

Polarographic Investigation of Dissolved Oxygen in Nonaqueous Solvent

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In a common aprotic solvent, the dissolved oxygen is reduced to superoxide, and then to peroxide with tetraalkylammonium salt as the supporting electrolyte. With alkali metal ion as the supporting electrolyte, it is reduced further to form the third wave. All of these waves are controlled by the successive chemical reaction; namely if the products due to the successive reaction are stable, the reduction potential shifts to more positive direction. When the solvated ion of the supporting electrolyte is small, it forms stable complex with oxygen radicals, hence the reduction waves shift to positive potentials.

The polarographic reduction of oxygen has been investigated in a number of nonaqueous aprotic solvents. In most aprotic solvents such as dimethylformamide, dimethylsulfoxide and acetonitrile, molecular oxygen undergoes two step reduction at the dropping mercury electrode; in the first step, oxygen is reduced to the superoxide anion, and then reduced further to the peroxide anion in the second step. The reaction mechanism of the first wave has been investigated by many authors,¹⁻⁴⁾ however, little attention has been drawn to the second wave process. Only a few papers by Johnson *etc.*⁵⁾ describe that the second reduction wave in 0.1 M Et₄NClO₄-DMSO solution is significantly affected by the addition of alkali metal ions. We found that oxygen was reduced further to form the third wave in the solution of alkali metal ion as the supporting electrolyte.

This paper deals with the results of detailed investigation on the electrolytic reduction of oxygen in aprotic organic solvents, especially with regard to the second and the third waves.

Apparatus and Reagents

Reagents. Dimethylacetamide (DMA) was purified by the double distillation under reduced pressure of nitrogen gas, first over calcium hydride and second over *p*-toluenesulfonic acid. Hexamethylphosphoramide (HMPA) and propylene carbonate (PC) were purified following the method in the previous paper.⁶⁾ Tetraalkylammonium perchlorates and alkali metal perchlorates were prepared and purified according to the method described in the previous paper.⁶⁾ Dodecyltrimethylammonium chloride was obtained commercially. The polarogram of oxygen was recorded in a solution which was saturated with dried air: air was dried by passing through concentrated H₂SO₄ bubblers before use.

Apparatus. A Yanagimoto polarograph, Type P 8-DP was used to record most current-potential curves. In AC polarography, the PAR (Princeton Applied Research Cooperation, Princeton, N. Y.) polarograph with IR-compensation using three electrodes system was used. The H cell used was the same as in the previous paper.⁶⁾ The silver-silver perchlorate electrode Ag/0.1 M AgClO₄ in the solvent was used as the reference electrode. The potential of the reference electrode against the aqueous SCE was +0.439 V, +0.750 V and +0.360 V in DMA, PC, and HMPA, respectively. The DME (A, B) used had *m* values of 1.61_s, 0.80_s mg/s at an open circuit and *h*=62 cm in DMA. The life times at -2.4 V in 0.05 M Et₄NClO₄-DMA were 3.21_s, 2.64_s, respectively. The DME used had *m* values of 0.63_s, and 0.89_s mg/s at an open circuit and *h*=65 cm, in PC and

HMPA, respectively. The drop time at -2.4 V in 0.05 M Et₄NClO₄-PC solution was 1.88_s. The drop time at -2.6 V in 0.05 M Et₄NClO₄-HMPA solution was 1.70_s.

Determination of the concentration of oxygen in nonaqueous solution by the iodometric method of Winkler is less satisfactory, especially PC is hardly soluble with water. Assuming that the solvation, if any, of the oxygen molecule should not be radically different in DMA, HMPA, PC, and DMSO, Walden's rule may be applied for the calculation of an approximate diffusion coefficient of oxygen in DMA, HMPA and PC as solvent. At 25 °C the viscosity of DMSO⁷⁾ is 1.95 cp, while those of DMA,⁷⁾ HMPA⁹⁾ and PC¹⁰⁾ are 0.92, 3.23 and 2.53 cp. The diffusion coefficient of oxygen in DMSO⁷⁾ is *ca.* 2.76 × 10⁻⁵ cm² s⁻¹. Hence from Walden's rule the diffusion coefficients of oxygen in DMA, HMPA and PC should be 5.85, 1.67, 2.13 × 10⁻⁵ cm² s⁻¹. Substituting into the Ilkovič equation, the concentrations of oxygen are *ca.* 0.923, 1.29, and 1.03 mM in DMA, HMPA and PC solution, respectively.

