Measuring oxygen diffusion coefficients with polarographic oxygen electrodes: I. Electrolyte solutions

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Measuring Oxygen Diffusion Coefficients with Polarographic Oxygen Electrodes:
I. Electrolyte Solutions

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The oxygen diffusion coefficient in aqueous solutions is an important factor leading to a successful chemical engineering process design. Unfortunately, few data are available in the literature, largely because accurate measurements are difficult and tedious. Different methods of measuring the oxygen diffusion coefficient have been reported.[1,2] The purpose of this work is to exploit a rapid method of measuring oxygen diffusion coefficients in electrolyte solutions with the commercially available membrane-covered oxygen electrode. The methodology is general and thus can be extended to gases other than oxygen.

When an electrode of noble metal such as platinum or gold is made 0.6–0.8 V negative with respect to a suitable reference electrode, for example, the calomel or Ag/AgCl, in a neutral potassium chloride (KCl) electrolyte as the electrode solution, dissolved oxygen is reduced at the surface of the cathode. By separating the cathode, anode, and KCl solution from the test medium with a plastic membrane permeable to oxygen but not to most of the ions, the polarographic oxygen electrode has been successfully used to measure oxygen tensions in the gas, liquid, or semisolid. This electrode has the property that the current output is directly proportional to the oxygen partial pressure in the immediate vicinity of the membrane surface. With proper interpretation, however, the measurement can be used to characterize the transport properties of oxygen in the bulk medium surrounding the electrode.

Takahashi and Fatt[3] used a Clark-type polarographic oxygen electrode, replacing its plastic membrane with a tissue segment, to make a direct measurement of the oxygen diffusion coefficient in corneas removed from steer and rabbit eyes. Eliminating the membrane, they avoided a multilayered system (the electrode solution, membrane, and tissue) on the electrode; hence, the data given by this dynamic process could easily be used to solve for the oxygen diffusion coefficient.

The method, however, is not applicable to an aqueous system because the electrode solution is prone to leak.

Two other methods measuring oxygen diffusion coefficients in the liquid were introduced by Lee.[4] One used an oxygen microelectrode with the unsteady-state analysis similar to that of Takahashi and Fatt.[3] The other was based on the fact that the response time of the bare cathode was inversely proportional to the value of the oxygen diffusion coefficient. However, these dynamic measurements are sensitive to external disturbances and are very difficult to perform.

This article describes findings concerning a convenient method using the steady-state analysis for characterizing oxygen diffusion coefficients in aqueous solutions. Furthermore, it reports on the effect of the ionic strength on the diffusion coefficients in various electrolyte solutions.

PRINCIPLE

Grunewald[5] has analyzed the steady-state oxygen concentration gradient near a hemispherical, membrane-covered cathode. A similar analysis was made by Gutherman and Goldstick[6] for a flat disk cathode of 25 μm diameter covered with a 30-μm-thick layer of electrode solution and a 10-μm-thick polyethylene membrane. In general, the steady-state oxygen transfer through the membrane-covered electrode immersed in a stationary liquid can be shown as in Fig. 1. By neglecting the gas–film resistance, it is reasonable to assume that the liquid at gas–liquid interface is saturated with oxygen in the air, and can be regarded as the source of oxygen transfer. The sink is the cathode surface where the oxygen is continuously engaged in the rapid electrochemical reaction. The rate of consumption of oxygen due to the reaction is much faster than the rate of diffusion; thus, the oxygen concentration at the cathode can be treated as nil. If a steady state is to occur, the fluxes of oxygen through the liquid layer, membrane, and electrode solution remain the same, that is,
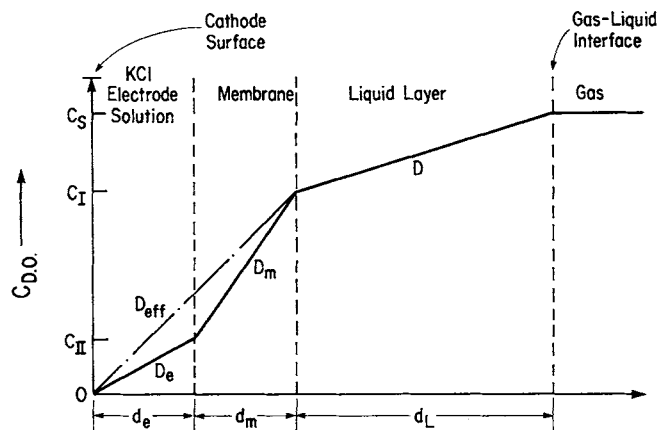
Figure 1. Schematic of the steady-state oxygen transfer through membrane-covered electrode immersed in stationary liquid.

