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

RECEIVED NOVEMBER 10, 1958

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).

$$\eta = \frac{\lambda_1}{\lambda_2\lambda_3} \times \frac{\kappa T}{\lambda^2_{\mathrm{v}} k_{\mathrm{v}}} = r\,\frac{\kappa T}{\lambda^2_{\mathrm{v}} k_{\mathrm{v}}} \qquad (3)$$

In eq. 3 the subscript v denotes parameters characteristic of viscous flow, λ_1, λ_2 and λ_3 denote, respectively, the distance between two layers of molecules in the liquid, between two neighboring molecules in the direction of viscous flow and between two adjacent molecules at right angles to the direction of viscous flow, κ is the Boltzmann constant and T the absolute temperature. Based on considerations of the phenomenological significance of activity coefficients as a measure of relative fugacity, it was concluded that

$$f = q\,\frac{k_{\mathrm{d}}}{k_{\mathrm{v}}} \qquad (4)$$

where q is a dimensionless numerical coefficient. A comparison of eq. 2, 3 and 4 makes it evident that eq. 1 holds whenever

$$\lambda_{\mathrm{d}} \approx \lambda_{\mathrm{v}} \qquad (5a)$$

$$r = \frac{\lambda_1}{\lambda_2\lambda_3} = \text{const.} \qquad (5b)$$

Equations 5a and 5b each represent a necessary condition for a Stokes–Einstein type relationship to hold; the simultaneous validity of eq. 5a and 5b fulfills a sufficient condition. The constancy of r implies the constancy of the inter-molecular distances in the presence of various amounts of "viscosity controller" (sucrose or glycerol). In the previous study this was accounted for by assuming that with increasing proportions of viscosity controller in the aqueous solvent, the over-all packing became closer and r remained invariant, "due to compensatory effects between increased average molecular solvent size and decreased intermolecular distance."[2] The failure of the Stokes–Einstein relation, reported previously in solutions approximating the viscosity of pure water, is interpreted as meaning that in the presence of relatively small amounts of viscosity controller the "ice-like structure" of liquid water[8] accounts for a greater amplitude of diffusive transitions than of viscous transitions, *i.e.*

$$\lambda_{\mathrm{d}} > \lambda_{\mathrm{v}} \qquad (6)$$

The ice-like structure in liquid water is known to collapse gradually as the temperature is increased,[8] as well as in the presence of relatively large solute species which exercise a quasi-internal pressure on the water structure.[9] In view of this situation, it was anticipated that a comparative study might be of interest, in order to elucidate as a function of temperature the relationship between viscosity and D_{a}. Results are reported in this paper which indicate that in the presence of sucrose at 37° and in the presence of glycerol at 80°, the Stokes–Einstein domain indeed extended to the lower viscosities the higher the temperature. The ice-like matrix of the aqueous solvent collapsed at specific "breakdown points." These corresponded to solvent compositions which depended on the nature of the viscosity controller: the molar ratio between water and viscosity controller was of the order of 100 and 10 in the presence of sucrose and glycerol, respectively.

Experimental

The experimental procedure was similar to that described previously.[2] However, in carrying out current–voltage determinations above room temperature, certain phases of the procedure were modified and special precautions were taken. The temperature of 37° was selected for one series of experiments because it approximates normal human blood temperature and was therefore considered of interest in connection with the polarographic behavior of oxygen in blood and body-fluids. The electrolysis cell was thermostated in a water-bath at 37.00 ± 0.08°. The constant temperature bath was stirred with the aid of air bubbles in order to obviate vibrations due to mechanical stirring devices. The electrolysis cell was equipped with a special cover, in order to minimize loss by evaporation. The cover was precision machined of Teflon with appropriate holes to insert the dropping mercury electrode, an inlet for nitrogen, air or oxygen and the "salt bridge end" of the reference electrode (v.i.). Solutions were deaerated with nitrogen or equilibrated with air and/or pure oxygen. Prior to entering the electrolysis cell, the appropriate gas was bubbled through a wash bottle containing the same solvent at the same temperature.

