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Polarographic Investigation of Alkali Metal Ions in Hexamethylphosphoramide

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The polarographic behavior of alkali metal ions in hexamethylphosphoramide (HMPA) has been found to be greatly influenced by the cations of the supporting electrolytes. With 0.05 M Et_4NClO_4 as the supporting electrolyte, cesium and rubidium ions give diffusion-controlled, reversible waves at -2.32 and -2.35 V, respectively, *vs.* the Ag/0.1 M $AgClO_4$ electrode, but sodium and lithium ions are not reduced until the reduction of the supporting electrolyte (-3.1 V). The potassium ion gives a wave at -2.37 V with a limiting current controlled by the rate of the preceding process. In 0.05 M Bu_4NClO_4 solutions, the reduction wave of the potassium ion is diffusion-controlled, but that of the sodium ion is kinetic and is very small. The lithium ion is not reduced until -3.1 V. In 0.05 M $LiClO_4$, even the sodium ion is reduced reversibly with $E_{1/2}$ at -2.47 V, while the reduction of the lithium ion starts from -2.6_5 V. In mixed supporting electrolytes, the presence of the tetraethylammonium ion is the determining factor of the electrode processes. From the measurements of the electrocapillary curves and of the conductivities, the effect has been attributed to the change in the double-layer properties with the cations of the supporting electrolytes.

Hexamethylphosphoramide(HMPA) is a dipolar aprotic solvent which is often used for organic reactions.[1] It has a highly basic character and solvates strongly to various metal ions.[2] Moreover, it can dissolve alkali metals to yield a blue solution; this solution has been attributed to the formation of solvated electrons.[3]

Voltammetric study at a rotated platinum electrode has been carried out by Dubois *et al.*[4] in HMPA and its mixtures with water. They used lithium and sodium perchlorates as the supporting electrolytes and observed that the behavior of the residual current-potential curves obtained in these two supporting electrolytes differ considerably from each other.

In the present study, the polarographic behavior of alkali metal ions has been investigated in order to elucidate some of the solvation phenomena of these ions in HMPA. The reductions of alkali metal ions in this solvent, being different from those in other aprotic solvents,[5] are greatly influenced by the supporting electrolyte. This effect was found to be due to the change in the double-layer properties with the cation of the supporting electrolyte.

Apparatus and Reagents

Apparatus. The DC polarograms were recorded with a Yanagimoto three-electrode polarograph, Type P8-DP, and the AC polarograms, with a Yanagimoto polarograph, Type 102. An H-type polarographic cell with a fine-porosity sintered glass disc between the two compartments was used. All the potentials were referred to a freshly-prepared Ag/0.1 M $AgClO_4$ (HMPA) electrode, which had a potential of $+0.36$ V *vs.* aq. SCE when both electodes were immersed in HMPA-0.05 M Et_4NClO_4. A platinum wire served as an auxiliary electrode. The dropping mercury electrodes had the following characteristics in HMPA-0.05 M Et_4NClO_4 and at the mercury head of 62 cm: the A electrode, $m=1.72$ mg/sec with the circuit open and $t=1.40$ sec at -2.6 V *vs.* the Ag/Ag^+ electrode, and the B electrode, $m=1.88$ mg/sec and $t=1.39$ sec. Except otherwise described, the A electrode was used. Most measurements were carried out at 25°±0.1°C.

Reagents. The cesium and rubidium perchlorates were prepared by adding silver perchlorate to the respective chloride solutions. The sodium perchlorate was prepared by recrystallizing it from its aqueous solution at 70—80°C. The potassium and lithium perchlorates were obtained commercially. All of these alkali perchlorates were vacuum dried at 200°C. The tetraethylammonium perchlorate (Et_4NClO_4), tetrapropylammonium perchlorate (Pr_4NClO_4), and tetrabutylammonium perchlorate (Bu_4NClO_4) were prepared following the procedures in the previous reports[6] and were dried at 80°C under a vacuum. Tetramethylammonium perchlorate (Me_4NClO_4) was prepared from $AgClO_4$ and Me_4NBr and was recrystallized from water.

