dissociation constants in acetic acid solution in a straightforward manner, and that these results are in better agreement with spectrophotometric results than are equilibrium constants derived from conductivity data.

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MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

Polarographic Diffusion Coefficients of Oxygen Defined by Activity Gradients in Viscous Media

BY JOSEPH JORDAN, EUGENE ACKERMAN AND ROBERT L. BERGER

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Fick diffusion coefficients of oxygen in aqueous sucrose solutions and in glycerol–water mixtures have been evaluated polarographically on the basis of the Lingane–Loveridge equation, in a range of viscosities (η) between 0.9 and 125 centipoise. These diffusion coefficients strikingly failed to satisfy the Stokes–Einstein relation. In terms of activity gradients, a new polarographic diffusion coefficient has been defined which varies linearly with η^{-1} between 2 and 125 centipoise. A phenomenological interpretation is presented on the basis of the Eyring discrete transition theory of diffusion and viscous flow. A corresponding polarographic diffusion current equation is derived.

The correlation between diffusion and viscosity coefficients in liquids warrants considerable fundamental interest as a possible clue to the detailed mechanism of the two processes and to the structure of liquids in general. Several studies have been reported in the literature devoted to the variation with viscosity of diffusion currents, i_d, at the dropping mercury electrode of ions and of oxygen in various solvents,[1,2] results being interpreted on the basis of the "original" Ilkovič Equation[1] which implies that

$$D_{\mathrm{Fick}} \propto i_d^2 \qquad (1)$$

where D_{Fick} denotes a conventional diffusion defined in terms of concentration gradients.[3] The determination at the dropping mercury electrode of the diffusion coefficient of oxygen is described in this paper on the basis of the "modified" (expanded) Ilkovič equation[4–9] in media covering a more than hundred-fold range of viscosities. In accordance with a suggestion by Hohn[10] a new polarographic diffusion coefficient D_a has been defined in terms of activity gradients in order to correlate diffusive and viscous properties in the several media. D_a satisfies at 25° a Stokes–Einstein type relationship

$$D_a\eta = \text{const.} \qquad (2)$$

in a range of viscosities between 2 and 125 centipoise, while D_{Fick} does not. A phenomenological interpretation is offered in terms of the "hole" theory of diffusion and viscous flow in liquids and a corresponding generalized form of the Ilkovič equation is presented and discussed.

Experimental

Chemicals.—C.P. chemicals and triply distilled conductivity water were used throughout.

Polarographic Procedure.—Solutions of desired viscosity were made up by mixing appropriate weight fractions of water and sucrose, or of water and glycerol. To serve as suitable supporting electrolytes, these solutions were made 0.1 *M* in potassium chloride and a phosphate buffer of *p*H 7 (0.01 *M* in total phosphate) was added. Buffering was considered desirable, because results by Foffani and Vecchi[2] seem to indicate that the polarographic diffusion coefficient of oxygen may vary with *p*H. As maximum suppressor, 0.01% gelatin was used, due precautions being taken to ascertain that it did not depress the relevant diffusion currents.[1,11] Gelatin was selected as maximum suppressor in preference to methyl red, because appreciable concentrations of the latter were found to be required in the viscous solutions (0.008%, as compared to 0.0001% customarily used in pure aqueous solutions) necessitating awkwardly large residual current corrections. A trace of a defoaming agent (Silicone Antifoam A, supplied by the Dow Corning Co., Midland, Michigan) was also added and had no measurable effect on the c.v. curves. Aliquots of the solutions at 25.00 ± 0.02° were equilibrated under the prevailing barometric pressure with air and with pure oxygen, respectively. This was accomplished by bubbling at a rate of 10 l./min. with the aid of an extra coarse Corning fritted glass gas dispersion cylinder for a period of 5 to 40 minutes. The time in each solution required for equilibration was ascertained polarographically and was found to increase with viscosity. The molarity of oxygen in the various solutions was calculated from its experimentally determined solubility in the given medium (*vide infra*) and the prevailing barometric pressure, the volume per cent. of oxygen in dry air being taken equal to 20.75.[12]

Current–voltage (c.v.) curves at the dropping mercury electrode (DME) were recorded at 25.00 ± 0.02° with a Leeds and Northrup Model E Electrochemograph, using an external Hume–Harris type saturated calomel reference electrode (SCE).[13] The DME was operated under a head of mercury of 60 cm. and had the following characteristics in 0.1 *M* aqueous potassium chloride solution: $m = 1.9657$

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Second Ed., Interscience Publishers, Inc., New York, pp. 43, 97, 100, 164; Vol. II, p. 552; 1952.

