BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 140—145 (1969)

Polarographic Studies of Dissolved Oxygen in DMSO-Water Mixtures

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(Received May 29, 1968)

The solubility and polarographic behavior of dissolved oxygen have been investigated in air-saturated DMSO-water mixtures at 25°C and 45°C. The first oxygen wave, which corresponds to one-electron reduction to superoxide ions in water-poor DMSO solutions of 0.1 M Et_4NClO_4, changes to a two-electron process in the range of water content between 10 and 30% because of the protonation reaction due to water. The rate of protonation is potential-dependent. The rate also depends on the species and the concentrations of the supporting electrolytes. The temperature effect is small. Using the solubility and polarographic data obtained, the polarographic diffusion coefficients of oxygen in the mixed solvent have been calculated.

The polarographic reduction of dissolved oxygen has been studied by a number of authors using different electrodes and solvents (for a survey, see Ref. 1). At tha dropping mercury electrode, dissolved oxygen in an aqueous solution usually gives two waves, each corresponding to a two-electron reduction. Recently, however, several authors have found that the reduction of oxygen in dipolar aprotic solvents occurs in two steps, and that the first wave is a one-electron process involving

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1) K. J. Vetter, "Elektrochemische Kinetik," Springer Verlag, Berlin (1961), p. 518; R. Takahashi, *Talanta,* **12,** 1211 (1965).

the formation of superoxide anion radicals.[2-7] The effects of acids[2,3,5] and metal cations[4,7] on oxygen waves in aprotic solvents have been studied, but a detailed investigation of the effect of water on the polarographic behavior of dissolved oxygen does not seem to have been undertaken yet. In the present work, we studied the behavior of oxygen in the mixed solvent of DMSO and water.

Apparatus and Reagents

Dc and ac polarograms were recorded with a Yanagimoto Polarograph, PA-102. The constant current source for chronopotentiometry was constructed from a high dc voltage source (225V) with large resistors. Potential-time curves were measured using a Shimadzu pH meter as a high input-impedance preamplifier and a Varicorder VR-100G as a voltage recorder. An H-type cell with a fine porosity sintered glass disk between the two compartments was used, except in the determination of the solubility of dissolved oxygen. In measurement, a sample solution was put in both compartments of the cell and aqueous SCE with a tip of fine porosity sintered glass disk was inserted in the reference compartment. Contamination from the aqueous SCE into the sample compartment of the H-type cell was negligible during measurement. The characteristics of the DME were $m=0.73$ mg/sec and $t=4.0$ sec at -0.4 V *vs.* SCE in a 0.1 M Et_4NClO_4 aqueous solution at 25°C. For the chronopotentiometric measurement, a glassy carbon disk electrode 3 mm in diameter was used. A mercury-coated rotating disk electrode with a diameter of 0.5 mm was prepared by plating gold on the surface of the platinum disk electrode and by amalgamating it. The electrode was rotated at 800 rpm in measuring the current-potential curves. The viscosity of the mixed solvent was measured with a Ostwald viscometer. Experiments were carried out at 25 ± 0.1°C or at 45 ± 0.1°C.

Dimethyl sulfoxide (DMSO) obtained from the Katayama Chemicals Co. was vacuum distilled twice. The water content just after distillation was less than 0.05%, as determined through a Karl Fischer titration. n-Bu_4NClO_4 was prepared from an aqueous solution of n-Bu_4NBr by adding an equivalent amount of concentrated perchloric acid, and was purified by recrystallization from ethanol solutions. n-Bu_4NBr was prepared by refluxing acetonitrile solutions of tri-*n*-butylamine and *n*-butyl bromide for 36 hr.[8] After evaporation of acetonitrile, n-Bu_4NBr was recrystallized several times from ethyl acetate. n-Pr_4NClO_4 was prepared by neutralizing 10% solutions of n-Pr_4NOH, obtained from the Wako Pure Chemicals Industries, Ltd., with perchloric acid and was purified by recrystallization from ethanol. Et_4NClO_4 was prepared by adding an equivalent amount of perchloric acid to Et_4NI in water and was recrystallized from water. Anhydrous $KClO_4$ was of analytical reagent grade and was used without further purification.