Results

Reduction of the Dissolved Oxygen in DMA. The dissolved oxygen gave three waves in DMA in the presence of 0.05 M alkali metal ion as the supporting

TABLE 1. POLAROGRAPHIC DATA OF OXYGEN IN DMA AT 25 °C

	<i>r_s</i> ^{a)}	(<i>E</i> _{1/2}) ₁	(<i>E</i> _{1/2}) ₂	(<i>E</i> _{1/2}) ₃
Me ₄ N ⁺	2.56	-1.35(1.18)	-1.75(0.78)	-2.52(0.01)
Et ₄ N ⁺	2.69	-1.40(1.13)	-2.15(0.38)	
Pr ₄ N ⁺	3.41	-1.40(1.13)	-2.70(-0.17)	
Bu ₄ N ⁺	3.90	-1.40(1.13)	-2.96(-0.43)	
Hex ₄ N ⁺	4.74	-1.40(1.13)		
TDDMB ion	4.80	-1.40(1.13)	-2.00(0.53)	
Dodecyltrimethylammonium ion		-1.41(1.12)	-1.91(0.62)	-2.63(-0.10)
Li ⁺	4.18	Max.		
Na ⁺	3.5	-1.31(1.22)	-1.71(0.82)	Max.
K ⁺	3.5	-1.31(1.22)	-1.82(0.71)	-2.37(0.16)
Rb ⁺	3.55	-1.31(1.22)	-1.81(0.72)	-2.22(0.31)
Cs ⁺	3.38	-1.31(1.22)	-1.57(0.96)	-2.04(0.49)

Underscripts of 1, 2, and 3 mean the first, the second and the third wave, respectively. Half-wave potentials in parentheses are referred to the reduction potential of rubidium ion. Concentration of the supporting electrolyte is 0.05 M. a); Ref. 7), 8).

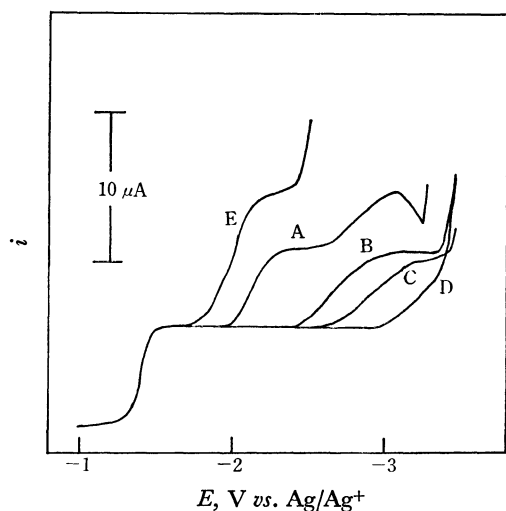


Fig. 1. Polarograms of dissolved oxygen in R_4NClO_4 -DMA solutions. Supporting electrolyte: A) Et_4NClO_4 , B) Pr_4NClO_4 , C) Bu_4NClO_4 , D) HeX_4NClO_4 and E) TDDMB ion. Each in 0.05 M. With the DME (A).

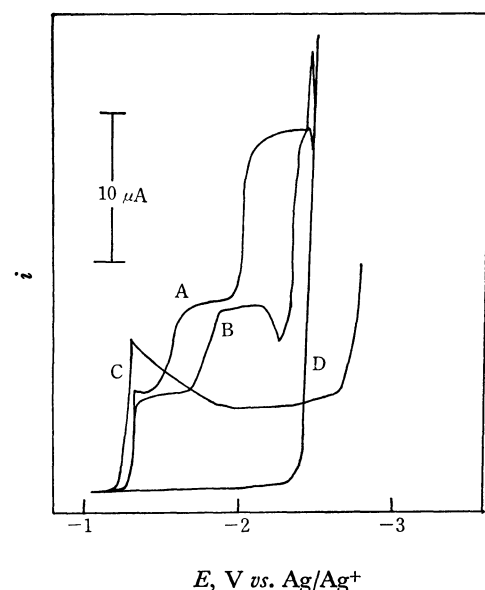


Fig. 2. Polarograms of dissolved oxygen in alkali metal ion-DMA solution. Supporting electrolyte: A) $CsClO_4$, B) $KClO_4$ and C) $LiClO_4$. Each in 0.05 M. D) Residual current in $CsClO_4$ -DMA solution. With the DME (A).