The HMPA was a product of the Nippon Oil Seal Co., Ltd. It was refluxed over barium oxide under reduced pressure for several hours and then vacuum-distilled. The middle fraction, about 70%, was collected (bp *ca.* 90°C). It was refluxed again over metallic sodium and vacuum-distilled from it. The distillations were carried out with an adiabatic vacuum fractional-distillation column (Shibata Chemical Apparatus Mfg. Co., Ltd.). The HMPA thus obtained gave a specific conductivity of $3—4\times10^{-8}$ ohm^{-1} cm^{-1}, and the water content, as determined by Karl Fischer titration, was approximately 0.01%. It was also confirmed to be pure enough both polarographically and UV-spectrophotometrically. The potential range applicable with a DME was from -0.1 V to -3.1 V *vs.* the Ag/Ag^+ electrode in HMPA-0.05 M Et_4NClO_4. Because the contact of HMPA with air produces an impurity which interferes with the polarographic investigation, the fresh distillate was usually used within a few hours after distillation. Storing at the temperature of dry ice and under a nitrogen atmosphere or under a vacuum was effective in keeping the distillate fresh for more than 24 hr.

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* Electrochemical Studies in Hexamethylphosphoramide. I.

[1] For review, see H. Normant, *Angew. Chem.*, **79**, 1029 (1967); *ibid., Int. Ed. Engl.*, **6**, 1046 (1967).

[2] V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer Verlag, Wien (1968).

[3] J. M. Brooks and R. R. Dewald, *J. Phys. Chem.*, **72**, 2655 (1968) and the references cited therein.

[4] J. E. Dubois, P. C. Lacaze, and A. M. de Fiquelmont, *Compt. Rend.*, **262C**, 181, 249 (1966).

[5] J. Broadhead and P. J. Elving, *J. Electrochem. Soc.*, **118**, 63 (1971) and the references cited therein.

[6] T. Fujinaga, K. Izutsu, K. Umemoto, T. Arai, and K. Takaoka, *Nippon Kagaku Zasshi*, **89**, 105 (1968).

Results and Discussion

Reductions of Alkali Metal Ions in Tetraalkylammonium Perchlorates as the Supporting Electrolytes. Cesium and Rubidium Ions: With 0.05 M tetraalkylammonium perchlorates as the supporting electrolytes, cesium and rubidium ions give diffusion-controlled, reversible reduction waves at −2.32 and −2.35 V respectively *vs.* the Ag/Ag$^+$ electrode. The reversibility of the waves was also confirmed AC polarographically. The results are summarized in Table 1 and Fig. 1.

Potassium Ion: When Bu_4NClO_4 or Pr_4NClO_4 is used as the supporting electrolyte, the potassium ion gives a diffusion-controlled wave with a diffusion current constant comparable to those of cesium and rubidium ions in 0.05 M Et_4NClO_4 (see Table 1). In both DC and AC polarographic methods, the wave is reversible and the temperature coefficient of the DC wave height is approximately 1.3%/°C.

If Et_4NClO_4 is used as the supporting electrolyte, however, the reduction of the potassium ion becomes rather complicated. Though the reduction seems to be fairly reversible, judging from both the analysis of the DC wave and the measurement of the AC polarogram, the DC wave height is considerably smaller than in the cases with Bu_4NClO_4 or Pr_4NClO_4 as the supporting electrolyte (Tabe 1) and its temperature coefficient is much larger (ca. 4%/°C in 0.05 M Et_4NClO_4). The test of the dependence of the DC wave height on the height of the mercury column shows that the limiting current is controlled partly by diffusion and partly by chemical reactions.

In Fig. 2, the values of $i_lC^{-1}h^{-1/2}$ are plotted against $h^{-1/2}$ for the reduction waves of 1, 2 and 3 mM potassium ions both in 0.05 M Bu_4NClO_4 and in 0.05 M Et_4NClO_4. Here, i_l is the limiting current in μA; C, the concentration of the potassium ion in mM, and h, the height of the mercury column corrected