$$N = D\frac{C_s - C_I}{d_l} = D_m\frac{C_I - C_{II}}{d_m} = D_e\frac{C_{II}}{d_e} \qquad (1)$$

For the polarographic electrode, properties of the membrane and the electrode solution would not change during a brief period of operation. It is thus possible to lump the effect of the membrane and the electrode solution into a parameter that is characteristic of the electrode used. Thus, eq. (1) can be simplified to the following expression:

$$D\frac{C_s - C_I}{d_l} = D_{\text{eff}}\frac{C_I}{d_{\text{eff}}} = KC_I \qquad (2)$$

where $K = D_{\text{eff}}/d_{\text{eff}}$ is the parameter, characteristic of the electrode. For the oxygen electrode, values of C_I can be read from the indicator. Rearranging eq. (2) leads to:

$$\frac{K}{D} = \left(\frac{C_s}{C_I} - 1\right)\Big/ d_l \qquad (3)$$

Hence, using a membrane-covered oxygen electrode to measure the oxygen concentration at a specified depth from the gas–liquid interface, d_l, which is exposed to a gas of known oxygen partial pressure, it is possible to obtain the (K/D) value of the test system.

Nonetheless, measuring the absolute distance between the membrane and the gas-liquid interface, d_l, has been proved very difficult; though moving the electrode for a known distance, Δd_l, is simple. Accordingly, eq. (3) can be transformed to:

$$\frac{K}{D} = C_s\left(\frac{1}{C_{I2}} - \frac{1}{C_{I1}}\right)\Big/ \Delta d_l \qquad (4)$$

where $\Delta d_l = d_{l2} - d_{l1}$ is the distance of the moving and C_{I1} and C_{I2} are the oxygen concentrations measured at d_{l1} and d_{l2}, respectively.

Since K is a characteristic constant of the electrode, its value can be deduced by conducting the same diffusion experiment with a reference solution of a known oxygen diffusion coefficient, D_o. Once the value of K

of the electrode is obtained, oxygen diffusion coefficients in various aqueous test solutions can be calculated using eq. (4).

EXPERIMENTAL APPARATUS AND PROCEDURE

Measurements of the oxygen diffusion coefficient were conducted in water and in aqueous solutions of four salts at 22°C and 1 atm pressure. The salts used were sodium chloride, KCl, sodium sulphate, and magnesium sulphate. The schematic of the experimental setup is shown in Fig. 2. The oxygen electrode was the YSI 5739 electrode manufactured by the Yellow Spring Instrument Co., Yellow Springs, Ohio. This electrode has a gold cathode and silver anode, using the half-saturated KCl aqueous solution plus the Kodak Photo-Flo Solution as the electrode solution. The current drawn from the electrochemical reaction was amplified and translated to the dissolved oxygen concentration with the YSI model 58 dissolved oxygen meter, and was recorded with the Hewlett–Packard (Palo Alto, California) 7132A strip-chart recorder.

Test solutions were contained in a glass jar with a magnetic stirrer at the bottom and a thermostat for temperature control. The electrode was fastened to a rod, which was held by a micromanipulator having a precision of ±2 µm. The electrode was completely immersed in the test solution with the membrane facing upward. Influence of the moving liquid on the performance of a polarographic oxygen electrode has been studied by Hudson.[7] His results indicated that to obtain reliable solubility data the polarographic oxygen electrode with a large cathode must have the test solution flowing over the membrane surface at the rate of 30 cm/s or more. The test solution was first aerated for at least 10 min to ensure its saturation. Then, the electrode was deeply immersed in the test solution and calibrated by gradually increasing the power input
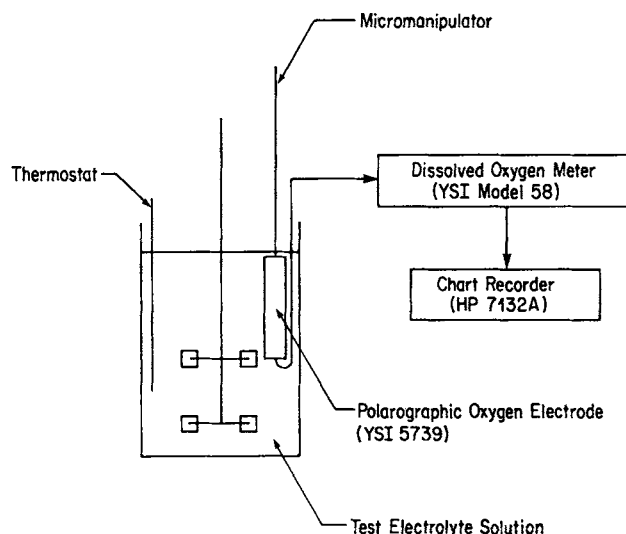