electrolyte, corresponding to one-electron, one-electron, and two-electrons process respectively; a maximum appeared at the third wave when sodium ion was used as the supporting electrolyte. When lithium ion was used as the supporting electrolyte, only the first wave was observed. When 0.05 M tetraalkylammonium ion was used as the supporting electrolyte, the dissolved oxygen gave two waves, each corresponding to one-electron process. Their half-wave potentials are summarized in Table 1. Some typical polarograms are shown in Figs. 1 and 2.

The half-wave potential shifted to negative side with

the increase of the radius of the solvated ion. The extent of the shift was the least pronounced with the first wave and more pronounced with the second wave. The third wave was most influenced by the radius of the supporting electrolyte cation, although in many cases except with cesium, rubidium, potassium, tetramethylammonium, and dodecyltrimethylammonium ion, the third wave shifted too negative to be observable before the final rise. In the case of alkali metal ion used as the supporting electrolyte, oxygen is reduced most easily in the presence of cesium ion and least in the presence of lithium ion. With tetraalkylammonium ion as the supporting electrolyte, oxygen is reduced most easily in the presence of tetramethylammonium ion. With the increase of the size of the solvated ion, the shift of the half wave potential to negative becomes pronounced. With 0.05 M tetrahexylammonium ion as the supporting electrolyte, the second wave shifts too negative to appear before the final rise. However, with 0.05 M tetradecyl-dimethyl-benzylammonium (TDDMB) ion, oxygen gave a well-defined second wave, although the size of the cation is larger than tetrahexylammonium ion.

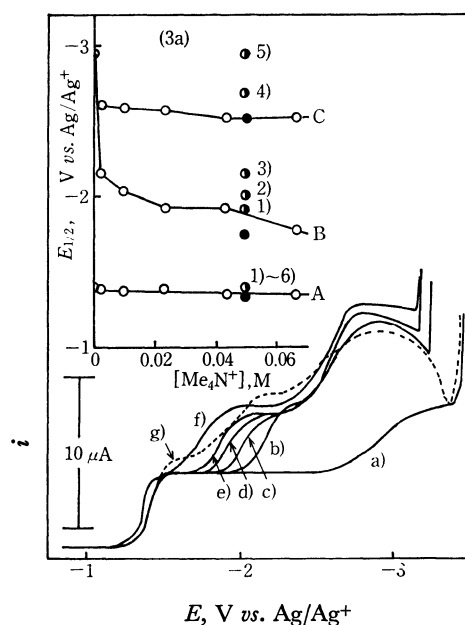


Fig. 3. Effect of methyl groups on the reduction of oxygen in 0.05 M Bu_4NClO_4 solution. With the DME (B).

Me_4NClO_4 concentration; a) 0, b) 2.5, c) 10.0, d) 24.0 and e) 43.6 mM.

f) 0.05 M Me_4NClO_4 solution, g) 0.05 M dodecyltrimethylammonium chloride solution.

Fig. 3a. Half wave potential of oxygen's reduction and concentration of tetramethylammonium ion.

○ A: the first wave, B: the second wave, C: the third wave in mixed with Me_4N^+ and Bu_4N^+ supporting electrolyte solution, ● 0.05 M Me_4NClO_4 solution, ○ 0.05 M other tetraalkylammonium ion solution; 1) dodecyltrimethylammonium ion, 2) TDDMB ion, 3) tetraethylammonium ion, 4) tetrapropylammonium ion, 5) tetrabutylammonium ion, 6) tetrahexylammonium ion. 1)~5) the first and the second waves, 6) only the first wave.

The presence of methyl groups may be responsible for the oxygen reduction at a relatively positive potential. Figures 3 and 3a show that the half wave potentials of the second wave of oxygen shift to the positive potential with the increase of the concentration of tetramethylammonium ion and that the numbers of methyl groups in the large cation are also responsible for the positive shift (See the cases of TDDMB ion and dodecyltrimethylammonium ion used as the supporting electrolyte).