[2] A. Foffani and E. Vecchi, "Proc. I. Internat. Polarographic Congress," Vol. I, Prague, Czechoslovakia, 1951, p. 64.

[3] E. A. Guggenheim, *Trans. Faraday Soc.*, **50**, 1048 (1954).

[4] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).

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

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

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

[8] O. H. Müller, N.B.S. Circular 524 (1953), p. 289.

[9] M. von Stackelberg and V. Toome, *Z. Elektrochem.*, **58**, 226 (1954).

[10] H. Hohn, *Chemische Analysen mit dem Polarographen*, Julius Springer, Berlin, 1937, p. 36.

[11] L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1955, p. 140.

[12] "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 393.

[13] D. N. Hume and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **15**, 465 (1943).

mg./sec., t (at −0.40 v. *versus* SCE) = 4.28 sec. The actual drop time at the relevant potentials where diffusion current readings were taken was determined in each viscous medium. The m value varied appreciably with viscosity (*e.g.*, it was about 10% larger in a glycerol–water mixture of 100 centipoise than in water) and was determined with the aid of an automatic device described by Lingane[14] slightly modified by the use of two suitably coupled electronic relays separated by an isolation transformer. At high viscosities, the DME appeared to be quite prone to contamination causing irregular dropping. This was minimized by coating the inside of the capillary with a water-repellent silicone product[15] (Dri-Film SC89 supplied by G.E.), a 1% solution in toluene being aspirated into the capillary, air-dried for 10 minutes and subsequently baked at 120° for 2 hours. Between experiments the coated capillary was cleaned with nitric acid in the usual manner.

A 150-ml. Pyrex beaker served as electrolysis cell. It was closed with a rubber stopper with appropriate holes through which were inserted the DME, inlets and outlets for nitrogen (or oxygen) and a Pyrex glass tube with a fritted glass disk bottom for holding a saturated KCl–agar salt bridge connected to the SCE. Fifty ml. of solution was used in each polarographic experiment. Residual currents in the working range of potentials were determined in solutions deaerated with high purity Linde nitrogen washed in vanadous sulfate solution.[16] Potentials reported in this paper are referred to the SCE and corrected for iR drops. Diffusion current values are appropriately corrected for residual current.

Solubility and Viscosity Determinations.—The solubility of oxygen at 25° in the various viscous media and the corresponding viscosities were determined under the actual experimental conditions, *i.e.*, in the presence of the supporting electrolyte, maximum suppressor, etc. Oxygen concentrations were determined by the Winkler method[17] and are considered accurate within ±1%. For the viscosity measurements a Cannon Type E viscometer was used in conjunction with a Westphal density balance.

Results

C.v. curves of oxygen determined in glycerol and sucrose solutions were of the same familiar double-wave shape as in pure water.[1] The following potentials were found best suited for measuring the two diffusion currents in all media: −0.40 v. for the "two electron current" (i_{2e}) of the first wave ($O_2 + 2e + 2H^+ \rightarrow H_2O_2$); −1.45 v. for the "four electron current" (i_{4e}) of the second wave ($O_2 + 4e + 4H^+ \rightarrow 2H_2O$). The half-wave potential of the first wave varied somewhat with the medium, between −0.05 v. (in the presence of 65% sucrose) and −0.1 v. (in 90% glycerol). The half-wave potential of the second wave was −0.9 v. in all media. In a given medium i_{2e} and i_{4e} were both proportional within ±1% to oxygen concentration in the working range. Fick diffusion coefficients were computed[8] from the modified Ilkovič equation