The temperature of 80° was selected for the second series of experiments, because this proved to be the highest temperature at which the current–voltage curves could be determined without resorting to unduly complicated experimental techniques. It was found that sucrose was not a suitable viscosity controller at 80°, because it hydrolyzed at a measurable rate and yielded reducing sugars which interfered with the determination of oxygen by the iodometric Winkler method.[2] Glycerol was used exclusively as the viscosity controller in the experiments at 80°. A constant temperature bath of dioctyl phthalate served for thermostating the polarographic cell at 80.0° ± 0.2°. Nitrogen, air or oxygen, passed through and/or over the solutions in the electrolysis cell, was preheated in a Pyrex glass tube wrapped in heating tape and bubbled through a solvent identical to the one in which the relevant current–voltage curves were recorded. Freshly distilled xylene was floated on the surface of the solution, in order to minimize loss by evaporation. By suitable blank experiments it was ascertained that xylene did not have any appreciable affect on the diffusion currents of oxygen.

Both at 37° and at 80°, a silver–silver chloride electrode salt bridge assembly described by Lingane[10] was used as a reference electrode. The reference half-cell was not immersed in the working thermostats but maintained at a room temperature of 25°. At this temperature, the potential of the silver–silver chloride reference electrode was −0.05 v. *versus* the saturated calomel electrode. For the sake of easy comparison with the previous study,[2] all potential values reported in this paper have been referred to the saturated calomel electrode at 25°. The ohmic resistance through the electrolysis cell was of the order of 500 ohms, obviating corrections for iR drops. The dropping mercury electrode was operated under mercury heads of 60 cm. The rate of flow of mercury was approximately 2 mg. per second and the drop times about 3.5 sec. at an applied potential of −0.35 v. (*versus* saturated calomel electrode) in pure aqueous 0.1 M potassium chloride at 25°. The actual m and t values prevailing under the experimental conditions were determined at the beginning of each experiment in the properly thermostated solutions. The m values were measured with the aid of an automatic device described by Lingane,[11] modified by using two coupled electronic relays. Drop times were determined with a precision and accuracy of ±0.5% using the method of F. L. English.[12]

Results

Polarograms of oxygen at 37 and 80° in the presence of sucrose and of glycerol were of the familiar double-wave shape. The waves were shifted toward positive potentials as the viscosity of the solution increased. Diffusion currents were generally measured at the optimum potential, *i.e.*, in the middle of the limiting current region. Typical character-

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(8) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, England, 1955, pp. 2–6.

(9) J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1954).

(10) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p. 263.

(11) J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1914).

(12) F. L. English, *Anal. Chem.*, **20**, 889 (1948).

TABLE I

CHARACTERISTICS OF OXYGEN POLAROGRAMS AT 37 AND 80°

Viscosity controller	Temp., °C.	Range of viscosities (cp.)	Half-wave potential[d] First wave[a]	Half-wave potential[d] Second wave[b]	Optimum potential[d] for measuring diffusion current First wave[a]	Optimum potential[d] for measuring diffusion current Second wave[b]
Sucrose	37.0	0.7 to 6	−0.08 to −0.05[c]	−0.96 to −0.79[c]	−0.45 to −0.30[c]	−1.35
Glycerol	80.0	0.4 to 9	−0.10 to −0.06[c]	−0.83 to −0.62[c]	−0.35 to −0.25[c]	−1.25

[a] Corresponds to 2-electron transfer: $O_2 + 2e + 2H^+ \rightarrow H_2O_2$. [b] Corresponds to 4-electron transfer: $O_2 + 4e + 2H^+ \rightarrow 2OH^-$. [c] Potentials shifted to more positive values with increasing viscosity. [d] Volt *versus* saturated calomel electrode.

istics of the current–voltage curves of oxygen have been summarized in Table I.

Fick diffusion coefficients of oxygen were calculated using the Lingane–Loveridge equation[2,4,7,13]

$$i_d = 607nm^{2/3}t^{1/6}CD^{1/2}_{\text{Fick}}(1 + 34m^{-1/3}t^{1/6}D^{1/2}_{\text{Fick}}) \quad (7)$$

D_a was calculated from the diffusion current equation derived in the previous article[2]

$$i_d = 607nm^{2/3}t^{1/6}\, aD_a^{1/2}(1 + 34m^{-1/3}t^{1/6}fD_a^{1/2}) \quad (8)$$

In eq. 7 and 8 i_d denotes the average diffusion current expressed in μa., n the number of electrons involved in the electrode reaction, m the rate of flow of mercury in mg./sec., t the drop time in sec., C the concentration of oxygen expressed in millimole/l., f the molarity activity coefficient and $a = fC$.

