Diffusivity of Oxygen in Electrolyte Solutions

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Diffusivities of oxygen dissolved in aqueous solutions of sodium decylsulfonate, sodium dimethylbenzenesulfone, sodium dodecylbenzenesulfonate, sodium sulfate, and sodium phosphate solutions have been measured utilizing a diaphragm cell technique. The diffusivity of oxygen in these solutions appears to be related to the fluidity through the Jones and Dole viscosity B coefficient. Utilization of Podolsky's lattice model for transport processes in electrolyte solutions seems to indicate a correlation effect between the self-diffusivity of water and the diffusivity of the dissolved oxygen.

In the work we report here, diffusion coefficients for oxygen dissolved in aqueous electrolyte solution have been measured. The diffusion measurements have been made in 1–1, 1–2, and 1–3 valence-type electrolyte solutions with the electrolyte concentration for each valence type varied over a significant range. The cation, sodium, was the same in all cases. The monovalent anions chloride, decylsulfonate, dimethylbenzenesulfonate, and dodecylbenzenesulfonate were used. Sulfate was used for the divalent anion and phosphate for the trivalent anion. All measurements were made at 25.0 ± 0.01°C.

Various workers have measured the diffusivity of oxygen in water and in a few aqueous solutions containing solutes not related in any systematic fashion (*3*). In addition, several different measuring techniques have been used. Since there is convincing evidence that aqueous electrolyte solutions are structured, it might be expected that oxygen diffusivities would vary in a fashion that could be related to other parameters generally recognized as being determined by solution microstructure, such as the Jones and Dole coefficients (*4*). Jordan and Bauer have reported diffusivities for oxygen in aqueous sucrose and glycerol solutions $0.1M$ in potassium chloride (*5*). The diffusivities reported by these workers varied inversely with concentration of dissolved solute. These workers attempted to correlate the measured diffusivities in a qualitative fashion with the solution viscosities. The interpretation was handicapped by the presence of the constant $0.1M$ potassium chloride concentration.

The objective of this work was to obtain a set of diffusivities of oxygen in electrolyte solutions in which the electrolyte concentration, anion valence, and anionic radius are varied in a systematic fashion. Also, the same technique would be used for all measurements. The primary reasons oxygen was chosen for these diffusion measurements were that no specific association with any of the components of the solution was to be expected, it was readily available, techniques for measuring the diffusivity were easily devised, and the measurements are of interest to workers in other areas.

EXPERIMENTAL

A diaphragm cell technique was used for these diffusion measurements. The diaphragm cell method has been described and analyzed by a number of investigators (*1*, *12*). In the more recent literature, a number of different styles of cells and types of diaphragms for measuring diffusivities have been described (*2*, *11*), and the one used here is again slightly different. The primary differences are that the diaphragm is mounted vertically rather than horizontally and oxygen-sensitive gavalanic cells are incorporated for continuous monitoring of the oxygen on either side or both sides of the cell.

The principal reason for the convention of mounting diaphragms horizontally rather than vertically was to avoid density gradients in unstirred cells and to facilitate the placement of stirrers to avoid concentration gradients in the cell reservoirs. In the measurement of oxygen diffusion, a density gradient would not be a problem because oxygen concentration, the variable component, does not make a measurable contribution to the overall solution densities (initial oxygen concentration 8–9 ppm). In the actual cell constant determination in which $0.1M$ KCl was in one compartment and water in the other (density ratio 1.003), density gradient effects should be apparent in the manner in which the measured concentrations were treated. One would expect that the rate of KCl transfer across the diaphragm, due to density gradients, would decrease as the density gradients would decrease as the density equalized—that is, log concentration difference vs. time plot would show a deflection. However, this was not observed. We therefore conclude that efficient stirring tends to eliminate density gradient effects.

Materials. Analytical grade reagents were used in all cases without further purification. The water for all measurements was double distilled.

Diffusion Cell. The diaphragm diffusion cell used in this work was constructed from two 50-ml round-bottomed flasks with 20/40 ground glass joints. The two flasks were connected with a piece of 20-mm glass tubing into which was sealed a 20-mm fritted glass disc of approximately 40-mμ pore size. The connecting tube was of minimum length, and the connections between the flask and tubes were flared as much as possible to allow free circulation of the solution. Ports for filling, fitted with stopcocks, were sealed into both flasks.