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

where 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 in millimole/l., D_{Fick} the conventional diffusion coefficient in cm.²/sec. and K a numerical factor assumed to be equal to 34.[7,9,18] Under the experimental conditions, values of D_{Fick} in a given medium calculated from i_{2e} and i_{4e}, respectively, agreed in most instances within ±2%. In general, however, it is felt that polarographic diffusion coefficients calculated from the four electron current may be considered to represent more reliable values than those derived from the two electron current, because at times i_{2e} was observed to be exalted by 5 to 10% (without exhibiting an actual maximum) when the gelatin concentration was less than 0.01%. In contradistinction to i_{2e}, i_{4e} was completely independent of the gelatin concentration in a range between zero and 0.01%.

In Tables I and II are listed the stochastic data describing the solubility, polarographic and diffusive characteristics of oxygen in the various

Table I

Solubility, Polarographic and Diffusive Characteristics (at 25°) of Oxygen in Aqueous Sucrose Solutions of Varying Viscosity[a]

Solution characteristics			Oxygen characteristics		
1	2	3	4	5	6
% Sucrose (w./w.)	Density (g./cm.³)	Viscosity $10^2 \times \eta$ (poise)	Equil. concn. when p_{O_2} = 1 atm.[b] (mmole/l.)	Conventional polarographic diffusion current constant (for i_{4e})[c]	$10^5 \times D_{\text{Fick}}$[d] (cm.²/sec.)
Zero	1.006	0.89	1.18	12.90	2.12
10.0	1.040	1.25	0.995	11.44	1.74
15.1	1.066	1.50	.872	10.03	1.40
30.0	1.149	3.00	.558	11.73	1.54
41.9	1.195	7.02	.439	9.68	1.32
52.0	1.248	17.5	.338	8.03	0.920
54.5	1.262	25.0	.316	6.72	.670
57.5	1.278	35.0	.294	6.65	.650
62.5	1.302	67.0	.267	5.46	.430
65.0	1.321	125	.249	4.05	.250

[a] Supporting electrolyte: 0.1 *M* KCl plus phosphate buffer of *p*H 7 (0.01 *M* in total phosphate); maximum suppressor: 0.01% gelatin. [b] Partial pressure of oxygen in gas phase. [c] $i_{4e}/(Cm^{2/3}t^{1/6})$. [d] Weighted average of several determinations, calculated from eq. 3.

Table II

Solubility, Polarographic and Diffusive Characteristics (at 25°) of Oxygen in Glycerol–Water Mixtures of Varying Viscosity[a]

Solution characteristics			Oxygen characteristics		
1	2	3	4	5	6
% Glycerol (w./w.)	Density (g./cm.³)	Viscosity $10^2 \times \eta$ (poise)	Equil. concn. when p_{O_2} = 1 atm.[b] (mmole/l.)	Conventional polarographic diffusion current constant (for i_{4e})[c]	$10^5 \times D_{\text{Fick}}$[d] (cm.²/sec.)
12.4	1.032	1.27	0.889	16.40	3.31
20.0	1.058	1.75	.735	14.14	2.99
34.9	1.077	2.24	.649	9.26	1.21
52.6	1.126	4.85	.478	8.99	1.15
68.0	1.163	10.8	.378	7.56	0.870
80.0	1.197	29.0	.302	5.86	.510
84.3	1.209	45.9	.280	5.31	.480
87.5	1.215	56.9	.264	5.36	.430
92.5	1.228	106	.238	3.99	.240

[a,b,c,d] Same as in Table I.

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[14] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1944).

[15] M. von Stackelberg and V. Toome, *Leybold Polarographische Ber.*, **1**, 4, 55 (1953).

[16] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

[17] American Public Health Association, *et al.*, "Standard Methods for the Examination of Water and Sewage," 9th Ed., New York, N. Y., 1947, p. 135.

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

viscous media. The "diffusion current constant"[19] (column 5 in both tables) has no exact significance. As recommended by Kolthoff and Lingane[20] it is nevertheless tabulated as a convenient approximation for correlating polarographic results.