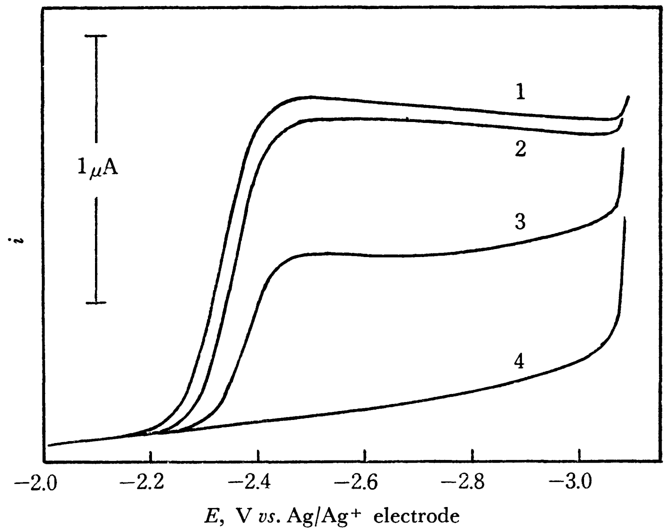

Fig. 1. Polarograms of alkali metal ions in 0.05 M Et_4NClO_4-HMPA. Curve 1, Cs$^+$; 2, Rb$^+$; 3, K$^+$; and 4, Na$^+$, Li$^+$ and the residual current. Concn. of each alkali metal ion is 1mM.

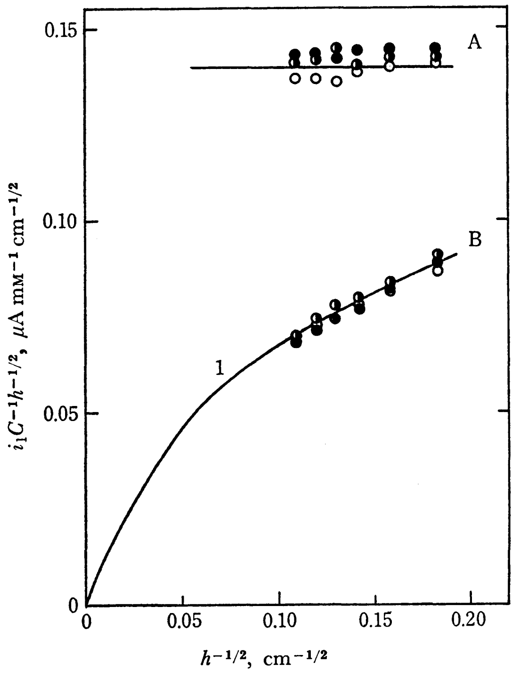

Fig. 2. Relations between $i_lC^{-1}h^{-1/2}$ and $h^{-1/2}$ for potassium waves in 0.05 M Bu_4NClO_4 (A) and in 0.05 M Et_4NClO_4 (B). Concn. of potassium ion: ○, 1 mM; ◑, 2 mM; ● 3 mM. Curve 1 is a theoretical i_l/i_d relation for $i_dC^{-1}h^{-1/2}$= 0.140 and $(Kk)^{1/2}$=1.23.

TABLE 1. POLAROGRAPHIC DATA OF ALKALI METAL IONS IN 0.05 M TETRAALKYLAMMONIUM PERCHLORATE-HMPA (25°C)[a)]

Alkali metal ions	$i_l/Cm^{2/3}t^{1/6}$ μA/mMmg$^{2/3}$ sec$^{-1/2}$	$E_{1/2}$ V *vs.* Ag/Ag$^+$	$E_{1/4}-E_{3/4}$ mV	$i_p/i_ln\tau^{1/2}$ [b)]	Remarks
Cs$^+$	0.74+0.03	−2.32	59	50	diffusion control
Rb$^+$	0.69±0.03	−2.35	60	46	diffusion control
	(0.71±0.03)	(−2.35)	(60)	(47)	diffusion control
K$^+$	0.40±0.03	−2.37	56	38	kinetic+diffusion
	(0.70±0.03)	(−2.38)	(59)	(48)	diffusion control
Na$^+$	—	—	—	—	not reduced
	(0.024)	(−2.42)[c)]	—	—	kinetic control
Li$^+$	—	—	—	—	not reduced

a) Values in parentheses are in 0.05 M Bu_4NClO_4 and others in 0.05 M Et_4NClO_4.

b) i_p: AC peak height in μmho; τ: drop time at the peak potential, in sec; i_l: limiting current in μA; n: number of electrons. The value of $i_p/i_ln\tau^{1/2}$ for Pb^{2+} in aq. 0.1 M KNO_3 (pH 2) was 101. Measured with the DME B.

c) This value is less negative than the reversible half-wave potential (Ref. 11, p. 376).

for the back pressure. In 0.05 M Bu_4NClO_4 the values of $i_lC^{-1}h^{-1/2}$ are almost independent of $h^{-1/2}$, as is to be expected for the diffusion-controlled current. In 0.05 M Et_4NClO_4, however, the values of $i_lC^{-1}h^{-1/2}$ are smaller than those in 0.05 M Bu_4NClO_4, and they increase with an increase in $h^{-1/2}$, showing that a kinetic factor is involved.