The effect of the supporting electrolyte cation on AC polarograms was also examined. The first peak is relatively sharp and high showing that the process is reversible. The peak height of the second wave is about one tenth of that of the first wave, and its shape is distorted. This fact suggests that the process is irreversible. The third peak is not appearing in AC polarogram.

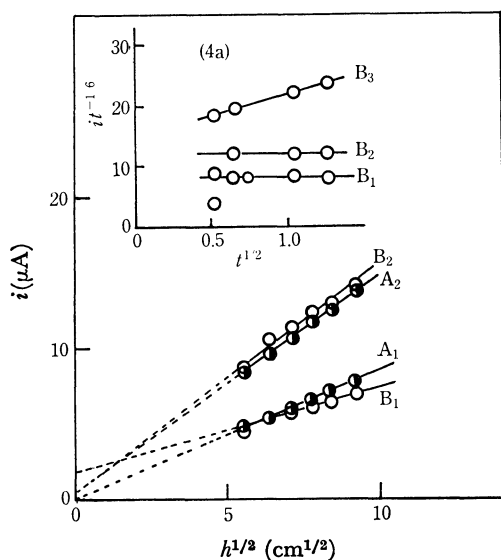


Fig. 4. Change of the limiting currents with the height of the mercury column in DMA solution. Supporting electrolyte: A) Et_4NClO_4 and B) CsClO_4 . Each in 0.05 M. Underscript 1, 2, and 3 mean the first, the second and the third wave. With the DME (A).

Fig. 4a. The relationship between $it^{-1/6}$ and $t^{1/2}$ in 0.05 M CsClO_4 -DMA solution.

Figure 4 shows the relationship between the square root of mercury height and the limiting current of oxygen in tetraethylammonium perchlorate and cesium perchlorate as the supporting electrolyte. With tetraethylammonium ion, the first wave is diffusion-controlled, and the second wave may include a little kinetic current. With cesium ion as the supporting electrolyte, both the first and the second waves may include a little kinetic current. At the potential of the third wave, the drop time increased extraordinary, therefore in Fig. 4a, the values of $it^{-1/6}$ are plotted against $t^{1/2}$ using the mechanical drop time controller. Here, i is the limiting current in μA ; t is the controlled drop time. For the first and the second waves, the values of $it^{-1/6}$ are almost independent of $t^{1/2}$, as is to be expected almost for the diffusion-controlled current,

but a little kinetic current. For the third wave, however, the values of $it^{-1/6}$ increase with an increase of $t^{1/2}$, showing that a kinetic factor is involved. This conclusion agrees well with the results of AC polarograms and Cyclic voltammograms as the following mention.

With the addition of water in the solution of 0.05 M tetrahexylammonium perchlorate in DMA, the second wave of oxygen begins to appear. With the increase of the concentration of tetrahexylammonium perchlorate over 0.075 M, the second wave also begins to appear.

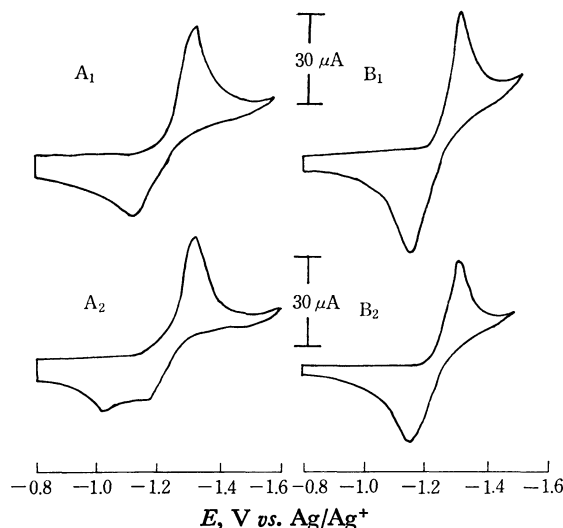


Fig. 5. Cyclic Voltammetry of oxygen in DMA solution. Supporting electrolyte: A) KClO_4 and B) CsClO_4 . Each in 0.05 M. Scan rate: 1, 100 mV/s and 2, 50 mV/s. Mercury drop is 0.1 μl .