Results and Discussion

Solubility of Oxygen in DMSO-Water Mixtures. The concentration of dissolved oxygen in air-saturated DMSO-water mixtures was determined polarographically, because the application of the Winkler method was difficult for systems containing 0.1 M Et_4NClO_4. The dissolved oxygen in the air-saturated 0.1 M Et_4NClO_4 solution of $(100-x)$% DMSO - x%water mixture was determined as follows: In a 100 m*l* tall beaker, thermostated at 25°C or 45°C, 40.0 m*l* of 0.1 N NaOH, 5.0 m*l* of x% DMSO - $(100-x)$% water mixture and a magnetic stirrer were taken. The beaker was closed with a silicon rubber stopper with holes through which DME and aqueous SCE were passed, and with inlets and outlets for nitrogen and an inlet for the sample solution. After the solution was deaerated with nitrogen, the residual current was recorded between -0.3 and -0.5 V *vs.* SCE. Then, while the solution in the beaker was being stirred with a magnetic stirrer and nitrogen gas passed over the solution, 5.00 m*l* of the sample solution of 0.1 M Et_4NClO_4 in a $(100-x)$% DMSO - x% water mixture, which has been saturated with air in a thermostat controlled at 25°C or 45°C, was put with a pipette into the bottom of the beaker. After the solution has been sufficiently mixed, stirring was stopped and the current recorded between -0.3 and -0.5 V *vs.* SCE. By comparing the

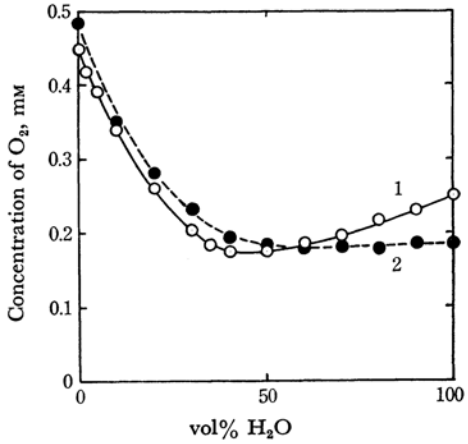

Fig. 1. Solubility of oxygen in air-saturated DMSO - water mixtures containing 0.1M Et_4NClO_4. Curve 1 is at 25°C and curve 2 at 45°C.

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[2] M. E. Peover and B. S. White, *Electrochim. Acta*, **11**, 1061 (1966); *Chem. Commun.*, **10**, 183 (1965).

[3] D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965).

[4] L. Johnson, K. H. Pool and R. E. Hamm, *ibid.*, **38**, 183 (1966).

[5] D. T. Sawyer and J. L. Roberts, Jr., *J. Electroanal. Chem.*, **12**, 106 (1966).

[6] M. E. Peover and J. S. Powell, *J. Polarog., Soc.*, **12**, 106 (1966).

[7] L. Johnson, K. H. Pool and R. E. Hamm, *Anal. Chem.*, **39**, 888 (1967).

[8] R. U. Lemieux and J. Hayami, *Can. J. Chem.*, **43**, 2162 (1965).