Figure 2. Schematic of experimental setup for oxygen diffusion coefficient measurement.

for stirring until no change of oxygen concentration readout was observed. At that stage, the dissolved oxygen was set to be 100% saturation.

The stirrer was turned off and the test solution was allowed to be quiescent. The electrode was then moved by the micromanipulator to have the membrane surface as close to the gas–liquid interface as possible, mainly for the purpose of minimizing the effect of side diffusion. Steady-state readings of the dissolved oxygen percent saturation at positions of known distances to one another were taken. By using eq. (4), K/D values of the test solutions could be determined with any pair of the readouts while those obviously influenced by the side diffusion effect were deleted. Experiments were repeated several times to ensure reproducibility.

RESULTS AND DISCUSSIONS

As previously stated, the oxygen diffusion coefficients can be obtained in all test solutions by first using pure water as the reference solution. Unfortunately, literature values of the oxygen diffusion coefficient vary considerably even under the same condition. For example, at 25°C, its values range from 1.87 to 2.60 × 10^{-5} cm^2/s.[1] It is thus advantageous to use the relative values of D/D_o instead of the absolute values of the oxygen diffusion coefficient (D) as a function of the electrolyte concentrations in the aqueous solutions. D_o is the oxygen diffusion coefficient of water at infinite dilution of salts. The results are shown in Fig. 3 and are listed in Table I.

The presence of ions results in a decrease in the diffusion coefficient, and the marginal effect of the
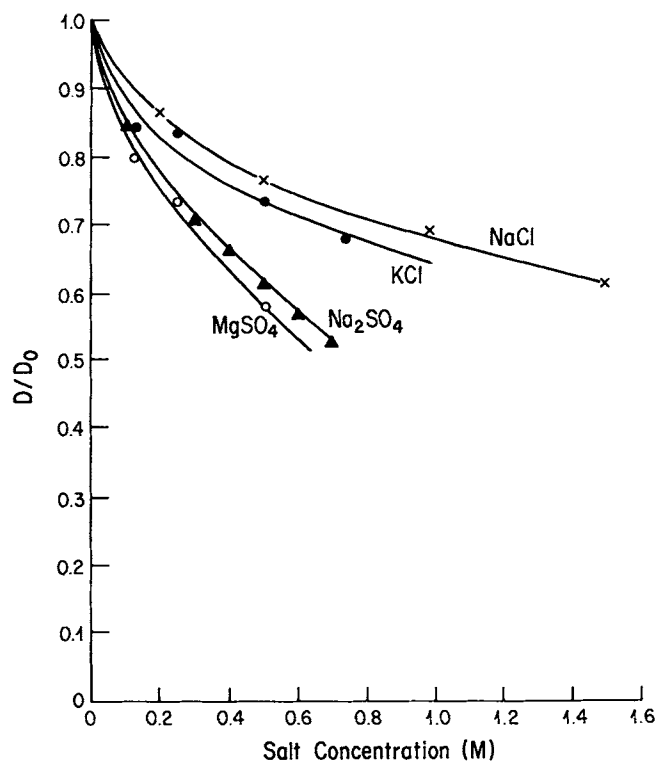

Figure 3. Relative oxygen diffusion coefficients as a function of salt concentrations in electrolyte solutions at room temperature.

electrolyte concentration on the diffusion coefficient decreases rapidly as the concentration increases. This, however, is inconsistent with the results reported by Ratcliff and Holdcroft[8] and Gubbins, Bhatia, and Walker.[9] By use of the Eyring's lattice model of the liquid, these authors proposed that the diffusion coef-

Table I. Oxygen diffusion coefficients in various electrolyte solutions at 22°C.

