[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKYLN]

Multilayer Membrane Electrodes. II. Preparation and Use in Double Concentration Cells[1]

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Multilayers of the alkaline earth salts of stearic, hexadecyl- and octadecylsulfuric and hexadecylorthophosphoric acids were prepared on two halves of a previously cracked glass slide; these were then cemented together to form a multilayer membrane electrode, such that alkaline earth cations could diffuse through the membrane from one contiguous solution phase to another in a direction *normal* to the axis of orientation of the long-chain acids. The electrodes had ohmic resistances ranging from 20 to 60 × 10^6 ohms for a given area (2 cm. × 2500 Å.), possessing a specific resistance of 2 × 10^4 ohm-cm. Potentials of double concentration cells containing varying concentration ratios of Ca(II), Ba(II) and Fe(III) salts were measured and found to agree closely with ones calculated for membranes ideally ion-selective for the cationic species. These membranes acted ideally in the range of ionic strengths from 3 × 10^{-4} to 15, or greater.

Introduction

This contribution is one of a series which describe the preparation and properties of membrane electrodes which are reversible to alkaline earth cations in the absence and presence of alkali metal cations. While specific membrane electrodes for the hydrogen ion are available, as are metallic electrodes for certain other cations measured under rather specific conditions, there are no electrodes available for the determination of the alkali metal and alkaline earth cations in the presence of other, similar species, particularly at different *p*H levels.

Experimental

A note has described an electrode composed of a barium stearate multilayer.[2] The preparation and properties of multilayers were studied extensively by Langmuir, Blodgett and others; excellent reviews have been contributed by Sobotka[3] and by Rothen.[4] In this communication, only a few of the essential experimental details are included; complete details and a review of unsuccessful methods are available in the thesis.[5]

Materials.—The stearic acid was quite pure, having a melting point range of 68–69.5°. Sodium octadecyl and sodium hexadecyl sulfate were provided in a pure state by Lever Brothers Company. Hexadecylorthophosphoric acid was supplied by the Victor Chemical Company. This product was found to be somewhat impure.

The solvents were of the highest grade obtainable from commercial sources and were used without further purification. Water, deionized by passage through a mixed-bed resin system, was used directly. Ordinary glass microscope slides, 50 × 75 mm. and 25 × 75 mm. in size and 1 mm. thick, were used; the grade was Pittsburgh noncorrosive precleaned glass.

Ferric stearate was prepared by adding a suspension of 10 g. of sodium stearate in 100 g. of water to 200 ml. of a concentrated solution of ferric chloride (~1 molar), shaking overnight, then filtering off the ferric stearate. A pure product was obtained, which was easily air-dried.

A number of different non-conducting cements were used to fasten the glass slides together. An epoxy resin especially designed for cementing purposes (6 parts of Stabilizer A-5 and 1 part of triethylenetetramine, both manufactured by the Carbide and Carbon Chemical Company) was found to be superior.

The Langmuir trough was constructed entirely of methyl methacrylate plastic, 100 × 30 × 1 cm. A rectangular well 10 cm. deep was built into the bottom of the trough near one end. The trough was mounted on adjustable legs to allow for proper leveling and was enclosed in a compartment with curtained holes cut into the sides to minimize atmospheric contamination. The trough surfaces were made hydrophobic by rubbing with ferric stearate to produce a monomolecular layer.

Trough Substrates.—For barium stearate Y-films, a phosphate buffer consisting of 2.6 volumes of a 0.1 *M* monobasic potassium phosphate solution and 7.4 volumes of a 0.1 *M* dibasic sodium phosphate solution was employed; its *p*H was 7.18. The trough substrate consisted of 1 ml. of a 0.1 *M* barium acetate solution and 2.5 ml. of the phosphate buffer in one liter of water; the final *p*H was 6.8. For calcium Y-films, the same substrate solution was employed, except that the calcium salt was used in place of the barium salt.

For X-type calcium films, it was found that the Langmuir–Schaefer buffers commonly described for this purpose[6] gave imperfect multilayers as regards their use for electrodes. A new buffer (designated S) for this purpose was prepared by adding 6 volumes of a 0.1 *M* sodium carbonate solution to 4 volumes of a 0.1 *M* sodium bicarbonate solution to produce a final *p*H of 9.6. Then, 100 ml. of this buffer and 2 ml. of a 0.1 *M* calcium acetate solution were diluted to 2 liters; the final *p*H was 9.0. Suitable calcium multilayers for electrodes could be prepared using this buffer. Barium multilayers of the X-type could not be prepared successfully.