Diffusion coefficients computed on the basis of the unexpanded (original) Ilkovič equation

$$i_\mathrm{d} = 607nm^{2/3}t^{1/6}CD_\mathrm{Fick}^{1/2} \qquad (4)$$

yielded two different sets of values, depending on whether they were calculated from the first or from the second diffusion current. Values obtained from $i_{2\mathrm{e}}$ were consistently higher by about 5%. Among the results obtained from eq. 3, any comparable systematic error trend was conspicuous by its absence. In agreement with recent findings by Sanborn and Orlemann,[21] this is interpreted as evidence of the adequacy of the modified Ilkovič equation for accurately evaluating diffusion coefficients. Mean diffusion coefficient values calculated from eq. 4 were between 10 and 25% higher than those obtained by using eq. 3.

Discussion

The Fick diffusion coefficient at 25° of oxygen in the pure aqueous supporting electrolyte (Table I, line 1) was 2.12×10^{-5} cm.²/sec. This compares with a value of 2.6×10^{-5} cm.²/sec. reported by Kolthoff and Miller in 0.1 *M* aqueous potassium nitrate.[22] With respect to both sign and order of magnitude the difference is accounted for by the fact that Kolthoff and Miller have used the unexpanded Ilkovič equation which was the only applicable relationship known at the time when their work was published.

The values of D_Fick for oxygen in the presence of sucrose and glycerol are plotted *versus* η^{-1} in Figs. 1 and 2 (curve I in both figures). As can be seen in the figures, the curves illustrate a striking failure of the Stokes–Einstein equation. The curve for glycerol (Fig. 2) exhibits a very pronounced maximum in 12% glycerol. The sucrose curve (Fig. 1) indicates slight minima and maxima in the presence of 15 and 30% sucrose, respectively (see Table I, column 5). In general, the variation of D_Fick with fluidity is non-linear and even non-monotonic. This is readily accounted for by the following considerations germane to the discrete transition ("jump") theory of diffusion and viscous flow in liquids.[23] On the one hand, the diffusion coefficient is given by the expression

$$D_\mathrm{Fick} = \lambda_\mathrm{d}^2 k_\mathrm{d} \qquad (5)$$

where the subscript d identifies parameters characteristic for the diffusion process, λ (expressed in cm.) denotes the distance a molecule is transported in each jump and *k* is the number of times a molecule moves per second from one equilibrium position to the next. On the other hand, the viscosity coefficient is identified as

$$\eta = \frac{\lambda_1 \kappa T}{\lambda_2 \lambda_3 \lambda_\mathrm{v}^2 k_\mathrm{v}} \qquad (6)$$

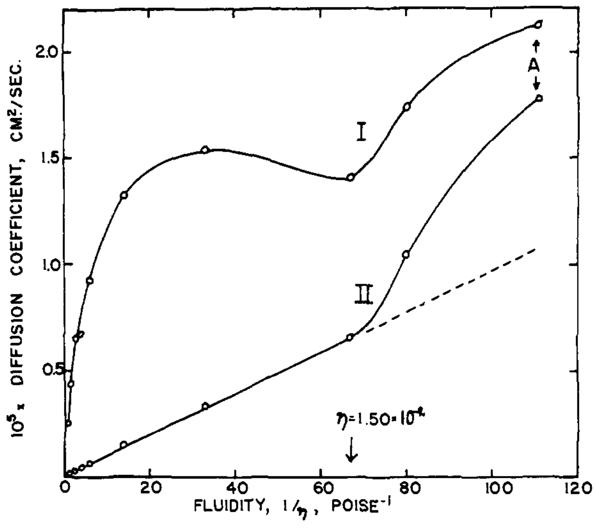

Fig. 1.—Plot of diffusion coefficient of oxygen *versus* fluidity in sucrose solutions. Supporting electrolyte: 0.1 *M* KCl plus phosphate buffer of *p*H 7, 0.01 *M* in total phosphate; I, D_Fick; II, D_a; A, pure aqueous supporting electrolyte.