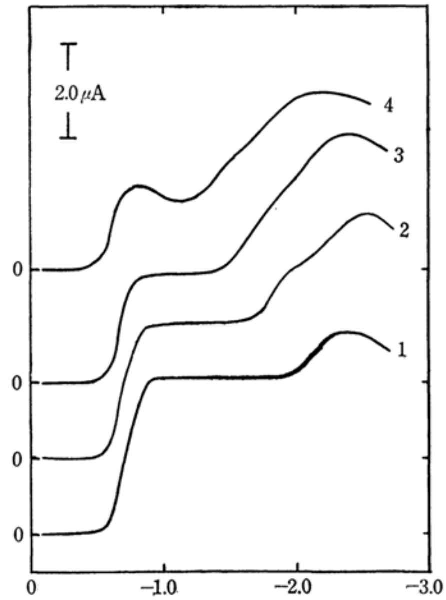
diffusion currents obtained for sample solutions of various values of *x*, the relative solubilities of oxygen in the air-saturated DMSO-water mixtures could be determined. The absolute solubilities could be calculated by measuring the diffusion current for a sample of air-saturated pure water and by assuming the solubilities of oxygen in the air-saturated pure water to be 0.254 mM at 25°C and 0.193 mM at 45°C, respectively.[9] The results are shown in Fig. 1 and Table 1. The reproducibility of the results was within ±2%. The solubility of oxygen at 25°C became minimum in the range 40 to 50% water. In a water-free, 0.1 M Et_4NClO_4 DMSO solution, the solubility was 0.44 mM, which is in agreement with the result of Sawyer and Roberts.[5] At 45°C, the solubility of oxygen was approximately constant over a water content of 50 to 100%. With a smaller water content, the solubility increased rapidly, as in the case at 25°C.

TABLE 1. SOLUBILITY AND DIFFUSION COEFFICIENT OF OXYGEN IN AIR-SATURATED DMSO-WATER MIXTURES CONTAINING 0.1M Et_4NClO_4

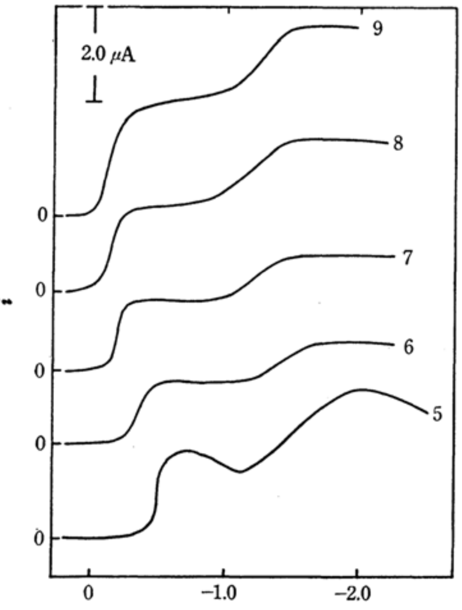
vol% H_2O	Solubility of O_2, mM	Viscosity η, cp	$D\times10^5$ cm^2/sec	$D\eta\times10^5$ $cp\cdot cm^2/sec$
		at 25°C		
0	0.44_6	1.95	(2.7_6)	(5.3_8)
10	0.34_0	2.55	1.7_2	4.3_8
20	0.26_0	3.25	1.3_5	4.3_9
30	0.20_5	3.65	1.1_9	4.3_5
40	0.17_5	3.42	1.0_9	3.7_3
50	0.17_5	2.95	1.1_5	3.3_9
60	0.18_2	2.26	1.3_9	3.1_4
70	0.19_5	1.81	1.4_9	2.7_0
80	0.21_8	1.42	1.5_5	2.2_0
90	0.23_0	1.05	1.7_8	1.8_7
100	0.25_1	0.85	1.9_9	1.6_9
		at 45°C		
0	0.49_2	1.39	(3.3_5)	(4.6_6)
10	0.35_2	1.72	2.4_7	4.2_5
20	0.28_1	1.97	2.1_6	4.2_6
30	0.32_3	2.18	1.8_6	4.0_5
40	0.19_3	2.07	1.9_1	3.9_5
50	0.18_6	1.83	1.9_2	3.5_1
60	0.18_0	1.44	2.0_4	2.9_4
70	0.18_2	1.14	2.3_0	2.6_2
80	0.17_9	0.93	2.5_6	2.3_8
90	0.18_4	0.72	2.7_4	1.9_7
100	0.18_5	0.60	2.9_0	1.7_4

D and *Dη* in water-free DMSO solution were determined from the height of the first wave.

The viscosities of DMSO-water mixtures containing 0.1 M Et_4NClO_4 were measured with an Ostwald viscometer at 25°C and 45°C. The results were almost in agreement with those of Cowie and Toporowski[10] determined for Et_4NClO_4-free mixed solvents.