Layering of Surface-active Substance.—Monolayers of stearic acid and of the alkaline earth metal stearates were formed by carefully layering onto the trough surface a sufficient quantity of a 0.05% solution of stearic acid in *n*-hexane, the proper quantity of acid being determined by adding the hexane solution until the first appearance of a "lens" on the surface. At that point the barrier was moved back to just allow the lens to spread. Prior to the addition of the spreading solution, the surface was swept several times with plastic barriers to remove any surface contamination which would cause faulty deposition of the multilayers. The proper salt was thereby formed *in situ* on the surface.

The inherent insolubility of the alkyl sulfates in most nonpolar solvents necessitated the use of a mixed spreading solvent. A 1:1 (equal volumes) ethanol–benzene mixture was found appropriate[7]; 0.05% solution of the alkyl sulfates was used as before. This solvent and the same concentration of surface-active material also was employed for the alkyl orthophosphates.

Plating and Assembly of Electrodes.—The constant film pressure device of Sher and Chanley[8] was employed. The problem was first to plate out a coherent multilayer, then to contain this multilayer between two electrolytic solutions such that transport of potential determining cations (calcium and barium) in a direction transverse to the axis of orientation of the molecules in the multilayer was possible. The single slide was scored by a diamond point at

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(1) Based on a portion of the Dissertation of Harold Schonhorn, to be submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the Polytechnic Institute of Brooklyn, June, 1959.

(2) H. P. Gregor and H. Schonhorn, THIS JOURNAL, **79**, 1507 (1957).

(3) H. Sobotka, "Medical Physics," Vol. II, Year Book Publishers, Inc., Chicago, Ill., 1950.

(4) A. Rothen, "Physical Techniques in Biological Chemistry," Vol. II, Ed., G. Oster and A. W. Pollister, Academic Press, Inc., New York, N. Y., 1956.

(5) H. Schonhorn, Dissertation, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., June, 1959.

(6) I. Langmuir and V. J. Schaefer, THIS JOURNAL, **59**, 2400 (1937).

(7) J. G. N. Thomas and J. H. Shulman, *Trans. Faraday Soc.*, **50**, 1131 (1954).

(8) I. H. Sher and J. D. Chanley, *Rev. Sci. Instr.*, **26**, 266 (1955).

the center of one edge, then cracked in half; this gave the most perfect fit obtainable. Only those pairs which cracked at nearly right angles to the face of the plate with no chipping were used. Elastic materials such as most plastics could not be used. The microscope glass slide sections were cleaned in chromic acid solution, washed with detergent, then rinsed carefully and dried. They were coated with a monolayer of ferric stearate, applied by mechanical rubbing, then mounted on a mechanical dipping device. The rate of dipping was such as to plate out 50 monomolecular layers in 1 hr., or at a rate of about 3 cm. min.$^{-1}$. The choice of 50 layers was made because thicker films tended to be imperfect and thinner ones had too high ohmic resistances, in addition to being too susceptible to imperfections.

After plating, the two slides were placed in a special clamping device which allowed application of the proper lateral pressure while the edges were observed under a microscope at high magnification (440×). The slit was aligned, then pressure applied by a screw, the proper pressure being judged by experience. A slide (50 × 50 mm.) with a 25 mm. hole drilled through the center was placed over the two halves, then cemented in place with the epoxy resin. After complete set, the other face plate was cemented into place, and contact with the two solutions was effected by cementing a curved section of 25 mm. thin walled glass tubing to each face plate opening (see Fig. 1).

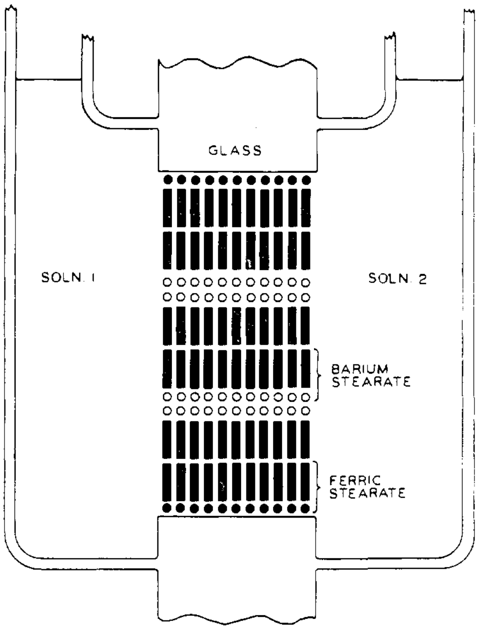

Fig. 1a.