Stirring was accomplished by placing small magnetic stirring bars in the bottom of the 50-ml flask on each side of the cell. The cell was then placed in the thermostat over magnetic stirring motors.

Oxygen-Sensitive Galvanic Cell. This detector is supplied by Precision Scientific Co. The only modification made was in the housing to allow it to fit securely into the diaphragm cell through the 20/40 ground glass joint. Rubber stoppers were utilized to make this fit. The characteristics of this cell have been extensively investigated and described by Mancy et al. (*10*). Cells freshly prepared and calibrated were used for each diffusion run. The sensitivity of these cells decreased with time. However, this decrease is linear with time for about two weeks so that sensitivity changes could be corrected in any given measurement.

The cell response to dissolved oxygen was measured in terms of potential drop across a 30K-Ω load resistor with a recording potentiometer. The measuring circuit also contained

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a standard potentiometer circuit for bucking out definite increments of the potential developed across the 30K resistor. Such a circuit has been described by Lipner et al. (*9*).

The cell was calibrated by determining the response in solution of known oxygen concentration. The techniques for preparing such solutions are described by Stone and Eichelberger (*15*). The cell response is essentially linear with concentration because it is sensitive to the activity of the dissolved oxygen, and Henry's law is obeyed.

The experimental data derived from the cell as related to time are utilized in an integrated form of Fick's first law to obtain the diffusion coefficient:

$$\log (C_h - C_o) = BDT + K \tag{1}$$

where C_h and C_o are the oxygen concentrations on the high and low side of the cell, respectively. On the right side of the equation, B, D, and T are cell constant, diffusion coefficient, and time in that order; K is an integration constant. Two conditions for the above equation to be applicable should be noted: Equal volumes are maintained in both cell compartments and a linear concentration gradient is maintained across the diaphragm. The linear concentration gradient was developed by allowing a period of time to elapse during which the diaphragm changed from a solvent only condition to a linear concentration gradient condition. Because the concentration of solute was being continuously recorded, we knew when the linear concentration gradient was obtained. The diffusion coefficient computed at the various points became constant when the gradient finally developed. Usually about 8 hr were allowed for this. The cell constant represents the diffusion cross section (i.e., area and length of diffusion path). Because this constant cannot be measured directly, it is determined by some reference standard with a well-known diffusion coefficient.

In this work, diffusion of aqueous potassium chloride in the diaphragm cell was monitored conductimetrically. The actual arrangement for measuring the KCl concentration consisted of substituting platinum electrodes for oxygen-sensitive detectors in the diffusion cell and measuring conductance with a General Radio model RC-18 conductance bridge. Diffusion runs lasted for approximately 2.5 days. Concentrations were read from an empirical plot of concentration vs. conductivity prepared by placing standard KCl solutions in the cell and recording conductance. The initial concentration of KCl was 0.1*M*. Common criteria for prediffusion time suggest that about 5 hr would be required for a linear concentration gradient to be established, but our measurements indicate the time is no more than 2 hr (*1*); that is, the plot of log $(C_h - C_o)$ vs. T was linear after 2 hr. The final concentration on the high side of the diaphragm was about 0.08*M*. From the plot of log concentration difference vs. time and using a value for the diffusion coefficient of KCl equal to 1.838×10^{-5} cm^2 sec^{-1} at 25°C, a cell constant of -4.567×10^{-2} cm^{-2} was obtained. Reproducibility of the values computed here was ±2.5%. The choice of the diffusion coefficient used for KCl here follows the suggestions of Gordon (*1*).

RESULTS AND DISCUSSION

Diffusion coefficients for oxygen in water and in aqueous electrolyte solutions determined in this investigation are presented in Table I. Other data tabulated in Table I, determined in this work because they did not appear in the literature, are fluidity values for aqueous sodium phosphate, *n*-decylsulfonate, dimethylbenzenesulfonate, and dodecylbenzenesulfonate solutions.