Values of the two types of polarographic diffusion coefficients of oxygen determined in solutions of varying viscosity at 37° and at 80° are listed in Tables II and III together with the pertinent solvent composition and oxygen solubility data.

Using data listed in Tables II and III, values of D_{Fick} and D_a were plotted *versus* fluidity in Fig. 1 (in the presence of sucrose at 37°) and in Fig. 2 (in the presence of glycerol at 80°).

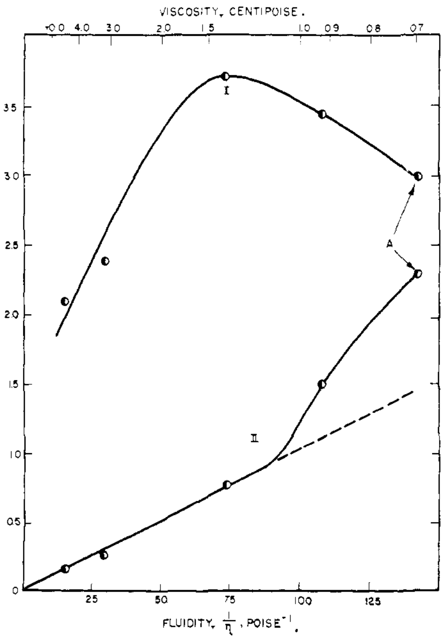

Fig. 1.—Plot of polarographic diffusion coefficients of oxygen *versus* fluidity at 37°: curve I, D_{Fick}; curve II, D_a; solvents, aqueous sucrose solutions listed in Table II; A, pure aqueous supporting electrolyte.

TABLE II

POLAROGRAPHIC DIFFUSION COEFFICIENTS AND SOLUBILITY AT 37° OF OXYGEN IN AQUEOUS SUCROSE SOLUTIONS OF VARYING VISCOSITY[a]

% Sucrose (w./w.) (1)	Density (gr./cm.³) (2)	Viscosity (cp.) (3)	Equilibrium concn. when p_{O_2} = 1 atm.[b] (mmole/l.) (4)	Molarity activity coefficient of oxygen[c]) (5)	$10^5 \times D_{\text{Fick}}$[d] (cm.²/sec.) (6)	$10^5 \times D_a$[e] cm.²/sec. (7)
0.00	0.999	0.704	0.93	1.15	3.0	2.3
9.63	1.038	0.924	.69	1.55	3.5	1.5
21.0	1.089	1.37	.50	2.14	3.7	0.79
40.0	1.147	3.42	.35	3.1	2.4 ± 0.4	0.25 ± 0.04
47.6	1.216	6.48	.30	3.6	2.1 ± 0.3	0.16 ± 0.03

[a] Supporting electrolyte: 0.1 M KCl plus phosphate buffer of pH 7 (0.01 M in total phosphate); maximum suppressor: 0.01% gelatin. [b] Partial pressure of oxygen in gas phase. [c] Reference state: dilute ($< 10^{-3}$ M) solution of oxygen in pure water at 37°. [d] Weighted average[2] calculated from eq. 7, based on replicate determinations of the oxygen double wave. [e] Weighted average[2] calculated from eq. 8, based on replicate determinations of the oxygen double wave.