The simplest mechanism considered is that the solvated potassium ion, which is the predominant species in HMPA, is converted into the electroactive state preceding its reduction:

$$K^+_{\text{solvated}} \underset{k'}{\overset{k}{\rightleftharpoons}} K^+_{\text{electroactive}} \overset{e}{\rightleftharpoons} K(Hg) \qquad (1)$$

$$K=k/k'$$

where the electroactive ion, $K^+_{\text{electroactive}}$, seems to be either a (partially) desolvated ion or a solvated ion which has approached to the electrode surface by penetrating through the layer of tetraethylammonium ions, as will be discussed later. According to the theoretical treatment by Koutecky,[7] the average limiting current, i_l, obtained for the above mechanism is shown by Eq. (2):

$$i_l = i_d\frac{0.886(Kkt)^{1/2}}{1+0.886(Kkt)^{1/2}} \qquad (2)$$

where i_d is the currnt which will be observed if the solvated potassium ion is reduced by diffusion control. ($t^{1/2}$ is equal to $9.1_6h^{-1/2}$ with the A electrode at −2.6 V in 0.05 M Et_4NClO_4.) It seems reasonable to use the limiting current in 0.05 M Bu_4NClO_4, corrected for the change in drop time (see Fig. 8), as the approximate value of i_d in 0.05 M Et_4NClO_4. Curve 1 in Fig. 2 was theoretically obtained by using Eq. (2) for $i_d\ C^{-1}h^{-1/2}=0.140$ and $(Kk)^{1/2}=1.23$. The good agreement of the curve with the experimental results seems to show that the mechanism expressed by Eq. (1) is valid.

The kinetic current is considerably affected by the experimental conditions. With 0.05 M Et_4NClO_4 as the supporting electrolyte, the values of $(Kk)^{1/2}$ are 0.4_8 at 12.4°C, 1.2_3 at 25°C, and $3._4$ at 41°C. The value of $(Kk)^{1/2}$ also increases with a decrease in the concentration of Et_4NClO_4; thus, $(Kk)^{1/2}$ at 25°C is 0.6_0 in 0.1 M Et_4NClO_4, 1.2 in 0.05 M Et_4NClO_4, and 2.1 in 0.02 M Et_4NClO_4.

Figure 3 shows the effect of water on the limiting current of the potassium ion. In 0.05 M Bu_4NClO_4, the limiting current decreases slightly upon the addition of water (probably due to the increase in viscosity), while, in 0.05 M and 0.1 M Et_4NClO_4, it increases and approaches the value of the purely-diffusion-controlled wave.

In Me_4NClO_4 as the supporting electrolyte, the potassium wave becomes diffusion-controlled again. (See below for a further discussion of the role of the supporting electrolyte.)

Sodium Ion: The polarograms of the sodium ion in HMPA and HMPA-H_2O mixtures containing 0.05 M Et_4NClO_4 as a supporting electrolyte are shown in Fig. 4. The sodium ion in water-free HMPA

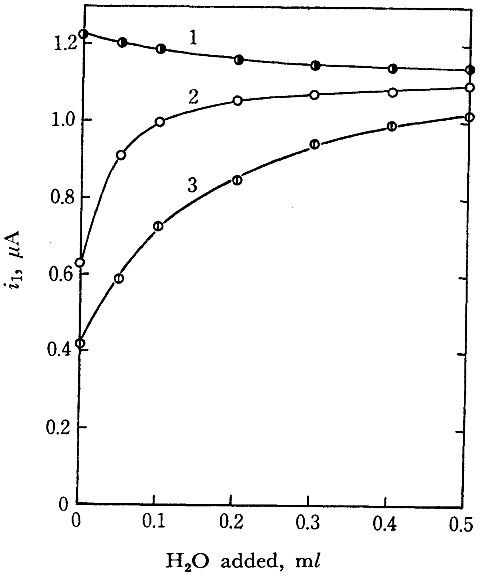

Fig. 3. Effect of water on the limiting current of potassium ions in HMPA. Original volume of the soln.: 10 ml. Concn. of potassium ion: 1 mM. Curve 1, in 0.05 M Bu_4NClO_4; 2, in 0.05 M Et_4NClO_4; and 3, in 0.1 M Et_4NClO_4. (Corrected for the volume change)