Figure 5 demonstrates the cyclic polarograms of oxygen in the solutions of cesium perchlorate and potassium perchlorate.

When tetraethyl or tetrabutylammonium perchlorate is used as the supporting electrolyte, electrode process of the first wave of oxygen is reversible, as has been studied already.¹¹⁾ With alkali metal perchlorate as the supporting electrolyte, the process, however, is not fully reversible: Figure 5 shows that the anodic peak appears at fairly more positive potential than the cathodic peak.

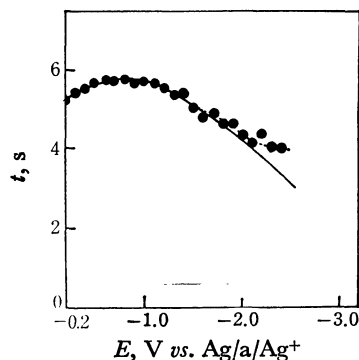


Fig. 6. Electrocapillary curve in 0.05 M CsClO_4 -DMA solution.

—●— With O_2 .
- - - Without O_2 . With the DME (A).

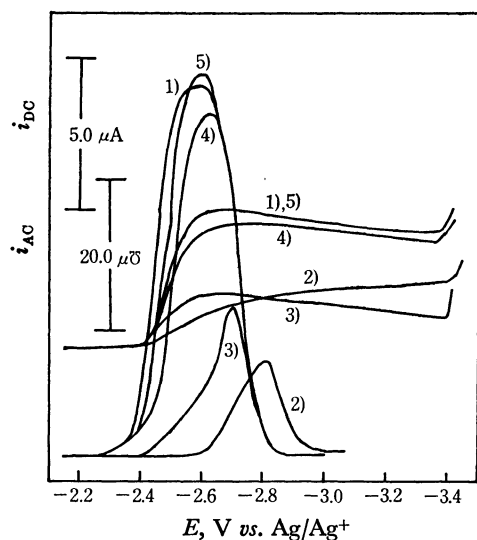


Fig. 7. Effect of oxygen on the reduction of 2.85 mM potassium ion in 0.05 M Bu_4NClO_4 -DMA solution. 1) nitrogen gas bubbled to remove oxygen thoroughly 2) air- O_2 saturated, 3), 4), and 5) nitrogen gas bubbled for 5, 10, 30 s in 2) solution, respectively. Gas flow rate: 12.10 ml/s. With the DME (B).

In the second and the third waves, no anodic peak appears probably because the successive chemical reactions will make the process irreversible.

Figure 6 shows the electrocapillary curves, in the presence and absence of oxygen in 0.05 M cesium perchlorate-DMA solution. In the figure, at a more negative potential than -2.0 V, the drop time is larger in the presence of oxygen than that in the absence. However, the difference can not be seen with the tetraalkylammonium ion as the supporting electrolyte.

Figure 7 shows that the reduction of alkali metal ion

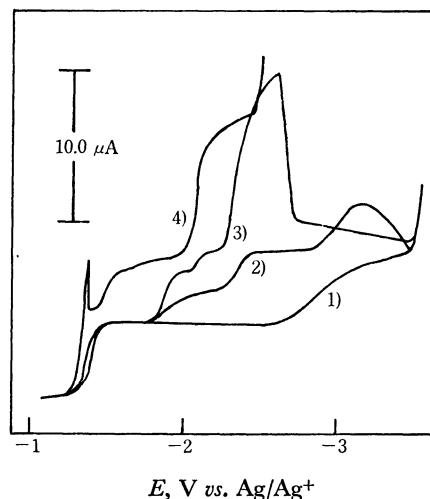


Fig. 8. Effect of the cesium ion on the reduction of oxygen in 0.05 M Bu_4NClO_4 -DMA solution. Cesium perchlorate concentrations are; 1) 0, 2) 2.5 and 3) 5.0 mM. 4) is 0.05 M CsClO_4 solution. With the DME (B).

is disturbed by the presence of oxygen.

The third wave of oxygen appeared in the presence of alkali metal ion in the tetraalkylammonium ion solution (Fig. 8).

Reduction of the Dissolved Oxygen in HMPA or PC.