Table I. Diffusivities and Viscosities of Oxygen in Water and in Aqueous Electrolyte Solutions at 25°C

Electrolyte	Concn, Mol/l.	Diffusivity, $10^5 \times$ cm^2/sec	Fluidity, $1/n$ P^{-1}
Pure water		3.40	111.91[a]
NaCl	0.25	2.69	109.32[a]
NaCl	0.50	2.08	106.91[a]
NaCl	1.00	1.75	102.30[a]
NaCl	2.00	1.12	92.60[a]
Na_2SO_4	0.05	3.00	110.92[a]
Na_2SO_4	0.10	2.50	109.61[a]
Na_2SO_4	0.30	1.91	104.90[a]
Na_2SO_4	0.90	1.47	92.93[a]
Na_3PO_4	0.005	2.61	111.31
Na_3PO_4	0.010	2.15	110.72
Na_3PO_4	0.020	1.79	109.63
Na_3PO_4	0.025	1.56	106.41
Na_3PO_4	0.050	1.25	101.50
$NaC_{10}H_{21}SO_3$	0.002	3.11	111.6
$NaC_{10}H_{21}SO_3$	0.004	2.67	111.4
$NaC_{10}H_{21}SO_3$	0.008	2.45	110.9
$NaC_8H_9SO_3$	0.002	2.93	111.7
$NaC_8H_9SO_3$	0.005	2.60	111.5
$NaC_8H_9SO_3$	0.010	2.05	111.0
$NaC_{18}H_{29}SO_3$	0.0003	3.24	111.8
$NaC_{18}H_{29}SO_3$	0.0007	3.04	111.4
$NaC_{18}H_{29}SO_3$	0.0014	2.74	110.8
$NaC_{18}H_{29}SO_3$	0.0029	2.30	110.0
$NaC_{18}H_{29}SO_3$	0.0057	1.51	107.8

[a] Fluidity values computed from viscosity reported in literature (*8*).

The diaphragm diffusion cell, although widely accepted and used because of experimental simplicity, provides data that may be subject to considerable uncertainty. Among these uncertainties is the fact that it is a comparison technique and relies upon a preliminary standardization. The reliability of the standard diffusion coefficient used for calibration then limits the measured diffusion coefficients. Another point of uncertainty in diffusion coefficients derived from diaphragm cell measurements is the possibility of surface interaction occurring at the pore walls of the diaphragm. Such an interaction cannot be ascertained from experimental data. Despite the various sources of uncertainty, diffusion coefficients determined with a diaphragm cell have been widely accepted.

The presence of added electrolyte increases the possibility that the measured diffusion coefficient may include other effects occurring within the diaphragm. Kolthoff and Miller (*7*) published a diffusion coefficient for oxygen (2.60×10^{-5} cm^2/sec) in 0.1*M* KNO_3 solution measured polarographically, which is comparable to the value measured here in 0.25*M* NaCl. Jordan and co-workers (*5*, *6*) also, using a polarographic method, measured a diffusion coefficient for oxygen (2.12×10^{-5} cm^2/sec) in 0.1*M* KCl and 0.01*M* K_3PO_4 which is in line with the values measured here in sodium phosphate solution. The comparison of the values for oxygen diffusivity in salt solution measured by other techniques reported in the literature and those measured here lead us to believe that the trends in oxygen diffusivity vs. electrolyte concentration are true solution effects and not experimental anomalies.

In the case of the organic sulfonic acid anions used here the possibility of adsorption of the sulfonic acid within the diaphragm pores and a consequent change in the cell constant is a possibility. We believe that this possibility has been minimized by maintaining concentrations below the critical micelle concentration. This was verified by conductivity measurements. Also the large pore size, 40 μ, would tend to reduce the effect. However the possibility of adsorption within the diaphragm does exist and is an open question.