Electrical Measurements.—Since the resistance of the electrode was found to be about 50 megohms and the potentials about 50 mv. or less, a highly sensitive potential-reading device was required. A Keithley model 200 B vacuum tube voltmeter in conjunction with a Keithley model 2008 Decade Shunt and a Keithley model 2004A regulated voltage supply allowed for the determination of reasonably accurate potentials and resistances alternately. A Keithley Coax Adapter model 2010 was attached to a shielded cable and to the Keithley electrometer, the other end of the cable being attached to the metal box which contained the membrane and reference electrode assembly. This voltmeter has an input impedance greater than 10^{14} ohms. The input grid current of less than 5×10^{-14} ampere is such as not to interfere with the current through the cell assembly, the latter being about 10^{-10} ampere. The measuring range was 8, 20 and 80 mv., with a listed accuracy of ±2% of the full-scale reading. The resistance readings were accurate to ±5%.

Its precision and accuracy was determined by calibration against a Leeds and Northrup Type K-2 potentiometer. At full scale the average deviation was less than ±0.4%, corresponding to ±0.03 mv. for the 8 mv. scale, ±0.10 mv. for the 20 mv. scale and ±0.3 mv. on the 80 mv. scale.

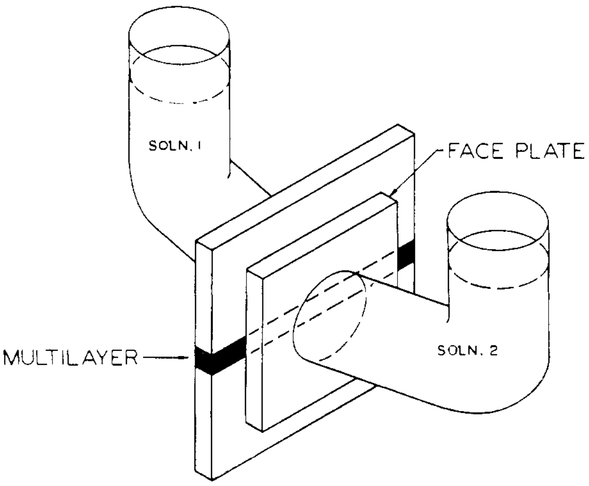

Fig. 1b.

The precision of the instrument was the same as its accuracy, being ±0.03 mv. on the 8 mv. scale at all scale readings, etc. This performance was substantially better than that claimed by the manufacturer.

The saturated calomel electrodes (S.C.E.) used were of the Beckman No. 270 fiber-type. The silver–silver chloride electrodes were prepared in the conventional manner and kept in the dark in 0.1 *m* (molal) potassium chloride solutions, all being grounded together. Their potentials usually did not differ by more than 0.1 mv. and did not vary for long periods of time. The difference in the potentials of the reference electrode in the same solutions was measured before and after each cell measurement, and the corrections applied; all potentials were corrected to 25°.

When reversible reference electrodes were used, exact theoretical potentials were calculated using the appropriate mean activity coefficient data listed by Harned and Owen[9] and Robinson and Stokes.[10] With calomel electrodes, the single ion activity coefficients given by Conway[11] were employed wherever possible. For the more concentrated solutions, it was assumed that the activity of the univalent anion present was the same as in a potassium chloride solution of the same ionic strength, and the single cationic activity was calculated from the mean activity; this method is described in some detail by Gregor and Sollner.[12] Corrections for the potential arising at liquid junctions were not made.

General Properties of Electrodes.—A résumé of the properties of the electrodes used in this study is presented in Table I. Individual electrodes are not identified because each was found to be ideally selective or not at all so. The determination as to whether an electrode was acting reversibly was made by measuring the potential of a given concentration cell and comparing the value obtained with the theoretical potential. The ohmic resistance of the electrode also was measured. Almost invariably defective electrodes or electrodes which had deteriorated were characterized by sharply decreased ohmic resistances, dropping from about 50 to 1 megohm, and potentials which were equal to the free diffusion potential of the electrolytic system in question. Once sufficient skill in the preparation of the electrodes was achieved, a large fraction (approximately 80%) of all membranes prepared were found to be functioning electrodes.