The values of the half-wave potentials of oxygen in HMPA and in PC are tabulated in Table 2.

In HMPA, similar results to those in DMA are obtained. However, with 0.05 M sodium perchlorate, the second wave overlaps with the third wave which is accompanied by a maximum. With 0.05 M lithium perchlorate, the second wave can be seen. The dependence of negative shift of each waves upon the size

TABLE 2. POLAROGRAPHIC DATA OF OXYGEN IN HMPA AND PC AT 25 °C

		r_s^a	$(E_{1/2})_1$	$(E_{1/2})_2$	$(E_{1/2})_3$
HMPA	Me_4N^+	3.22	-1.35^b (1.00)	-1.67^b (0.68)	
	Et_4N^+	2.73	-1.32 (1.03)	-1.89 (0.46)	
	Pr_4N^+	3.73	-1.32 (1.03)	-2.08 (0.27)	
	Bu_4N^+	4.33	-1.32 (1.03)	-2.35 (0.00)	
	Hex_4N^+	5.68	-1.33 (1.02)		
	TDDMB ion		-1.27 (1.08)	-1.75 (0.60)	
	Li^+	4.88	$(-1.36)_{\text{max}}$	-1.92 (0.43)	
	Na^+	4.38	-1.32 (1.03)	$(-2.0)_{\text{max}}$	
	K^+	4.20	-1.24 (1.11)	-1.71 (0.64)	-2.13 (0.22)
	Rb^+	4.20	-1.22 (1.13)	-1.66 (0.69)	-2.05 (0.30)
	Cs^+	3.98	-1.17 (1.18)	-1.52 (0.83)	-1.86 (0.49)
PC	Me_4N^+	2.18	$(-1.61)_{\text{max}}$	-2.31^b (0.46)	
	Et_4N^+	2.34	-1.64 (1.13)	-2.45 (0.32)	
	Bu_4N^+	3.47	-1.62 (1.15)	-2.92 (-0.15)	
	Hex_4N^+		-1.62 (1.15)	-3.31 (-0.54)	
	TDDMB ion		$(-1.54)_{\text{max}}$	b)	
	Li^+	3.37	$(-1.24)_{\text{max}}$		
	Rb^+	2.31	$(-1.58)^c$ (1.19)	$(-2.26)^c$ (0.51)	
	Cs^+		$(-1.47)_{\text{max}}$		

Subscripts of 1, 2, and 3 mean the first, the second and the third wave, respectively. Concentration of the supporting electrolyte is 0.05 M. a); Ref. 9) and 12). b); Measurements are difficult. c); With the controlled drop time 0.40 s used in Fig. 10.

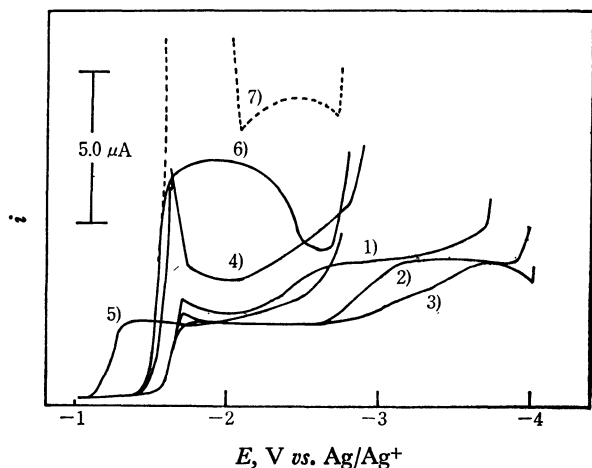


Fig. 9. Polarograms of dissolved oxygen in PC solution. Supporting electrolyte; 1) Et_4NClO_4 , 2) Bu_4NClO_4 , 3) $\text{Hex}_4\text{NClO}_4$, 4) TDDMB-perchlorate, 5) LiClO_4 , 6) RbClO_4 and 7) CsClO_4 . Each in 0.05 M.

of the cation is more remarkable in HMPA than that in DMA.