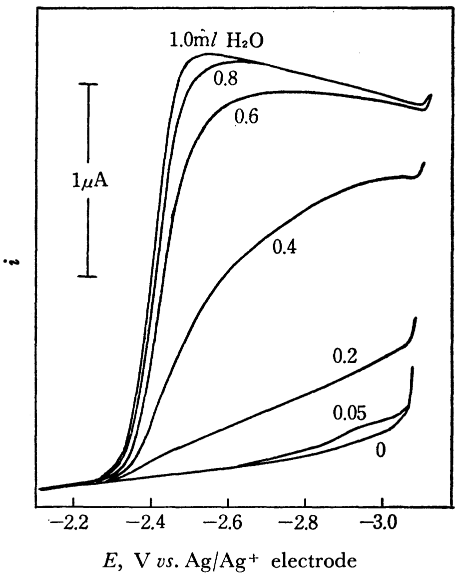

Fig. 4. Effect of water on the sodium wave in HMPA-0.05 M Et_4NClO_4. Water was added to 10 ml of 2.24 mM Na^+ solution. Corrected for the volume change.

does not give a reduction wave up to the potential of the reduction of the supporting electrolyte. A fairly large amount of water should be added in order to obtain a well-defined sodium wave. In Bu_4NClO_4 (or Pr_4NClO_4) as the supporting electrolyte, the sodium ion gives a very small wave (probably kinetic in nature) at about -2.4_2 V *vs.* the Ag/Ag+ electrode (Fig. 5); the wave height is increased more easily by the addition of water than when Et_4NClO_4 is the supporting electrolyte.

Lithium Ion: The reduction of the lithium ion in HMPA-tetraalkylammonium perchlorate solutions is more difficult than that of other alkali metal ions (Fig. 1), and no further experiments were carried out.

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[7] J. Koutecky, *Collect. Czech. Chem. Commun.*, **18**, 597 (1953).

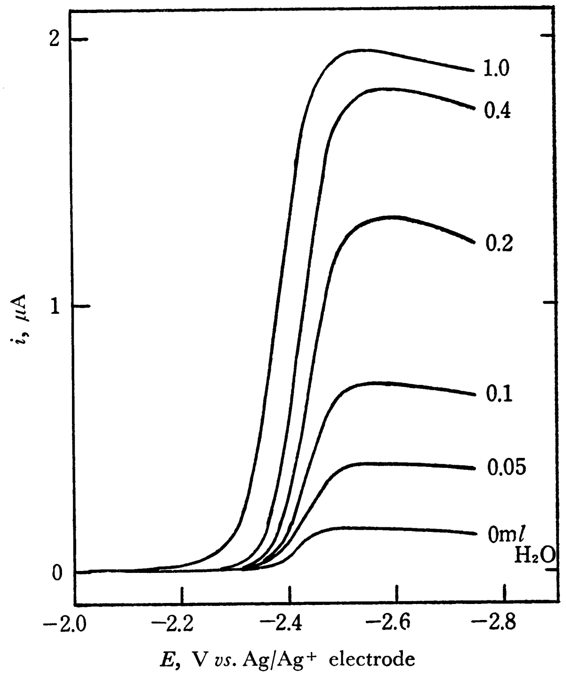

Fig. 5. Effect of water on the sodium wave in 0.05 M Bu_4NClO_4-HMPA. Water was added to 10 ml of 2.21 mM Na^+ solution. Corrected for the residual current and the volume change.