Once an electrode was assembled, about 0.5 hr. of contact with an electrolytic solution was required to obtain steady potentials. Thereafter, constant potentials were measured almost instantly after changes in concentration. The useful life of a given electrode was not determined. Usually, these were stored dry when not in use. Electrodes have been used for a total solution contact time of over 100 hr. without any apparent deterioration. Electrodes pre-

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[9] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1958.

[10] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955.

[11] B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, N. Y., 1952.

[12] H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **50**, 53 (1946).

TABLE I

PROPERTIES OF MULTILAYER MEMBRANE ELECTRODES

	Composition	Buffer[a]	*p*H	Plating pressure, dynes cm.$^{-1}$	Type
A	Barium stearate	P	7	30	Y
B	Calcium stearate	P	7	37	Y
D	Calcium stearate	S	9	37	X
F	Barium hexadecylsulfate	P	7	10	Y
G	Barium octadecylsulfate	P	7	10	Y
H	Calcium hexadecylorthophosphate	S	9	48	Y
J	Ferric stearate	P	7	30	Y

[a] Buffers: P is phosphate; S is special bicarbonate-carbonate.

pared over one year ago are still apparently perfect. The resistance of the multilayer membrane electrodes was quite high, averaging from 10^7 to 10^8 ohms for an exposed length of 2 cm. The resistance of the blank, *i.e.*, of the cell itself, not including that of the multilayer, was determined by constructing an identical cell, except that an uncracked slide was employed. The resistance of this cell was 5.0×10^{11} ohms, such that no correction to the cell potential was required. As an additional check, the potential of a multilayer membrane electrode was measured using a grounded guard ring about one of the cell arms; no significant difference in the potential of the cell with or without the guard ring was observed. The resistance of the calomel electrodes and of the most dilute solution employed was about 10^4 ohms.

The resistance at 25° of a 100-layer barium stearate Y-film electrode was 5.8×10^7 ohms. Large differences in the resistances of X-type electrodes or of systems with different cations or different long-chain anions were not observed. Electrodes which had resistances below 10 megohms were found, from their potential measurements, to be imperfect.

Certain experimental problems connected with the preparation of various types of electrodes deserve mention. The only usable X-type film prepared was a calcium stearate multilayer plated out using the special buffer S at *p*H 9, and a higher than normal pressure (electrode E). The characteristics of the plating operation were unusual since during the first several layers a Y-film was formed, because plating-out occurred during both the downward and upward strokes. After about the eighth layer had been deposited on the downward path, ordinarily the film would have been hydrophobic on the upward path; however, this time the film slipped as the slide moved out of the trough and the film emerged still dry. Thereafter, X-films were deposited during the downward stroke only of the slide, not during its upward stroke. Certain Z-films have been reported which apparently are plated out during only the upward stroke.

It must be emphasized that the criteria for a usable electrode are probably more stringent than are those for the deposition of a given film. It was observed several times that an apparently good film was plated out as regards movement of the barrier, the lack of striations, etc., but the resulting multilayer was not usable as an electrode. An electrode appears to require a particularly perfect multilayer.

The calcium hexadecylphosphate electrode (H) showed unusual plating characteristics. It was a Y-film, plating on both descending and ascending strokes. Most unusual, it was wet after the upward stroke, a phenomenon apparently peculiar to this system.

The use of the long-chain alkyl sulfate materials for the preparation of multilayers was investigated because these substances are not *p*H dependent as are the alkyl carboxylic acids. Accordingly, these films could be entirely in the salt form at neutral *p*H levels and might also be usable at lower *p*H values as compared with the stearate films. This system should be more stable and might exhibit greater specificity between the alkaline earth cations than would the alkyl carboxylic acids.

A barium hexadecylsulfate electrode (F) was prepared by spreading a solution of 0.05% sodium hexadecylsulfate (which is water insoluble) in the ethanol-benzene solvent. These barium hexadecylsulfate monolayers exhibited a relatively low surface pressure with a particularly shallow force-area isotherm. A condensed film was not obtained until a pressure of 8 dynes cm.$^{-1}$ was reached, and the film collapsed at pressures above 12 dynes cm.$^{-1}$. A surface pressure of 10 dynes cm.$^{-1}$ was found suitable for casting purposes. In general, it was found advisable to plate at a pressure just below that required to collapse the condensed monolayer. In the case of stearic acid, a wider range of pressures is available, with the collapse point at about 42 dynes cm.$^{-1}$. A usable barium octadecylsulfate electrode (G) was prepared using the same procedure as with electrode (F). It appeared to offer no advantages over the barium hexadecylsulfate electrode (F).

