papers comprising the Symposium on Fire Retardant Paints, presented before the Division of Paint, Plastics, and Printing Ink Chemistry at the 123rd meeting of the American Chemical Society, Los Angeles, Calif., March 1953

Edited by the staff of
Industrial and Engineering Chemistry

CONTENTS

Introduction	1
<i>Mark W. Westgate, National Paint, Varnish and Lacquer Association, Washington, D.C.</i>	
Value of Fire-Retardant Paints	3
<i>George S. Cook, Chemical Materials Department, General Electric Co., Schenectady, N.Y.</i>	
Some Theoretical Aspects of the Flameproofing of Cellulose	7
<i>H. A. Schuyten, J. W. Weaver, and J. David Reid, Southern Regional Research Laboratory, New Orleans, La.</i>	
Effectiveness of Fire-Retardant Paints in Fire Prevention	21
<i>Joe R. Yockers, California State Fire Marshal, Los Angeles, Calif.</i>	
Fire-Retardant Coatings on Acoustical Surfaces and Test Methods for Their Evaluation	28
<i>Alice C. Weil, George W. Mod, and Chapman A. Watson, The Celotex Corp., Chicago, Ill.</i>	
Practical Aspects of the Formulation of Fire-Retardant Paints	35
<i>T. M. Murray, Felix Liberti, and Austin O. Allen, Vita-Var Corp., Newark, N.J.</i>	
Testing Fire-Retardant Paints under Simulated Service Conditions	48
<i>Robert Grubb and Walter W. Cranmer, Industrial Test Laboratory, U.S. Naval Shipyard, Philadelphia 12, Pa.</i>	
Fire-Retardant Coatings for Aircraft Use	67
<i>H. W. Lasch and Elmer E. Jukkola, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.</i>	
High Heat- and Flame-Resistant Mastics	82
<i>John C. Zola, Ideal Chemical Products, Inc., Culver City, Calif.</i>	

94 pages

paper bound

\$2.50 per copy

Published June 1954, by
American Chemical Society
1155 Sixteenth St., N. W.
Washington, D. C.

WILEY

BOOKS

*Theory—applications—and techniques**in the only complete handbook on*

X-RAY DIFFRACTION PROCEDURES

for Polycrystalline and Amorphous Materials

By HAROLD P. KLUG and LEROY E. ALEXANDER

Both of the Mellon Institute

Here is the first complete work on all the major applications of X-ray diffraction to polycrystalline materials. It is fully up-to-date and sufficiently broad in scope to serve both the beginner and the experienced worker. It offers complete, practical details on all the techniques involved—and backs them up with enough basic theory to provide an understanding of the procedures. Over 325 illustrations and copious examples give maximum help in visualizing and carrying out the experimental operations. Adequate bibliographical material is provided, but the major topics are so amply treated that no other references are needed except for very special and infrequently used techniques.

Much of the material in *X-Ray Diffraction Procedures* has never before appeared in book form. In general, it presents within a single, convenient volume a great mass of information hitherto available only in scattered references. All this material is arranged for ease of reference and study. Here are a few of the highlights:

- The Debye-Scherrer method and powder techniques in general are treated more fully than ever before in a work of reference.
- A full chapter—80 pages—devoted to the first comprehensive discussion of Geiger-counter spectrometry.
- Complete treatment of such topics as small-angle scattering methods and radial-distribution techniques.
- Full coverage of qualitative and quantitative analysis of powder mixtures.
- A 55 page critical evaluation of all work on the precision determination of lattice constants.
- Discussion of recent theoretical and experimental developments in crystallite size determination.
- Material on diffraction laboratory layout and on the handling and processing of X-ray film.

Written by two of the nation's leading specialists in this field, *X-Ray Diffraction Procedures* calls for no special previous experience. Its first 3 chapters provide all the necessary background. The work is vital to every research worker as a guide to the power and utility of the various methods in a wide range of research problems.

1954.

716 pages.

Illus.

\$15.00.

The TECHNOLOGY of SOLVENTS and PLASTICIZERS

By ARTHUR K. DOOLITTLE, *Carbide and Carbon Chemicals Company*. Here is a monumental work that treats not only the theoretical aspects of the subject but also covers the practical technology. September, 1954. Approx. 838 pages. Probably \$15.00.

*Send now for on-approval copies***JOHN WILEY & SONS, Inc. 440 Fourth Ave., New York, 16, N.Y.**