Discussion

It is considered conclusively established that under the experimental conditions prevailing in this study, the significant parameter, determinative of the diffusion of oxygen, was D_a rather than D_{Fick}. This conclusion is in agreement with the findings set forth in the previous study.[2] That investigation was limited to a temperature of 25° and—*per se*—may therefore have left room for some skepticism as to the more general significance of activ-

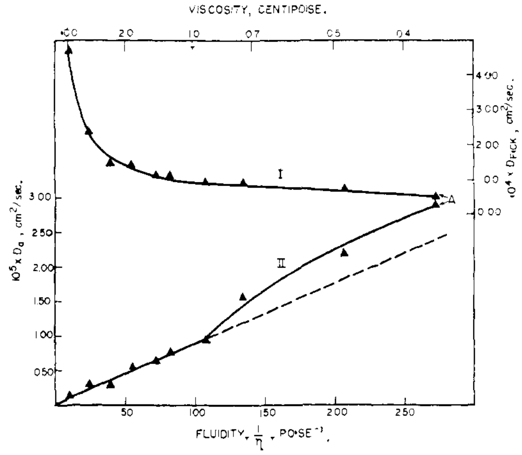

Fig. 2.—Plot of polarographic diffusion coefficients of oxygen *versus* fluidity at 80°: curve I, D_{Fick} (right side ordinate scale); curve II, D_a (left side ordinate scale); solvents, aqueous glycerol solutions listed in Table III; A, pure aqueous supporting electrolyte.

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(13) W. Hans, W. Henne and E. Meurer, *Z. Elektrochem.*, **58**, 836 (1954).

TABLE III

POLAROGRAPHIC DIFFUSION COEFFICIENTS AND SOLUBILITY AT 80° OF OXYGEN IN AQUEOUS GLYCEROL SOLUTIONS OF VARYING VISCOSITY[a]

(1) % Sucrose (w./w.)	(2) Density (g./cm.^{3})	(3) Viscosity (cp.)	(4) Equilibrium concn. when pO$_2$ = 1 atm.[b] (mmole/l.)	(5) Molarity activity coefficient of oxygen[f])	(6) $10^4 \times D_{\text{Fick}}$[d] (cm.^{2}/sec.)	(7) $10^5 \times D_a$[e] (cm.^{2}/sec.)
0.00	0.981	0.366	0.645	1.30	0.59	2.90
15.4	1.014	.484	.492	1.71	.71	2.19
31.1	1.053	.738	.347	2.42	.91	1.55
40.5	1.074	.934	.276	3.04	.89	0.960
49.7	1.096	1.22	.217	3.87	1.16	.779
53.8	1.105	1.38	.194	4.32	1.18	.637
60.6	1.123	1.81	.158	5.31	1.48	.525
69.0	1.145	2.58	.121	6 94	1.50	.313
75.4	1.176	3.61	.095	8.9	2.4	.30
89.4	1.201	9.41	.036	23	4.7	.14

[abde] Same as in Table II. [f] Reference state: dilute (< 10^{-3} M) solution of oxygen in pure water at 80°.

ity diffusion coefficients. However, the combined data reported in the previous paper and in the present investigation cover altogether a range of temperatures between 25 and 80° and a range of fluidities between 0.8 and 270 reciprocal poises. Within this extensive range of conditions no single instance was found where D_{Fick} behaved in accordance with the requirements of the Stokes–Einstein equation. Under certain circumstances D_{Fick} exhibited a non-monotonic variation as a function of fluidity yielding maxima in the corresponding plots (*e.g.*, Fig. 1, curve I); in one series of experiments D_{Fick} *increased* continuously with decreasing fluidity (Fig. 2, curve I) which is even qualitatively contrary to eq. 1. These striking anomalies in the behavior of D_{Fick} cannot be accounted for by any known theoretical considerations. In contradistinction to D_{Fick}, D_a exhibited a consistent behavior throughout the entire range of conditions investigated. Figure 3 represents a synoptic plot of the relationship between D_a and fluidity, based on all the available pertinent information. It is evident from the figure that the variation of D_a was generally characterized by two distinct patterns of behavior corresponding to two domains: (1) a "non-Stokes–Einstein domain" prevailing in media containing only moderate concentrations of viscosity controller, where the solvent consisted predominantly of water; (2) a "Stokes–Einstein domain" extending to high viscosities in the presence of large concentrations of viscosity controller. Irrespective of temperature or of the specific nature of the viscosity controller (sucrose or glycerol) the curves in Fig. 3 were similar in shape. They were rigorously linear in the Stokes–Einstein domain and showed marked positive deviations at fluidities approximating that of pure water. At the transition points between the two domains, the plots of diffusion coefficients *versus* fluidity exhibited well-defined breaks. Solvent compositions prevailing at these "break-down points" of the Stokes–Einstein equation are summarized in Table IV.