Salts / C (M) Variables	NaCl					KCl				
	0	0.2	0.5	1.0	1.5	0	0.125	0.25	0.5	0.745
$\dfrac{K^a}{D}$	9.50	10.94	12.34	13.77	15.20	9.28	10.98	11.13	12.60	13.58
$\dfrac{D}{D_o}$	1.0	0.868	0.770	0.690	0.625	1.0	0.845	0.834	0.737	0.683
D^b (× 10^5) (cm^2/s)	2.08	1.80	1.60	1.44	1.30	2.08	1.76	1.73	1.53	1.42

Salts / C (M) Variables	Na$_2$SO$_4$							MgSo$_4$		
	0	0.1	0.3	0.4	0.5	0.6	0.7	0	0.125	0.25	0.5
$\dfrac{K^a}{D}$	9.49	11.12	13.45	14.31	15.43	16.93	18.37	10.06	12.60	13.74	17.46
$\dfrac{D}{D_o}$	1.0	0.853	0.706	0.663	0.615	0.561	0.517	1.0	0.798	0.732	0.576
D^b (× 10^5) (cm^2/s)	2.08	1.77	1.47	1.38	1.28	1.17	1.08	2.08	1.66	1.52	1.20

[a] Different K/D values for pure water are due to different membranes used for different salts.

[b] Based on D_o = 2.08 × 10^{-5} cm^2/s, adjusted by the Wilke–Chang equation, and literature data of D_o = 2.10 × 10^{-5} cm^2/s at 25°C (refs. 2 and 13).

ficients of gas solutes in electrolyte solutions would vary approximately linearly with the electrolyte concentrations. Actually, the assumption they made for the lattice model that the presence of the electrolyte does not affect the lattice spacing, i.e., that the lattice spacing remains the same as that of pure water, appears crude. The induced electric field of ions alters the orientation of the dipole molecules of water, distorting the ice-like water structure and also compressing them (the electrostriction effect).

By considering the relation between viscosity and diffusion, Eyring and Jhon[10] developed an expression of the diffusion coefficient as:

$$D = \frac{\lambda_1 kT}{\xi \lambda_2 \lambda_3 \eta} \frac{d\ln a}{d\ln c} \simeq \frac{kT}{\xi \lambda \eta} \qquad (5)$$

since $d\ln a/d\ln c \simeq 1$ and λ_i's are similar in magnitudes. Parameter ξ, which is the number of the nearest neighbors of the diffusing molecule, is usually a constant. Therefore, at constant temperature, the diffusion coefficient, D, is inversely proportional to the product of the distance between two adjacent molecules, λ, and the viscosity of the solution, η.

Studying with several electrolyte solutions, Jones and Dole[11] have found the following empirical correlation to be valid at constant temperature,

$$\eta = \eta_0(1 + A\sqrt{c} + Bc) \qquad (6)$$

This has been modified by Asmus[12] as:

$$\eta = \eta_0(1 + A'\sqrt{I} + B'I) \qquad (7)$$

where $I = (1/2) \Sigma_i c_i z_i^2$ is the ionic strength of the electrolytes, and A, B, A', and B' are constants. The term $A'\sqrt{I}$ is usually important only at very low electrolyte concentrations, since $|A'|$ is usually much smaller than $|B'|$. Qualitatively, viscosities of the electrolyte solutions vary linearly with the ionic strength in the range of concern.

On the other hand, based on the theory of Debye and Hückel, every ion in the electrolyte solution is surrounded by an "ionic atmosphere" with an average charge opposite that of the "central ion." The thickness, or so-called characteristic distance, of the ionic atmosphere was found to be inversely proportional to the square root of the ionic strength. Similar effects should be expected with λ. Combining the effects of the ionic strength on viscosity and the distance between the diffusing molecule and as neighboring molecules, it can thus be expected that the diffusion coefficient varies linearly with the square root of the ionic strength of the solution rather than the concentration of the electrolytes.