The correlation between fluidity and diffusivity has long been recognized. However, there are no generally accepted relationships for predicting the diffusivity of gases dissolved in electrolyte solutions. Ratcliff and Holdcroft (*14*) have suggested a number of relationships while attempting to correlate their measured diffusivities of carbon dioxide in electrolyte

Table II. Relative Fractional Change in Diffusivity vs. Square Root of Electrolyte Concentration and Jones and Dole Viscosity B Coefficients

Electrolyte solution	$[D/D_o - 1]/C = K$	α^a	Jones and Dole B coefficient	α^a
NaCl	−0.479	0.003	−0.078	0.003
$NaC_{10}H_{21}SO_3$	−3.200	0.034	−0.877	0.011
$NaC_8H_9SO_3$	−3.979	0.036	−0.944	0.007
$NaC_{18}H_{29}SO_3$	−7.617	0.033	−7.016	0.021
Na_2SO_4	−0.619	0.045	−0.152	0.004
Na_3PO_4	−2.924	0.039	−2.308	0.068

[a] α is standard deviation of linear least-square fit.

solutions. One of their simpler equations is $D = D_o\ (1 - AC)$, where D and D_o are the diffusivities in electrolyte solution and in pure water, respectively, A is an empirical constant, and C is the concentration of electrolyte. However, we find that the relative fractional change in diffusivity, $[(D/D_o) - 1]$, where D and D_o are as before, is apparently linear with respect to the square root of electrolyte concentration. An equation is followed of the form, $D = D_o\ (1 - k\sqrt{C})$, where k is an empirical constant and the other terms are the same as for the Ratcliff and Holdcroft equation above. In Table II, the k values in the above equation for the electrolytes used here are tabulated. Also included in the table are the standard deviations for the k values computed from a least-square technique. The deviation for the sodium sulfate electrolyte solution is somewhat large, but the others are quite satisfactory.

Podolsky (*13*) previously showed that the relative change in self-diffusivity of water in electrolyte solutions should be, at a given concentration of electrolyte, a linear function of the Jones and Dole viscosity B coefficient. Podolsky used the data of Wang (*16*) for the self-diffusivity of water in ionic solutions to support his idea. His relationship for the dependence of the self-diffusivity of water on electrolyte concentration is $(D/D_o) - 1 = (B/1 + r)C$. B is the Jones and Dole viscosity B coefficient and r is the ratio of the perturbation of activation energy of an ion by an adjacent water molecule to the perturbation of the activation energy of a water molecule interacting with an ion. The other terms are as before. Podolsky's treatment of the self-diffusivity of water-electrolyte dependence, together with our previous correlation of the diffusivity of dissolved oxygen with electrolyte concentration when equated through the concentration terms, suggests that the relative change in the diffusivity of dissolved oxygen is proportional to the square root of the relative change in the self-diffusivity of water. The proportionality constant would be the product of the term $(1 + r)/B$ (the symbols are defined previously) and another term characteristic of the particular electrolyte, which is the proportionality constant listed in Table II.

The Jones and Dole viscosity B coefficients for the electrolytes used have been computed either from viscosity data taken from the literature or recorded in the course of this investigation and are listed in Table II. The relationship, when compared with the B coefficients of the Jones and Dole equation, gives one group of electrolyte solutions (sodium chloride, sodium sulfate, sodium dimethylbenzenesulfonate, and sodium decylsulfonate) which fits a linear equation ($k = 0.107 + 3.79\ B$). The points for sodium phosphate and sodium dodecylbenzenesulfonate scatter quite far from the line. The cation, sodium, is the same in all cases; consequently any change in diffusivity of oxygen with respect to electrolyte concentration, and likewise for the viscosity of the electrolyte solutions, is due to the change in anions. The B coefficients are recognized as being characteristic of the particular ion. In the case of sodium phosphate solutions, because of hydrolysis and the consequent existence of several different ions in the solution, we might expect the behavior observed with respect to the other electrolytes. The behavior of the measurements with the other electrolyte, sodium dodecylbenzenesulfonate, with a very negative B coefficient indicating a high degree of disordering of the solvent structure, is not so easily rationalized.

The lattice model upon which Podolsky based his derivation has been extensively used to explain and develop theories interpreting the various phenomena associated with solutions. The data collected here seem to indicate that yet another effect exists in common between ionic solids and electrolyte solutions—i.e., a correlation effect between the diffusion of the lattice matrix particles and the solute particles. If this is the case, then the anomalous behavior of oxygen diffusivity in sodium dodecylbenzenesulfonate solution might be due to a severe distortion of the solution lattice, such as might be experienced prior to micelle formation.

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