(a) *E*, V *vs.* SCE



(b) *E*, V *vs.* SCE

Fig. 2. Oxygen waves in air-saturated DMSO-water mixtures containing 0.1M Et_4NClO_4 at 25°C.
Water contents are:
1, water-free; 2, 1%; 3, 6%; 4, 15%, 5, 25%; 6, 40%; 7, 60%; 8, 80%; and 9, 100%.

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[9] "Mizu no Bunseki (Analysis of Water)," ed. by Hokkaido Div. of Japan Soc. for Analytical Chemistry, Kagakudojin, Kyoto (1966), p. 181.

[10] J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, **39**, 2280 (1961).

Polarographic Behavior of Oxygen in Mixed Solvents. The curves in Fig. 2 are polarograms of dissolved oxygen in air-saturated 0.1 M Et_4NClO_4 solutions in DMSO-water mixtures. In a water-free solution, two waves were obtained at -0.77 and -2.2 V, respectively. The first wave corresponded to a one-electron reduction to superoxide anion radicals and the second wave to the formation of peroxide anions.[2-7] As reported in the literature,[4] the height of the second wave is smaller than that of the first, even after correction for change in drop-time. The second wave was very sensitive to a small amount of water and, in the presence of more than 0.1% water, the wave shifted to more positive potentials and the wave height was much increased. Increase in the second wave height occurred because peroxide ions were further reduced to hydroxyl ions. The effects of water on the half-wave potential of the first wave and on the potential at which the second wave began to occur are given in Fig. 3. When the water content was 6%, the first wave still corresponded to a one-electron reduction, but the total wave approximately to a four-electron reduction (formation of hydroxyl ions). If the water content became greater than 10%, the current at the beginning of the plateau of the first wave increased because some superoxide ions became protonated by water and were further reduced to peroxide ions. Thus, between a water content of 15 and 30%, a distinct minimum was obtained just before the second wave. When the water content was greater than 35%, the minimum disappeared and the first and the second waves became approximately equal in height, both corresponding to two-electron reductions. A similar minimum to that obtained in a 0.1M Et_4NClO_4 solution containing water between 15 and 30% was observed even in solutions containing other supporting electrolytes, such as 0.1M n-Bu_4NClO_4, 0.1M n-Pr_4NClO_4 and 0.1M $KClO_4$. The addition of surface active substances, halide ions and hydroxyl ions did not influence the shape of the oxygen wave. Moreover, such a minimum was obtained even at a mercury-coated disk electrode rotating at 800 rpm. This is probably due to the fact that the rate of the protonation reaction of superoxide ions is potential dependent, and the reaction is faster at more positive potentials. This potential dependence of the protonation reaction may be caused by a change in the surface concentration of superoxide anions with electrode potential: when the potential becomes more negative, negatively charged superoxide ions will be repelled more strongly from the electrode and the surface concentration will become smaller.

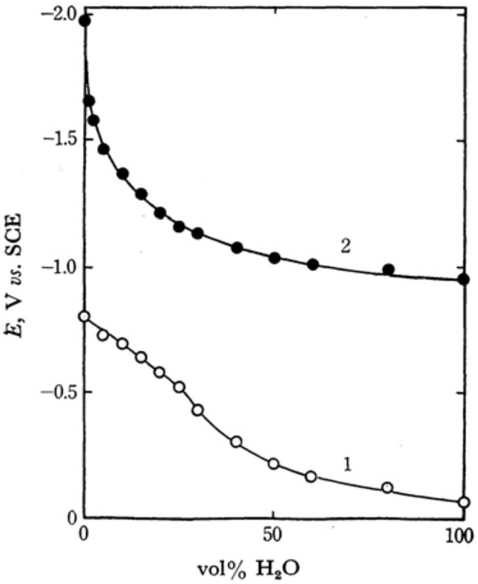

Fig. 3. Half-wave potential of the first wave (curve 1) and the potential at the beginning of the second wave (curve 2) of oxygen in air-saturated DMSO-water mixtures containing 0.1M Et_4NClO_4 at 25°C.