Fig. 4 shows the results of the experimentally determined D/D_o as a function of $\sqrt{I}$. Agreement between the experimental results and the theoretical consideration is good. Mathematically, the results can be expressed as:
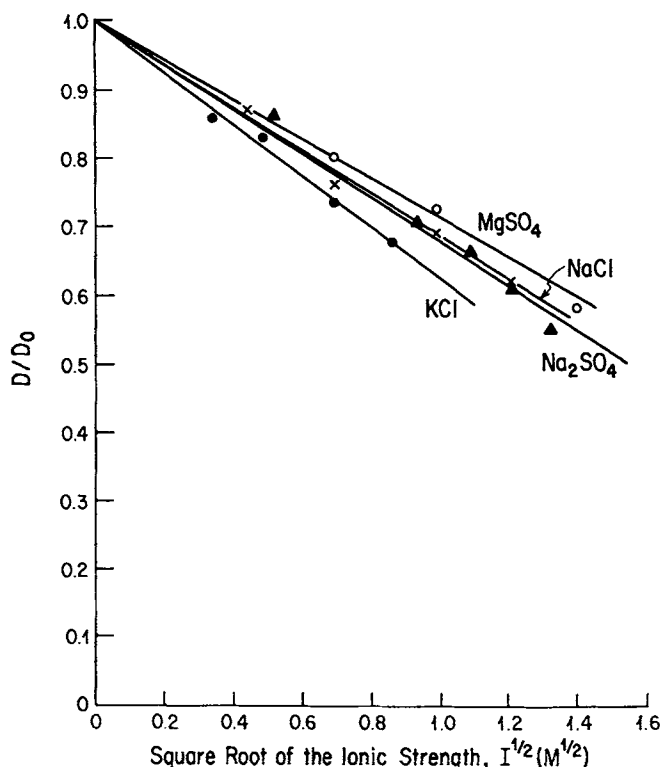
$$D = D_o(1 - f\sqrt{I}) \qquad (8)$$

Figure 4. Relative oxygen diffusion coefficients as a function of the square root of the ionic strength of electrolyte solution.

where f is the slope of the line and its value depends on the nature of the salt.

CONCLUSIONS

A method of measuring the oxygen diffusion coefficient in aqueous solutions was introduced. It is much easier and faster than other existing methods in terms of its operation. By measuring the steady-state concentrations of dissolved oxygen at two different depths with a commercially available polarographic oxygen electrode, the ratio of the diffusion coefficients of oxygen in liquid solutions to that in distilled water can be obtained.

According to experimental results, the oxygen diffusion coefficients in electrolyte solutions vary approximately linearly with the square root of the ionic strength of the electrolytes. This can be interpreted with Eyring's significant liquid structure theory. It is our opinion that further studies relating to the feature subject are needed.

NOMENCLATURE

A, A'	constants in eqs. (6) and (7)
B, B'	constants in eqs. (6) and (7)
C_{DO}	dissolved oxygen concentration in liquid solution (mol/L)
C_s	oxygen saturation concentration (mol/L)
C_I	oxygen concentration at liquid-membrane interface (mol/L)
C_{II}	oxygen concentration at membrane-electrode solution interface (mol/L)

C	salt concentration in electrolyte solution (mol/L)
c_i	concentration of ion i in electrolyte solution (mol/L)
D	oxygen diffusion coefficient in liquid solution (cm^2/s)
D_e	oxygen diffusion coefficient in the electrode solution in the probe (cm^2/s)
D_{eff}	effective oxygen diffusion coefficient for the probe, including the membrane and electrode solution (cm^2/s)
D_m	oxygen diffusion coefficient in membrane (cm^2/s)
D_o	oxygen diffusion coefficient in pure water (cm^2/s)
d_e	thickness of the electrode solution within the probe (cm)
d_{eff}	effective thickness ($= d_m + d_e$) (cm)
d_l	thickness of the liquid solution between the gas–liquid interface and the membrane (cm)
d_m	thickness of the membrane (cm)
f	slope as defined in eq. (8) (mol/L)$^{-1/2}$
I	ionic strength of the electrolyte solution (mol/L)
K	characteristic constant of oxygen probe ($= D_{\text{eff}}/d_{\text{eff}}$) (cm/s)
k	a constant
M	molarity (mol/L)
N	flux of oxygen (mol cm)/(L s)
T	temperature of the aqueous solution (K)
z_i	valence of ion i
ξ	effective number of molecules surrounding the diffusing molecule
λ	distance between the surrounding molecules and the diffusing molecule (cm)
η	viscosity of the electrolyte solution (P)
η_0	viscosity of the pure solvent (P)

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