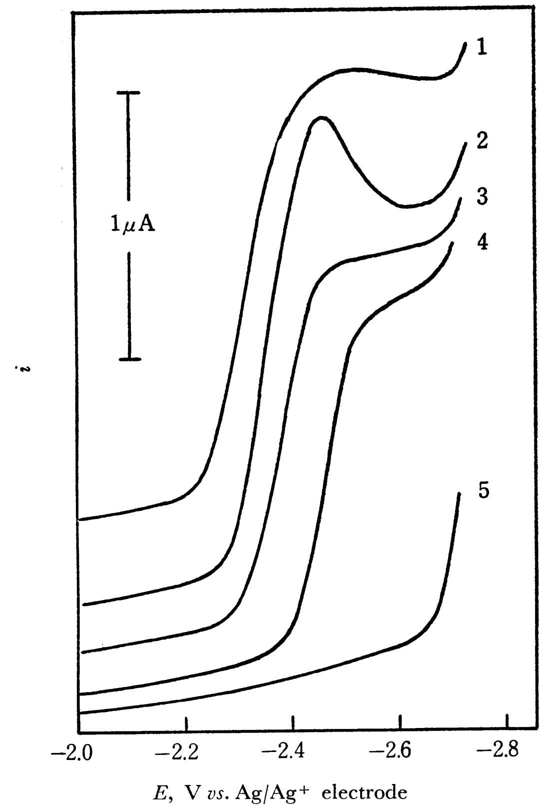

Fig. 6. Polarograms of alkali metal ions in 0.05 M $LiClO_4$-HMPA. Curve 1, Cs^+; 2, Rb^+; 3, K^+; 4, Na^+; and 5, the residual current. Concn. of each alkali metal ion is 1 mM. With the DME B.

Reductions of Alkali Metal Ions in Lithium Perchlorate as the Supporting Electrolyte. As is shown in Fig. 6, the behavior of alkali metal ions in 0.05 M $LiClO_4$-HMPA solutions is quite different from that in tetraalkylammonium perchlorate solutions. The reductions of cesium and rubidium ions in these solutions occur at approximately the same potentials as with the Et_4NClO_4 supporting electrolyte (−2.32 and −2.35 V respectively), though maxima are observed in these waves. The potassium ion also gives a diffusion-controlled wave at −2.37 V, and even the sodium ion, which can not be reduced in the Et_4NClO_4 solution, gives a reversible wave at −2.47 V. The reduction of the lithium ion starts from -2.6_5 V.

Reductions of Sodium and Potassium Ions in Mixed Supporting Electrolytes. The effect of Et_4NClO_4 on the reduction of the sodium ion in 0.05 M $LiClO_4$ was examined. The results are shown in Fig. 7. The sodium wave, which is controlled by diffusion in the absence of the tetraethylammonium ion, is markedly interfered with by the presence of very small amounts of Et_4NClO_4. The presence of Et_4NClO_4 also decreases the drop-time significantly, as is shown in Fig. 7a, indicating that the tetraethylammonium ion is preferentially attracted onto the electrode surface. The reduction of the lithium ion, which starts from about −2.65 V in the absence of the tetraethylammonium ion, is also inhibited by the presence of small amounts of Et_4NClO_4 (Figs. 6 and 7).

In mixed supporting electrolytes, such as $LiClO_4$+Et_4NClO_4, Bu_4NClO_4+Et_4NClO_4, and Pr_4NClO_4+Et_4NClO_4, the reduction of the potassium ion is again

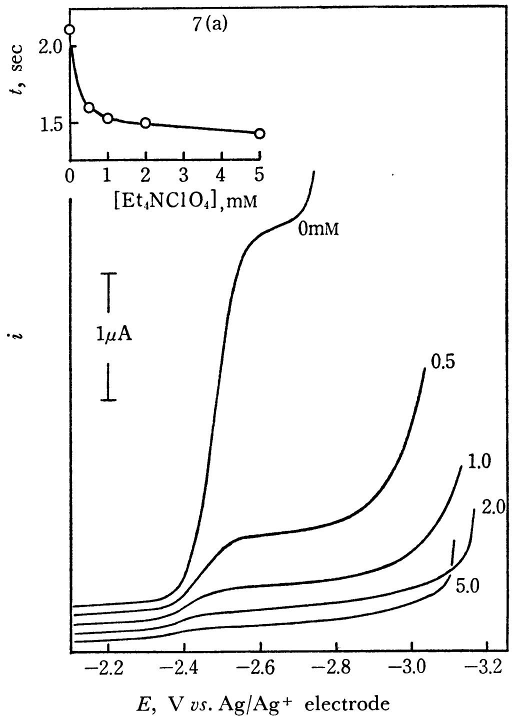

Fig. 7. Effect of Et_4NClO_4 on the sodium wave in 0.05 M $LiClO_4$-HMPA. Concn. of sodium ion: 2.27 mM. Concn. of Et_4NClO_4 is shown on the curves. With the DME B.
Fig. 7(a). Effect of Et_4NClO_4 on the drop time in 0.05 M $LiClO_4$-HMPA.

controlled by the tetraethylammonium ion and a kinetic current is observed, just as when the supporting electrolyte is Et_4NClO_4 only.