In principle, there appear to be no limitations on the applicability of multilayers for the preparation of reversible electrodes for any cationic or anionic species. For example, there is no reversible electrode system for the Fe(III) ion. Accordingly, a multilayer of ferric stearate was prepared using the same conditions as with electrode (1) utilizing ferric chloride as the substrate salt. Fifty Y-type monolayers were deposited to form electrode (1).

All of the multilayer membrane electrodes showed an appreciable asymmetry potential, as measured between two identical solutions. This potential was as high as 2 mv., averaging about 1 mv. This asymmetry potential was apparently constant throughout the life of the electrode.

Potentials of Double Concentration Cells.—A series of double concentration cells consisting of the chain

Ag/AgCl/Solution (1)/Membrane/Solution (2)/AgCl/Ag

were measured (Table II). Table III presents less extensive data obtained with a number of different electrode systems.

TABLE II

POTENTIALS WITH MULTILAYER MEMBRANE ELECTRODES

Chain: Ag/AgCl/Solution (1)/Membrane/Solution (2)/AgCl/Ag

Solution (1), *m*	Solution (2), *m*	E.m.f., mv. Meas.	E.m.f., mv. Calcd.
Calcium stearate electrode B–calcium chloride solutions			
0.000100	0.0000100	. .	. . .
.00100	.000100	85.4	86.60
.00200	.00100	25.4	25.05
.0200	.0100	23.9	23.20
.0250	.0125	23.8	24.05
.0500	.0250	22.7	22.20
.200	.100	23.7	23.60
1.000	.500	29.5	30.80
5.000	2.500	94.5	93.25
5.000	0.500	190	188
Barium hexadecylsulfate electrode F–barium chloride solutions			
0.00200	0.00100	26.3	25.80
.0200	.0100	23.8	23.62
.200	.100	22.8	22.15
Barium stearate electrode A–barium chloride solutions			
0.00200	0.00100	25.8	25.80
.0100	.00500	25.0	24.10
.0200	.0100	23.4	23.62
.0400	.0200	20.0	21.60
.200	.100	22.8	22.15
.400	.200	23.1	22.85
.100	.0100	75.6	74.10

The value of the mean activity coefficient for calcium chloride in 0.0001 *m* solutions (Table II) was taken to be the same as the value for barium chloride in a solution of the same molality ($\gamma_{\pm} = 0.939$), as measured by Lewis and Linhart[13] using freezing point methods. At these concentrations, the multilayer membrane electrode responded in the normal manner. However, in 0.00001 molal solutions, constant and meaningful potential measurements could not be obtained. Whether this was due to the solubility of the

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[13] G. N. Lewis and G. A. Linhart, THIS JOURNAL, **41**, 1952 (1919).

TABLE III

RESULTS WITH VARIOUS ELECTRODES

Memb.	Reference electrode	Electrolyte	Soln. (1), m	Soln. (2), m	E.m.f., mv. Meas.	E.m.f., mv. Calcd.
A	S.C.E.	Barium acetate	0.00200	0.00100	7.65	7.88
A	S.C.E.	Barium acetate	.0100	.00100	25.2	24.21
A	S.C.E.	Barium acetate	.0200	.0100	6.65	6.55
A	S.C.E.	Barium acetate	1.000	.500	5.28	4.96
G	S.C.E.	Barium acetate	0.0200	.0100	6.60	6.55
D	Ag/AgCl	Calcium chloride	.0200	.0100	23.5	23.20
D	S.C.E.	Calcium chloride	.0200	.0100	7.60	7.70
H	S.C.E.	Calcium chloride	.0200	.0100	7.55	7.70
J	Ag/AgCl	Ferric chloride	.500	.250	30.0	...
J	Ag/AgCl	Ferric chloride	.250	.125	34.0	...
J	S.C.E.	Ferric chloride	.250	.125	5.10	...

reference electrodes or to the calcium stearate multilayer was not determined.

Discussion

The apparently perfect fit of the two half-slides is quite remarkable. Here, each slide has been coated with a layer which is approximately 1,000 Å. thick, but the two halves apparently fit perfectly. The diameter of the chloride ion is approximately 5 Å., so any larger holes through the membrane could not be present. It is to be expected that some crushing of the multilayer crystal occurs as the halves are joined together, and this may act to seal holes.