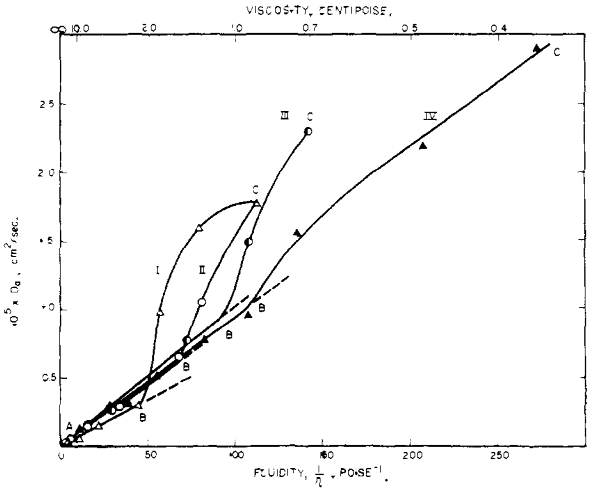

Fig. 3.—Synoptic plot of activity diffusion coefficients *versus* fluidity: I, in the presence of glycerol at 25°; II, in the presence of sucrose at 25°; III, in the presence of sucrose at 37°; IV, in the presence of glycerol at 80°; AB, Stokes–Einstein (closely packed) domain; B, breakdown point of Stokes–Einstein equation; BC, non-Stokes–Einstein (ice-like) domain.

TABLE IV

STOCHASTIC CHARACTERIZATION OF BREAK-DOWN POINTS OF STOKES–EINSTEIN EQUATION

(1) Viscosity controller	(2) Temp., °C.	(3) Fluidity (poise^{-1})	(4) Concn. of viscosity controller (moles/l.)	(5) Mole fraction ratio of water to viscosity controller	(6) Plot no. in Fig. 3
Sucrose	25.0	68	0.43	120	II
Sucrose	37.0	94	0.43	120	III
Glycerol	25.0	45	3.6	11	I
Glycerol	80.0	108	4.7	8	IV

The break-down points can conveniently be characterized by the corresponding mole fraction ratios between viscosity controller and water. Numerical values, shown in column 5 of the table, indicate that the mole fraction ratio depended primarily on the viscosity controller. The temperature dependence—if any—was small. In the presence of sucrose the relative abundance of water at the break-down point was an order of magnitude greater than in the presence of glycerol.

The shape of the plots in Fig. 3, as well as the mole fraction ratio values in Table IV, are accounted for by this phenomenological interpretation. Each domain of "diffusion-fluidity behavior" is postulated to correspond to a discrete solvent structure domain. The non-Stokes–Einstein sections of the relevant curves reflect the properties of a solvent which has the quasi "ice-like" structure of pure liquid water at room temperature, *i.e.*, a hydrogen bonded tetrahedral configuration interspersed with appreciable "quasi empty" space.[8] Qualitatively the ice-like structure accounts for a relatively enhanced rate of diffusion compared to viscous flow, because free interstitial space is available for diffusive transitions of oxygen molecules. In contradistinction, the Stokes–Einstein domain of the curves corresponds to a closely packed solvent matrix in which the ice-like structure has completely broken down. The effect of thermal motion favoring the collapse of the ice-like structure is quite evident in Fig. 3: on all curves the Stokes–Einstein domain extends to higher fluidities the higher the temperature.