Effect of the Supporting Electrolytes on the Electrical Double Layer. The electrocapillary curves obtained by measuring the drop time are shown in Fig. 8. The drop time at extremely negative potentials changes considerably with the supporting electrolytes used; it is largest in 0.05 M $LiClO_4$, smallest in 0.05 M Et_4NClO_4, and between these two in 0.05 M Bu_4NClO_4. The charge densities on the electrode, calculated from the slopes of these electrocapillary curves, are plotted in Fig. 9. The negative charge on the electrode is much larger in 0.05 M Et_4NClO_4 than in 0.05 M Bu_4NClO_4 and $LiClO_4$, showing that the tetraethylammonium ion is more easily attracted to the electrode surface. This difference is probably due to the difference in the sizes of the solvated ions. Figure 10 shows the Stokes law radii of mono-valent cations in HMPA, calculated from the results of conductivity measurements.[8] Though it is questionable to consider that the Stokes law radii are a direct measure of the sizes of solvated ions, it is reasonable to assume that, among the ions in Fig. 10, the tetraethylammonium ion is smallest and the lithium ion is largest. It is natural that the tetraethylammonium ion, which is the smallest cation, is the most easily (or preferentially in the mixed electrolytes) attracted onto the negatively-charged electrode surface.

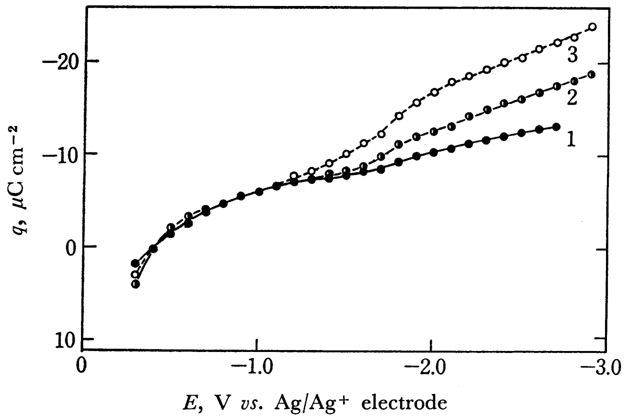

Fig. 9. Charges on the electrode surface obtained from the electrocapillary curves in Fig. 8. Curve 1, in 0.05 M $LiClO_4$; 2, in 0.05 M Bu_4NClO_4; and 3, in 0.05 M Et_4NClO_4.

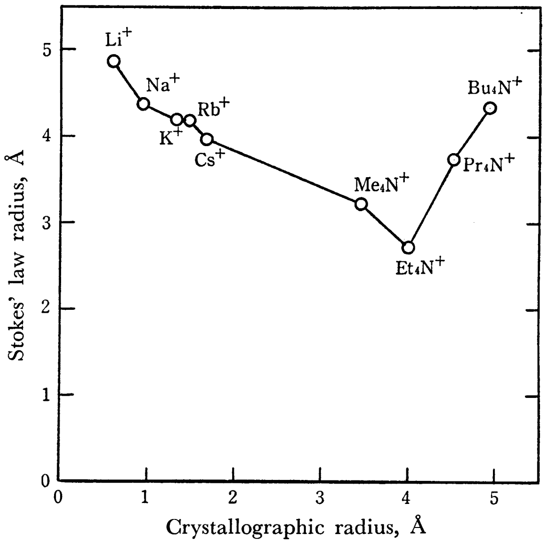

Fig. 10. Stockes' law radii of various mono-valent cations in HMPA.