As was stated previously, multilayer electrodes prepared from calcium or barium stearate in either the X- or Y-form or from the various sulfates or phosphates did not show significant differences in their ohmic resistances. In general, the ohmic resistance of the membrane varied from approximately 20 to 60 megohms. These results are somewhat unexpected in view of the known differences in the degrees of ionization of these salts. These effects are being investigated and will be reported in a future paper of this series.

The specific resistance of a barium stearate multilayer was approximately 2×10^4 ohm-cm. in a direction *transverse* to the axis of molecular orientation. This corresponds to the resistance of a solution of barium stearate which is approximately 2×10^{-4} molal.

Several biologists have speculated upon the fundamental nature of natural membranes which possess a high degree of selectivity, and have attributed their properties to the presence of a multilayer row of molecules. On the basis of the results obtained here, it would appear that a multilayer membrane which is 50 Å. thick, composed of a ten-molecule multilayer row, would have an area ohmic resistance of 0.01 ohm-cm.^{2} This resistance is probably lower than that of ion-specific natural membranes. While there is no valid reason to support the view that natural membranes are composed, wholly or in part, of multilayers, it is interesting to observe that a simple multilayer membrane electrode can exhibit a high degree of selectivity, while being based upon such a simple configuration. As will be shown in subsequent papers, the simple multilayer system is also highly ion-specific.

An examination of Tables II and III shows that the multilayer membrane electrode allows the transport of only the appropriate alkaline earth cation over a wide range of solution concentration, extending to those which are at least 5 molal. From a preliminary consideration of the nature of the electrode material itself, it seems surprising that the electrode functions as perfectly as it does. The stearate multilayers are composed of both the acid and the alkaline earth salt, usually in approximately equal amounts. While it is to be expected that the barium ions in a barium stearate multilayer would be mobile because of the unusual configuration of the lattice, the hydrogen ions would be expected to have a comparable mobility. However, the latter is not a matter of consequence as regards the functioning of the electrode in neutral solutions because here the concentration of hydrogen ions in the solution phase is negligible as compared with that of the barium ions. This means that the *net* flux of hydrogen ions across the multilayer must be negligible compared with that of the barium ions; therefore, the barium ions are solely potential determining.

The situation which exists here is comparable to that with an ion-exchange carboxylic resin-type electrode. These have been investigated by a number of authors, including the work on the oxidized collodion permselective membranes of Gregor and Sollner[12,14] and the interpolymer membranes of Gregor and Wetstone[15] prepared from a copolymer of maleic acid. In these cases the concentration of mobile hydrogen ions was appreciable, but these ions were not potential determining. It is for these same reasons that the multilayer membrane electrodes were able to function in the *p*H range from 4 to 10 with no difficulties.

Multilayer membrane electrodes can be used to determine mean activity coefficients of a large number of electrolytes over almost any desired range of concentration. On one side of the cell, measurements can be made of concentrations as dilute as 10^{-4} molal, at which concentrations simple Debye–Hückel extrapolations can be made. This is particularly important when dealing with polyvalent electrolytes, because here specific ion effects, deviations from the limiting law and other phenomena (as described by Brönsted) make the estimation of reliable activity coefficients difficult.

Future papers in this series will consider the general physico-chemical properties of multilayer membrane electrodes, in particular their conductivity as a function of temperature and ionic composition;

(14) H. P. Gregor and K. Sollner, *J. Phys. Chem.*, **58**, 409 (1954).

(15) H. P. Gregor and D. M. Wetstone, *ibid.*, **61**, 147 (1957).

measurements of transport numbers and mobilities will also be reported. The next paper in this series will consider the use of the multilayer membrane electrode for the determination of the activity of barium and calcium salts in the presence of sodium and potassium salts of varying concentrations. Following papers will describe mixed electrolytic systems containing high concentration of alkali metal cations and low concentration of alkaline earth cations, systems which approximate those of biological composition.

As will be shown in subsequent papers, multilayer membrane electrodes, properly fabricated, can be used to determine the activity of one alkaline earth cation in the presence of high concentrations of other alkaline earth cations. These electrodes can be used to determine the activity of an alkaline earth cation of higher atomic weight in the presence of one of lower atomic weight. For example, barium can be determined in the presence of strontium, strontium in the presence of calcium, calcium in the presence of magnesium, etc.