Differences in the "mole fraction ratio at the break-down point" in the presence of sucrose and of glycerol are ascribed to specific effects of the viscosity controlling molecules. Three categories of interactions can be visualized by which a polyalcohol type viscosity controller may contribute to the break-down of the ice-like structure and engender closer packing in the solvent matrix[9,14,15]: (a) an "internal pressure effect" on the loosely bound tetrahedral solvent aggregates by the sucrose or glycerol molecules (which cannot fit into normal lattice positions) "wedged" between them; (b) removal of water molecules from the tetrahedral structure due to the formation of primary ("inner shell") solvate bonds between water and viscosity controller; (c) long range interactions such as secondary ("outer shell") hydration which may compete with the relatively weak "intra ice-like structure bonds." Perturbation of the tetrahedral structure by these long-range effects can be envisioned as a distortion of the normal orientation of the water dipoles under the influence of the electrostatic fields in the vicinity of the polar viscosity controller molecules. The order of magnitude of the mole fraction ratio at the break-down point in the presence of sucrose clearly indicates that the breakdown of the ice-like structure cannot be due to an internal pressure effect in this instance. Inspection of reasonable tridimensional models of sucrose and water makes it evident that a sucrose molecule cannot possibly exert a wedge effect on more than an average of 5–10 water molecules. This compares with a mole fraction ratio of 120 water molecules per sucrose at the experimentally determined breakdown point. Primary hydration can only account for about four water molecules per sucrose.[16] Consequently, long-range effects of the viscosity controlling molecules, such as outer shell hydration, apppear to be the paramount factor in the breakdown of the ice-like solvent structure upon addition of sucrose. This is the only plausible explanation for the collapse of the ice-like water matrix in the presence of only one sucrose molecule per 120 water molecules. Glycerol, with a mole fraction ratio at the breakdown point of the order of 10, presents an entirely different picture. Wedge and primary hydration effects *can* readily account for the breakdown of the ice-like structure in the presence of glycerol.

We cannot offer as yet a satisfactory rationalization for explaining the variance in the mechanisms by which glycerol and sucrose cause the breakdown of the ice-like structure of water. However, the following analogy may be pertinent. Sound velocity measurements indicate that the prevalence of the ice-like structure is affected appreciably and specifically by monohydric alcohols.[17] For instance, in an aqueous solution containing 0.4 mole fraction methanol, the mole fraction of associated water molecules was 0.2 as compared to 0.8 in pure water; *ceteris paribus*, a mole fraction of ethanol as high as 0.6 was required to reduce water association to the same level. Because of the similarity between methanol and ethanol, this difference cannot reasonably be accounted for by internal pressure effects nor by primary solvation. Long range effects of outer shell hydration or an unknown type of interaction evidently must be involved. Since convincing experimental evidence shows that such a situation can prevail in the case of two simple homolog alcohols, it is perhaps not surprising that appreciable differences were found in this study between the behavior of a disaccharide (sucrose) and a triol (glycerol).

Acknowledgment.—This investigation was supported by research grants H-2342, H-2342(C) and H-2342(C2) from the National Institutes of Health, Public Health Service.

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[14] W. E. Bauer, Thesis, Pennsylvania State University, 1959.

[15] D. G. Miller, THIS JOURNAL, **80**, 3576 (1958).

[16] H. Shiio, *ibid.*, **80**, 70 (1958).

[17] O. Nomoto, *J. Phys. Soc. Japan*, **11**, 1146 (1956).

UNIVERSITY PARK, PENNSYLVANIA

[CONTRIBUTION NO. 486 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Polarographic Behavior of Some 1,4-Substituted-2,3,5-pyrrolidinetriones

BY E. A. ABRAHAMSON

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A polarographic study has been made of the behavior of 1,4-substituted-2,3,5-pyrrolidinetriones at the dropping mercury electrode. A parallelism has been found between their behavior and the behavior of such compounds as pyruvic acid and phenylglyoxylic acid which can exist in both anion and undissociated forms, both of which are reducible. Application of theory derived by Delahay has given rates of recombination of the order of 10^9 to 10^{11} l. mole^{-1} sec.$^{-1}$.

Synthesis of pyrrolidinetriones having a strong electron-attracting group in the 4-position[1] prompted a polarographic study of these compounds because of the paucity of information on the polarographic reduction of tricarbonyl compounds. Although a number of experimenters have investigated dicarbonyl compounds of aliphatic, aromatic and heterocyclic types,[2] the only published work on tricarbonyl compounds has been that on the reduction of croconic acid[3] and diphenyl-

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[1] E. G. Howard, A. Kotch, R. V. Lindsey, Jr., and R. E. Putnam, THIS JOURNAL, **80**, 3924 (1958).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 676, 691, 811.

[3] F. Arcamone, C. Prevost and P. Souchay, *Bull. soc. chim. France*, 891 (1953).