In PC, generally oxygen is more easily reduced than in DMA or HMPA. (See the values of half-wave potentials referred to the reduction potential of rubidium ion in Tables 1 and 2). The typical results are shown in Fig. 9. Even in 0.05 M tetrahexylammonium ion as the supporting electrolyte, oxygen gave two waves. With alkali metal ion such as cesium or rubidium ion as the supporting electrolyte, the reduction products of oxygen react with them more strongly in PC than in DMA or HMPA. At the potential of the first wave, the strong adsorption of the reaction product occurs and the drop time becomes 1.3 times larger than that with tetraalkylammonium ion. If polarograms are measured by controlling the drop time of the DME to be very short (0.40 s) using a mechanical

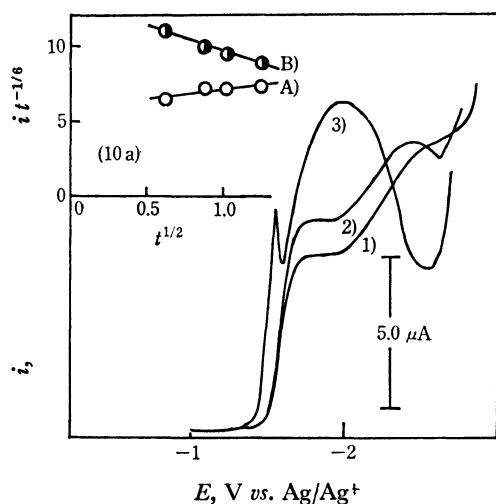


Fig. 10. Polarograms of dissolved oxygen in 0.05 M RbClO_4 -PC solution. Using the controlled drop time: 1) $t=0.40$, 2) $t=0.80$ s and 3) natural drop time.

Fig. 10a. The relationship between $it^{-1/6}$ and $t^{1/2}$ of Fig. 10.

A) the first wave, B) the second wave

drop time controller, well-defined two waves appear. (Fig. 10)

From Fig. 10a which shows the relationship between $it^{-1/6}$ and $t^{1/2}$, both the first and the second waves may be concluded to be kinetic in nature.

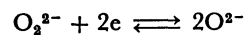
The most important determining factor influencing these waves is the degree of solvation of the supporting electrolyte cations in the solvents. The solvation is known to become stronger in the order: $\text{PC} \ll \text{DMA} < \text{HMPA}$.

Discussion

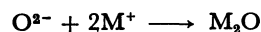
When tetraalkylammonium perchlorate is used as the supporting electrolyte, molecular oxygen is carried to the electrode surface by diffusion and is reduced to the superoxide ion by one-electron process, followed by further one-electron reduction process to the peroxide ion. Complex formation between the anion radical and tetraalkylammonium cation influences the reduction potential of oxygen and the reversibility of the process. In the first wave, the process is reversible and diffusion-controlled and in the second wave, process is irreversible because of the presence of successive chemical reaction.

When alkali metal perchlorate is used instead as the supporting electrolyte, oxygen is reduced similarly as in the case of tetraalkylammonium perchlorate, but the superoxide, the reaction product of the first wave and the peroxide, that of the second wave, both react consecutively with alkali metal ions. Therefore, the first and the second waves appear as kinetic current. The fact that the reduction of alkali metal ion is disturbed by the presence of trace of oxygen (Fig. 7) also indicates the presence of the consecutive reaction between the oxygen anion radicals and the alkali metal ions.

Moreover, when sodium, potassium, rubidium and cesium perchlorates are used as the supporting electrolyte, a third new wave appears at the potential a little in advance to their final rise (the metal reduction); the reduction seemed to proceed by two electron process. (Fig. 2) The reduction process for the third wave may therefore be written as;



From the behaviors of the third wave, which is extremely irreversible and kinetically controlled and from the facts that the third wave appears in the presence of alkali metal ions, it may be concluded that the following consecutive reaction may be taking place at the electrode solution interface;



In the solution containing alkali metal ions, the drop time is remarkably increased by the presence of air. It is also due to the fact that chemical reaction between oxygen anion radical and alkali metal ion occurred in the electrical double layer or on the electrode surface strongly.

The chemical reactions mentioned above seem to correlate closely with the size of the solvated ions of the supporting electrolyte. In spite of a large radius

of TDDMB ion, however, the half-wave potential of oxygen is relatively positive in both HMPA and DMA. The presence of methyl groups may be responsible for the oxygen reduction at a relatively positive potential. (Figs. 3 and 3a).

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