Multilayer membrane electrodes should prove invaluable for a study of complex ion formation. They can be used to determine the activity of a metallic cation in exactly the same manner as the glass electrode is now used for hydrogen ion activities. In conjunction with other measurements, they should allow for a precise and definitive determination of instability constants. The problem of aquo-ion formation, particularly by Fe(III) and Al(III) cations, is being examined by the use of appropriate multilayer membrane electrodes and will be reported subsequently.

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BROOKLYN 1, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY]

Correlations between Solvent Structure, Viscosity and Polarographic Diffusion Coefficients of Oxygen[1]

BY JOSEPH JORDAN AND WILLIAM E. BAUER

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Compelling experimental evidence is presented that "activity diffusion coefficients" (D_a), rather than Fick diffusion coefficients, are quite *generally* the significant parameters determinative of the diffusion of oxygen under boundary conditions prevailing at the dropping mercury electrode. Data obtained in a range of temperatures between 25 and 80°, and at viscosities between 0.4 and 125 centipoise, are discussed critically. The viscosity was controlled by the addition of sucrose or glycerol to aqueous supporting electrolytes. Plots of D_a *versus* fluidity yielded a family of curves which were similar in shape, irrespective of temperature and viscosity controller. Two domains of diffusion–viscosity behavior were found to exist, corresponding to two types of solvent structure: (1) an ice-like, "non-Stokes–Einstein" domain, in media the viscosity of which approximated (within a factor of two) that of pure water; (2) a closely packed, Stokes–Einstein domain, extending over a range of viscosities covering two orders of magnitude. The transition between the two domains corresponded to the breakdown point of the Stokes–Einstein equation and was characterized by a specific mole fraction ratio (m.f.r.) between viscosity controller and water. This m.f.r. depended on the nature of the viscosity controller and was independent of temperature. The m.f.r. values in the presence of glycerol and sucrose were 10 and 120, respectively. This difference is interpreted as indicating that glycerol caused the collapse of the ice-like structure of liquid water due to an internal pressure ("wedge") effect and by primary hydration, while the breakdown of the ice-like structure by sucrose is accounted for by long-range interactions, such as secondary (outer-shell) hydration.

In a previous paper[2] conventional polarographic diffusion coefficients (called "Fick diffusion coefficients"), which are defined in terms of classical concentration gradients, were determined at 25° at varying viscosities on the basis of the Lingane–Loveridge equation.[3–7] Results obtained in aqueous sucrose and glycerol solutions indicated that Fick diffusion coefficients (D_{Fick}) of oxygen at 25° strikingly failed to obey a Stokes–Einstein type relationship at viscosities between 0.9 and 125 centipoises. However, a newly defined "activity diffusion coefficient" was found to obey the Stokes–Einstein type equation

$$D_a\eta = \text{const.} \qquad (1)$$

where D_a denotes the activity diffusion coefficient of oxygen and η the viscosity of the solution. Equation 1 was found to hold at 25° between an upper limit of 125 centipoise (which is the highest viscosity studied so far) and a lower limit of 1.5 and 2.2 centipoise in the presence of sucrose and glycerol, respectively. At viscosities below 1.5 centipoise at 25°, eq. 1 failed for D_a as well as for D_{Fick}. These experimental results were interpreted by correlating the activity diffusion coefficient with the frequency and amplitude of the corresponding diffusive transitions, in accordance with the "hole" theory of diffusion and viscous flow in liquids.[2] Accordingly, it was postulated that

$$D_a = \frac{\lambda^2_d k_d}{f} \qquad (2)$$

where λ_d denotes the distance a molecule is transported in each diffusional transition, k_d is the frequency of the transitions and f is the activity coefficient of the diffusing species. The viscosity coefficient was similarly correlated with corresponding jump amplitudes and frequencies as

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(1) Based on a doctoral thesis by William E. Bauer.

(2) J. Jordan, E. Ackerman and R. L. Berger, THIS JOURNAL, **78**, 2979 (1956).

(3) J. J. Lingane and B. A. Loveridge, *ibid.*, **72**, 438 (1950).

(4) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(5) T. Kambara and I. Tachi, *Bull. Chem. Soc., Japan*, **25**, 284 (1952).

(6) T. Kambara, *ibid.*, **25**, 281 (1952).

(7) J. Koutecky, *Czechoslov. J. Phys.*, **2**, 50 (1953).