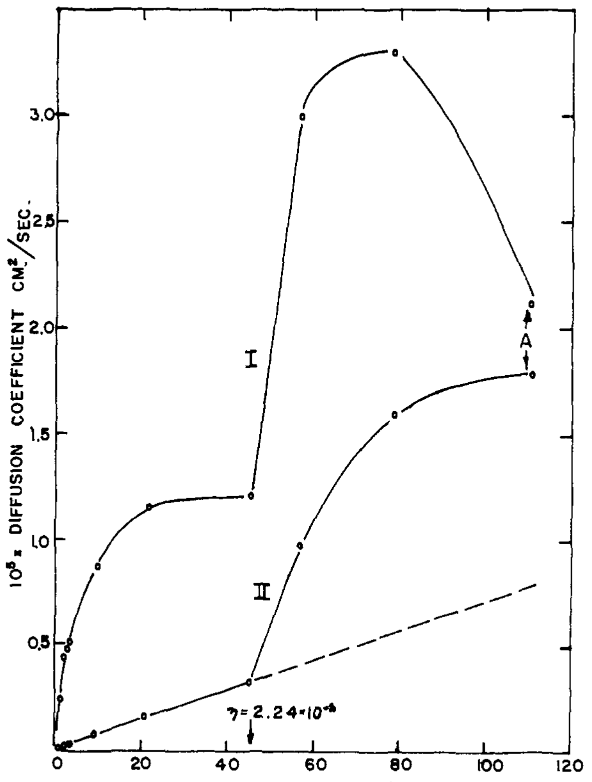

Fig. 2.—Plot of diffusion coefficient of oxygen *versus* fluidity in glycerol–water mixtures. Supporting electrolyte, same as in Fig. 1; I, D_Fick; II, D_a; A, pure aqueous supporting electrolyte.

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[19] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 588 (1943).

[20] Reference 1, p. 382.

[21] R. H. Sanborn and E. F. Orlemann, THIS JOURNAL, **77**, 3726 (1955).

[22] I. M. Kolthoff and C. S. Miller, *ibid.*, **63**, 1013 (1941).

[23] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 477 ff.

where the subscript v denotes parameters specific for viscous flow, κ is the Boltzmann constant, T the absolute temperature; λ_1, λ_2 and λ_3 are 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 motion, respectively. A Stokes–Einstein type equation is expected to hold[23]

if $$\lambda_d = \lambda_v \tag{7}$$

and $$k_d = k_v \tag{8}$$

The distance a molecule is transported in each transition is likely to be primarily dependent on the over-all average packing in the liquid. Under the experimental conditions (*i.e.*, in a homogeneous solution at 25°) it appears plausible that

$$\lambda_1 \approx \lambda_2 \approx \lambda_3 \approx \lambda_d \approx \lambda_v \approx \Lambda \tag{9}$$

However, the frequency of transitions ought reasonably to be expected to be greater for oxygen than for any of the solvent species, because less free energy of activation should be needed for a solute molecule to jump from one equilibrium position to the next than is required for a component of the "solvent lattice" proper; *i.e.*

$$k_d > k_v \tag{10}$$

On the basis of the following stringent fundamental considerations it was further concluded that D_{Fick} does not represent an adequate significant parameter for comparatively characterizing the diffusion current at the DME of oxygen in the various viscous media. In the derivation of the Ilkovič equation,[1] the diffusive flux, F, is assumed to be determined by a concentration gradient of the diffusing species

$$F = -D_{\text{Fick}} \frac{\partial C}{\partial r_t} \tag{11}$$

where r_t denotes the radius at time t of the DME. The assumption on which eq. 11 is based is not valid for a situation which involves comparison between solutions of oxygen in media in which its solubilities differ. Consider, for instance, a solution of oxygen in pure water and one in a glycerol–water mixture. Assume that both solutions are equilibrated with gaseous oxygen at a given partial pressure. The chemical potential of oxygen is obviously the same in both media although the corresponding equilibrium concentrations of oxygen may be appreciably at variance (Tables I and II, column 4). Equation 11 implies a tendency for oxygen to diffuse between the two solutions, which is energetically impossible because there is no difference between the relevant chemical potentials. It is therefore proposed that eq. 11 (and the Ilkovič equation which represents its integrated solution) be replaced by a diffusion equation of more general validity.