The big influence of the supporting electrolyte on the reductions of alkali metal ions can be explained by the effect of a competitive approach to the electrode surface of the cation of the supporting electrolyte and of the depolarizing cation. With $LiClO_4$ as the supporting electrolyte, for example, all the alkali metal ions can easily approach the electrode surface and can be reduced. With the Et_4NClO_4 supporting electrolyte, on the other hand, the tetraethylammonium cation is attracted preferentially and its layer inhibits the approach of the bigger solvated cations to the electrode surface. In this case, either the penetration of the solvated cations through the layer or some chemical reactions, such as the (partial) desolvation of the solvated cation, should precede the reduction. If the preceding process is rapid, the reduction is diffusion-controlled (the cases of cesium and rubidium ions), but if it is very slow, the reduction does not occur at all (the cases of sodium and lithium ions). When the rate of the preceding process is in between these two extremes, a kinetic current is observed, as in the case of the potassium ion. With 0.05 M Bu_4NClO_4 as the supporting electrolyte, the inhibition by the tetrabutylammonium ion is less than that by the tetraethylammonium ion, and the potassium ion can be reduced by diffusion control. The reduction of the sodium ion, however, is still controlled by the rate of the preceding process.

The influence of the supporting electrolyte can

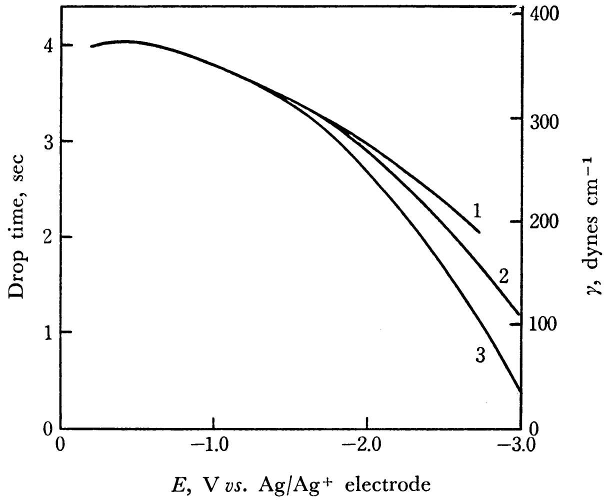

Fig. 8. Drop time-potential curves. Curve 1, in 0.05 M $LiClO_4$; 2, in 0.05 M Bu_4NClO_4; and 3, in 0.05 M Et_4NClO_4. For conversion of drop time t to surface tension γ, the values of t and γ at the ecm in aq. 0.1 M KCl were used as reference. The values of γ at very negative potentials are approximate because correction was not made for the variation of back pressure. With the DME B.

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[8] K. Izutsu, S. Sakura, and T. Fujinaga, unpublished results; C. Atlani, J. C. Justice, M. Quintin, and J. E. Dubois, *J. Chim. Phys.*, **66**, 180 (1969).

also be explained qualitatively by means of the double-layer effect. Recently, the kinetics of electrode reactions have been treated by taking into account separately the distance of the outer Helmholtz plane from the geometrical electrode surface (x_2) and that of the plane at the charge center of the reacting species in the transtion state (x_r).[9,10] In HMPA, x_2 is expected to increase with the size of the cation of the supporting electrolyte in the order $Et_4N^+ < Bu_4N^+ < Li^+$, and the x_r values for potassium and sodium ions seem to be between x_2 in $LiClO_4$ and that in Et_4NClO_4. Thus, the potential, ϕ_r, at the plane of the closest approach of these ions will be more negative in $LiClO_4$ than in Et_4NClO_4. The preceding reactions of the depolarizing cations, as shown by Eq. (1), are accelerated significantly when the ϕ_r-potential becomes more negative.[11]

The above explanations are still only tentative. Further studies are now in progress in this laboratory on the electrode double layer at extremely negative potentials and its effects on electrode processes in HMPA and other organic solvents.[12,13]

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[9] W. R. Fawcett, *J. Electroanal. Chem.*, **22**, 19 (1969); W. R. Fawcett and M. D. Mackey, *ibid.*, **27**, 219 (1970); W. R. Fawcett, D. J. Bieman, and M. D. Mackey, *Collect. Czech. Chem. Commun.*, **36**, 503 (1971).

[10] N. Tanaka, Y. Aoki, and A. Yamada, 16th Symposium on Polarography, Kyoto (1970).

[11] J. Heyrovsky and J. Kuta, "Principles of Polarography," Academic Press, New York (1966), p. 351.

[12] K. Izutsu, S. Sakura, K. Kuroki, and T. Fujinaga, *J. Electroanal. Chem.*, **32**, App. 11 (1971).

[13] Quite recently similar inhibiting effect of Et_4N^+ on the reductions of sodium and lithium ions was observed by Gal and Yvernault. J. Y. Gal and T. Yvernault, *Bull. Soc. Chim. France*, **1971**, 2770.