The ratio of the total wave height $(i_d)_t$ to that of the first wave $(i_d)_1$ was calculated after correction for change in drop time. A simple Ilkovic equation was assumed for this correction. The results are shown in Fig. 4. Curve 1 was obtained by measuring the height of the first wave at the potential at which the current became maximum, and curve 2 at the potential at which the current became minimum. From these curves, it is apparent that the total wave, which is approximately a two-

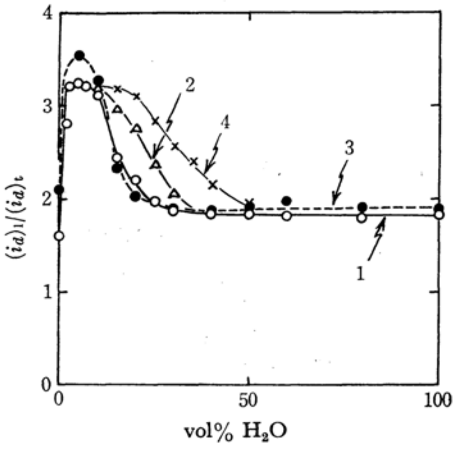

Fig. 4. Ratio of the total wave height to that of the first wave of dissolved oxygen in air-saturated 0.1M (curves 1, 2 and 3) and 0.01M (curve 4) Et_4NClO_4 solutions. Curves 1, 2 and 4 are at 25°C and curve 3 at 45°C. Curves 1 and 3 were obtained by measuring the maximum current of the first wave and curves 2 and 4 the minimum current.

electron reduction in water-free DMSO solution, approaches a four-electron reduction by the addition of several percents of water. The ratio does not become four and is much smaller, probably due to the fact that the drop time at the second wave is so small compared to that at the first wave that the diffusion current may significantly deviate from that given by the Ilkovic equation. The first wave, on the other hand, changed from a one- to a two-electron process between a water content of about 10 and 30%, both at 25°C (curves 1 and 2) and at 45°C (curve 3). The temperature effect was not large. The water content necessary to convert the first wave from a one-electron reduction to a two-electron reduction changed considerably with species and concentrations of supporting electrolytes. When the concentration of the supporting electrolyte decreased, the necessary water content increased, as in curve 4, Fig. 4. The necessary water content also increased with the species of supproting electrolyte in the following order (Fig. 5):

$KClO_4 < Et_4NClO_4 < n\text{-}Pr_4NClO_4 < n\text{-}Bu_4NClO_4$

The larger the ionic radius of the cation of the supporting electrolyte, the more water was necessary for the first wave to change from a one-electron process to a two-electron one.

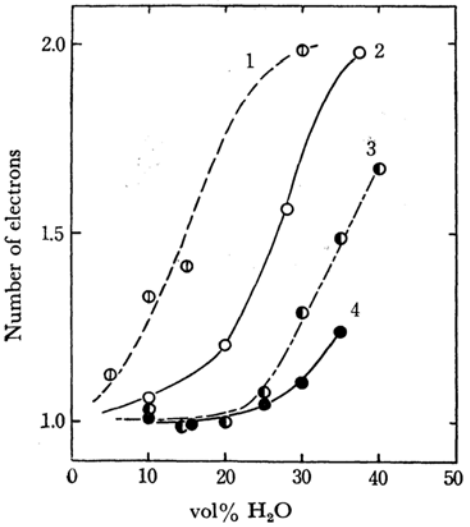

Fig. 5. Number of electrons taking part in the first wave of oxygen in various supporting electrolytes at 25°C.
Supporting electrolytes are: 1, 0.1M $KClO_4$; 2, 0.1M Et_4NClO_4; 3, 0.1M $n\text{-}Pr_4NClO_4$; and 4, 0.1M $n\text{-}Bu_4NClO_4$. Estimated from the current at the minimum of the first wave.

The addition of Et_4NOH to the solution containing water between 15 and 30% did not influence the behavior of the oxygen wave, though a big increase in pH was expected due to hydroxyl ions. From this result, the protonation reaction seems to occur as a reaction between a superoxide anion and a water molecule, and not through a reaction between a superoxide anion and a proton produced by the dissociation of water.