If all oxygen solutions are referred to a unique standard state, the activity (a) of oxygen represents a convenient measure of its chemical potential. The molarity activity coefficients (f) of oxygen in the viscous media used in this investigation, referred to a dilute solution of oxygen in pure water (in the absence of any supporting electrolyte), were computed from solubility data and are shown in Table III (columns 2 and 4).

TABLE III

MOLARITY ACTIVITY COEFFICIENT[a] OF OXYGEN IN VARIOUS VISCOUS SOLUTIONS[b]

In presence of sucrose 1 Viscosity $10^2 \times \eta$ (poise)	 2 Activity coefficient[c]	In presence of gycerol 3 Viscosity $10^2 \times \eta$ (poise)	 4 Activity coefficient[c]
0.89[d]	1.09	1.27	1.44
1.25	1.29	1.75	1.75
1.50	1.47	2.24	1.98
3.00	2.30	4.85	2.68
7.02	2.92	10.8	3.39
17.5	3.79	29.0	4.26
25.0	4.07	45.9	4.59
35.0	4.37	56.9	4.85
67.0	4.81	106	5.38
125	5.15		

[a] Referred to a solution of oxygen in pure water as the standard state, where the equilibrium concentration of oxygen (when $p_{O_2} = 1$ atm.) was taken equal to 1.28 mmole/l. [b] Same solutions as in Tables I and II. [c] Calculated from data in column 4 in Tables I and II. [d] No sucrose added; aqueous supporting electrolyte only.

In order to arrive at a diffusion current equation in which i_d is proportional to a,[10] an "activity diffusion coefficient" was defined by the equation

$$F = -fD_a \frac{\partial a}{\partial r_t} \tag{12}$$

where

$$a = fC \tag{13}$$

Combination of eq. 12 and 13 yields

$$F = -f^2 D_a \frac{\partial C}{\partial r_t} \tag{14}$$

Solving for the boundary conditions prevailing at the DME[4-7] the following integrated diffusion current equation was obtained

$$i_d = 607nm^{2/3}t^{1/6}aD_a^{1/2}(1 + Km^{-1/3}t^{1/6}fD_a^{1/2}) \tag{15}$$

This is a generalization of the conventional expanded Ilkovič equation (eq. 3) to include the effect of the varying media. The two equations become identical if $f = 1$ ($D_{\text{Fick}} = D_a$). The conventional polarographic diffusion coefficient and the activity diffusion coefficient are correlated as

$$D_{\text{Fick}} = f^2 D_a \tag{16}$$

From the numerical data in Tables I, II and III, values of D_a were calculated for the various solutions and plotted *versus* fluidity in Figs. 1 and 2 (curve II in both figures). As can be seen in the figures, D_a in the presence of sucrose is rigorously proportional to η^{-1} in a range of viscosities between 1.5 and 125 centipoise and extrapolates to zero for $\eta \rightarrow \infty$. In the presence of glycerol D_a is proportional to η^{-1} between 2 and 106 centipoise and also extrapolates to zero for $\eta \rightarrow \infty$. In the range between 0.9 centipoise on the one hand and 1.5 or 2 centipoise on the other, D_a is appreciably larger than expected by extrapolation from the linear "Stokes–Einstein region."

The existence of a Stokes–Einstein region extending over a more than fifty-fold range of viscosities is considered compelling evidence for the significance of D_a and the validity of eq. 15.

Reconsidering accordingly eq. 5 and 11 on the one hand, and eq. 12 on the other, it is postulated that

$$fD_a = \lambda_d^2 k_d \tag{17}$$

and

$$F = -\lambda_d^2 k_d \frac{\partial a}{\partial r_t} \tag{18}$$

This implies the assumption that the driving force of diffusion is determined by the activity gradient $\partial a/\partial r_t$, rather than by the conventional concentration gradient $\partial C/\partial r_t$.