The first wave of oxygen in water-free dipolar aprotic solvents has been reported to be very reversible ac polarographically.[2,6] In an aqueous, unbuffered neutral solution, on the other hand, only a small ac wave can be obtained.[11] In this report, ac polarograms were measured in DMSO-water mixtures and the values of $i_{ac}/i_{dc}\cdot t^{1/2}$ were calculated as a measure of the reversibility of the first oxygen wave. The results are shown in Fig. 6.

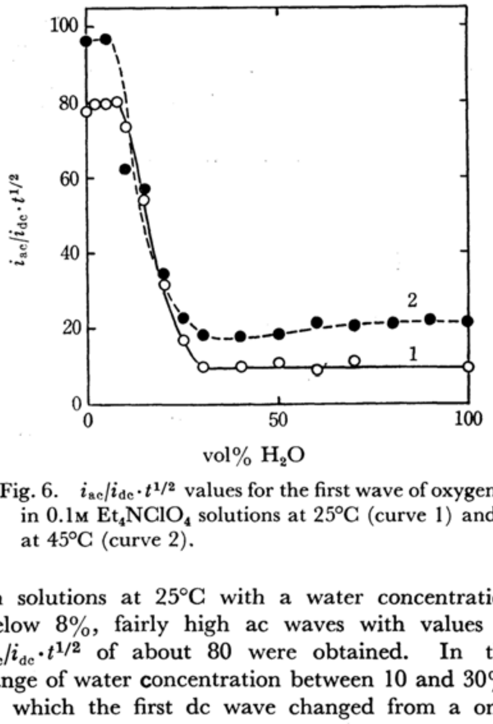

Fig. 6. $i_{ac}/i_{dc}\cdot t^{1/2}$ values for the first wave of oxygen in 0.1M Et_4NClO_4 solutions at 25°C (curve 1) and at 45°C (curve 2).

In solutions at 25°C with a water concentration below 8%, fairly high ac waves with values of $i_{ac}/i_{dc}\cdot t^{1/2}$ of about 80 were obtained. In the range of water concentration between 10 and 30%, in which the first dc wave changed from a one-electron to a two-electron process, the value of $i_{ac}/i_{dc}\cdot t^{1/2}$ decreased gradually, showing a decrease in the reversibility of the electrode reaction. At a water content above 30%, it was almost constant at 10. The ac polarographic behavior at 45°C was approximately similar to that at 25°C.

Reverse chronopotentiometry at the glassy carbon electrode seems to provide, though qualitatively, knowledge concerning the lifetime of superoxide anion radicals. In oxygen-saturated DMSO-water mixtures, potential-time curves for the reduction of oxygen at constant current were measured. Before the transition time of the first wave was attained, the direction of the current was reversed and the potential-time curves for the re-oxidation of the superoxide ions were recorded. From the chronopotentiograms obtained, the time intervals

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[11] S. Hacobian, *Australian. J. Chem.*, **6**, 211 (1953).

for the reduction (τ_{red}) and the transition time for the re-oxidation (τ_{ox}) were measured. In Fig. 7, the values τ_{ox}/τ_{red} are plotted for the case in which $\tau_{red}=30$ sec. Because the mechanisms of further reductions of superoxide anion radicals at the glassy carbon electrode are still unestablished and are probably somewhat different from those at the dropping mercury electrode, the results cannot be analysed theoretically to determine the lifetime of the radical anions. The value of τ_{ox}/τ_{red} for a water concentration below 10%, however, seems to show that the superoxide anions are fairly stable chronopotentiometrically. The rapid decrease of the ratio between 10 and 30% water indicates that superoxide ions disappear rapidly in water-rich solutions in agreement with the results of dc and ac polarography at the dropping mercury electrode.

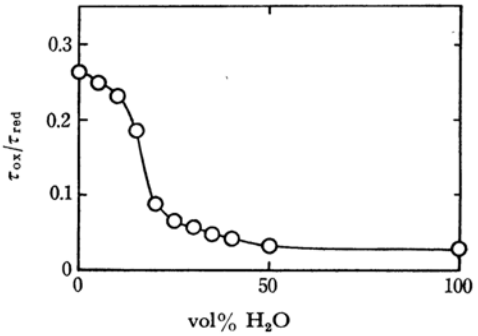

Fig. 7. Ratio of τ_{ox}/τ_{red} obtained by reverse chronopotentiometry at the glassy carbon electrode in oxygen-saturated 0.1M Et_4NClO_4 solutions. τ_{red} = 30 sec.

Polarographic Diffusion Coefficients of Dissolved Oxygen in Mixed Solvents. From the oxygen waves in DMSO-water mixtures, the polarographic diffusion coefficients was calculated using the modified Ilkovic equation:

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}(1 + AD^{1/2}m^{-1/3}t^{1/6}),$$

where the value of A was assumed to be 25. The limiting currents used in the calculation of these diffusion coefficients were confirmed to be diffusion-controlled by the linear proportionality of the currents to the oxygen concentration, and also to the square root of the height of the mercury reservoir. The results are shown in Fig. 8 and Table 1. Curves 1, 2 and 3 are the results at 25°C, and curve 1′ at 45°C. Curves 1 and 1′ were calculated using the total wave heights (assuming four-electron reduction), whereas curves 2 and 3 were calculated from the heights of the first wave. Here, the first wave was supposed to be a one-electron process at a water content below 5% (curve 2) and to be a two-electron process at a water content above 30% (curve 3). In these curves, the diffusion coefficients obtained by measuring the first wave are always larger than the values calculated from the total wave heights. This may be due to several reasons, such as the incompleteness of the diffusion current equation used, the occurrence of the reduction of a small amount of hydrogen peroxide at the potential at which the first wave height was measured, and the depletion effect of the depolarizer which is more pronounced at the potential of the total wave height because of the absence of appropriate maximum suppressors.[12] Moreover, when the water content is small (5% to 15%), the accuracy of the diffusion coefficients obtained from the total wave heights may decrease to some extent because the drop time is very small. Though the polarographic diffusion coefficients suffer from these limitations, they provide sufficient knowledge concerning their variation with composition of mixed solvent. From Fig. 8, the diffusion coefficient becomes a minimum at a water concentration between 30 and 50%, both at 25°C and 45°C. Curves 4 and 4′ are the products $D\eta$ of the diffusion coefficient and the viscosity of the solvent. Both at 25°C and 45°C, when the water content is greater than 30%, the value of $D\eta$ is not constant and increases almost linearly with decrease in water content, but below 30%, it is approximately constant.

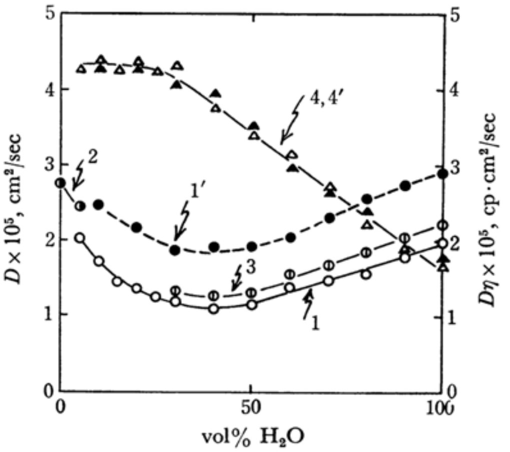

Fig. 8. Diffusion coefficient, D, of oxygen (curves 1, 2, 3 and 1′) and the product, $D\eta$, of the diffusion coefficient and the viscosity (curves 4 and 4′) of the solution containing 0.1M Et_4NClO_4. Curves 1, 2, 3 nd 4 are at 25°C and curves 1′ and 4′ at 45°C. Curves 1 and 1′ were obtained from the total wave heights, curves 2 and 3 from the first wave heights and curves 4 and 4′ were calculated using the values of curves 1 and 1′.

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[12] I. M. Kolthoff and K. Izutsu, *J. Am. Chem. Soc.*, **86**, 1275 (1964).