The activity coefficient of oxygen represents an obvious measure of its relative fugacity in the various media. The fugacities can be visualized as depending on the relative frequency of jumps to the solution surface of oxygen and solvent molecules, *i.e.*

$$f \propto \frac{k_d}{k_v} = g \frac{k_d}{k_v} \tag{19}$$

Combining eq. 19, 17, 6 and 9, it is readily seen that

$$D_a\eta = \frac{\lambda_d^2 k_d}{f}\eta = \frac{\kappa T}{q\Lambda} \tag{20}$$

At a given temperature, eq. 20 indicates that $D_a\eta$ is a constant as long as approximation (9) is valid. Under the experimental conditions this appears to be the case at all viscosities greater than about 2 centipoise. This is accounted for by assuming that with increasing proportions of glycerol or sucrose in the solvent, the over-all packing becomes comparatively closer and the average Λ value remains invariant due to compensatory effects between increased molecular size and decreased intermolecular distances.

The failure of eq. 20 in the low viscosity region ($\eta < 2$ in the presence of glycerol, $\eta < 1.5$ in the presence of sucrose) indicates that approximation (9) does not hold in solutions consisting predominantly of pure water as solvent. This anomaly is attributed to the "ice-like structure" of liquid water at room temperature which implies the availability of appreciable intermolecular space between loosely packed tetrahedral aggregates of water molecules.[24,25] The presence of other molecules, such as sucrose or glycerol, is known to cause the ice-like structure to collapse by a quasi pressure-like strain-action engendering closer packing.[24] The fact that the Stokes–Einstein region extends to lower viscosities in the presence of sucrose than in the presence of glycerol can be ascribed to the reasonably greater efficiency of the larger sucrose molecules in destroying the ice-like structure of water. Qualitatively, increased pressure and/or higher temperatures are expected to have a similar effect. An extensive program of subsequent studies is anticipated in these laboratories with a view to elucidating the relevant quantitative correlations.

Acknowledgments.—This investigation was supported in part by a grant-in-aid from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council. Thanks are due to Richard A. Javick for carrying out solubility determinations.

[24] J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1954).

[25] R. A. Robinson and R. M. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 3.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Thermodynamics of the Liquid Solutions in the Triad Cu–Ag–Au. II. The Cu–Au System[1]

BY RUSSELL K. EDWARDS AND MERWYN B. BRODSKY

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The thermodynamics of the liquid solutions in the Cu–Au system have been investigated by effusion vapor pressure measurements carried out over a number of solution compositions in the temperature range 1500–1600°K. The activities of both components demonstrate marked negative deviation from ideal solution behavior over most of the composition range. Corresponding values for the partial and integral enthalpies and the excess partial and integral entropies of mixing are negative. However, for copper the activities, partial molar enthalpies, and excess partial molar entropies of mixing show small positive deviations as the solutions approach pure copper in composition. The work demonstrates the practicability of computing the activities of both components in a series of solutions of a binary mixture from measurements of the total rates of effusion—without experimental measurements of gas phase compositions.

Introduction

Edwards and Downing[2] initiated the titled general study with their investigation of the liquid Cu–Ag system by the effusion vapor pressure method. Concurrent with the present work, Oriani[3–5] carried out experimentally an e.m.f. investigation in the liquid Cu–Au system.

In the present investigation, the thermodynamics of the liquid solutions in the Cu–Au system were obtained from rate of effusion measurements carried out over a number of solutions in the temperature range 1500–1600°K. Partial rates of effusion for both components were related to those of the pure materials, similarly measured in the same apparatus, to obtain self-consistent data from which activities were calculated.

The total rate of effusion from Cu–Au solutions was measured by the weight-loss method. The Cu–Au solutions were contained in porcelain Knudsen crucibles, situated in a heated, evacuated porcelain

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[1] (a) Based on part of a thesis by M. B. Brodsky, submitted by Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, May, 1955. (b) This work was supported by the U. S. Office of Naval Research through Contract N7-onr-329, Task Order II, and Contract NONR 1406, Task Order II.

[2] R. K. Edwards and J. H. Downing, *J. Phys. Chem.*, **60**, 108 (1956).

[3] R. A. Oriani, private communication enclosing a manuscript prepared for publication and including large scale plots of his e.m.f. data, June 8, 1955.

[4] R. A. Oriani, private communication, Sept. 13, 1954.

[5] R. A. Oriani, private communication, Oct. 4, 1954.