The Polarographic Reduction of Various Ammonium Cations in Hexamethylphosphoric Triamide**

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Synopsis. The reductions of tetradecylammonium, tetradodecylammonium, benzyldimethyl(tetradecyl)ammonium, and ammonium ions were examined in hexamethylphosphoric triamide. The reduction behavior of these ions was found to be a function of the size and the charge of the cation of the supporting electrolytes.

The present authors have studied the polarographic reductions of various metal ions in hexamethylphosphoric triamide (HMPA) which is the most basic solvent in the aprotic solvents available thus far. The reduction behavior of certain kinds of metal ions is remarkably influenced by the cations of the supporting electrolyte. For example, in a 0.05 M (1 M=1 mol dm^{-3}) tetraethylammonium perchlorate (Et_4NClO_4) solution, the sodium ion is not reduced until the reduction of the supporting electrolyte is observed. In contrast, in a lithium perchlorate ($LiClO_4$) solution, the reduction of sodium ion is diffusion-controlled.[1] From the measurements of the electrolytic conductivities, it was found that the solvated radius of the lithium ion is much larger than that of the tetraethylammonium ion, while that of the sodium ion is between them.[2] With the use of the larger cation as the supporting electrolyte, the reduction of the metal ion is promoted.

The above phenomena suggest that the relative difference in size between the supporting electrolyte cation and the depolarizing ion must control the electrode reaction. If various ammonium ions are used as the depolarizing ions, the situation is as follows; the chemical character and charge are the same, and there is only a difference in size. Therefore, it is expected that the relationship between the cation of the supporting electrolyte and that of the depolarizing ion could be made more clear.

The physical characters of various ammonium ions in HMPA have already been investigated.[3] Some of them are reduced at a very negative potential, while the others are reduced at a less negative potential. The latter were used as the depolarizing ions for the purposes of this research.

Experimental

The equipment used was a Yanagimoto polarograph, Type P8-DP. All the experiments were carried out at 25 °C±0.1 °C. All the potentials were referred to a freshly-prepared Ag/0.1 M $AgClO_4$(HMPA) electrode. The dropping mercury electrode used had the following characteristics in 0.05 M Et_4NClO_4–HMPA at h=62 cm: m=1.760 mg s^{-1} with an open circuit and t=1.450 s at −2.6 V *vs.* Ag/0.1 M Ag^+.

All the solutions were prepared from the perchlorate salts. The supporting electrolytes were 0.05 M Et_4NClO_4, tetrabutylammonium perchlorate (Bu_4NClO_4), and $LiClO_4$. As the depolarizing cation, the ammonium, benzyldimethyl(tetradecyl)ammonium (BDT^+), tetradecylammonium (Dec_4N^+), and tetradodecylammonium (Dod_4N^+) cations were used. The methods of preparing these reagents and the purification of HMPA have been described in previous papers.[1]

Results and Discussion

In Figs. 1 and 3, the polarograms of various ammonium ions in Et_4NClO_4, Bu_4NClO_4, and $LiClO_4$ solutions are shown.

Ammonium Ion: In the Et_4NClO_4 solution, the reduction of the ammonium ion was very irreversible, judging from the log-plot of the wave analysis, which was obtained by means of the plots of the values of $\log i/(i_l-i)$ and E (where i is the current at potential E and where i_l is the limiting current) (see Fig. 1 and Table 1).

When Bu_4NClO_4 was used as the supporting electrolyte, the reduction potential shifted in the positive direction. In the solution of $LiClO_4$, the potential of the reduction was shifted towards a more positive value. As the reduction wave showed a large maximum in this case, the measurement of the current heights was impossible (see also Table 1). The value of the I ($=i_l c^{-1} m^{-2/3} t^{-1/6}$; c is the concentration) of NH_4^+ in the Bu_4N^+ solution showed 0.67 μA $s^{1/2}$ mM^{-1} $mg^{-2/3}$ (1 mM=10^{-3} mol dm^{-3}). The caesium ion in Et_4NClO_4 has the I value of 0.74 μA $s^{1/2}$ mM^{-1} $mg^{-2/3}$, as was shown in previous papers.[1] The reduction of the caesium ion is reversible and diffusion-controlled. From the value of the caesium ion, the diffusion coefficient should be assumed to be 1.486×10^{-6} cm^2 s^{-1}. Using this, the value of n (the mol equivalent electron number) in the case of NH_4^+ reduction was obtained as 0.88 in Bu_4N^+. Therefore, the reduction, by one electron, to the neutral radical (NH_4·Hg) seems to have occurred, as has been reported in other aprotic solvents.[4]

Figure 2 shows the dependence of the limiting current of the ammonium ion on the square root of the height of the mercury column in the Et_4NClO_4 and Bu_4NClO_4 solutions. In the Bu_4NClO_4 solution, the height of the limiting current (i_l) was proportional to the square root of the mercury height. This means that, in this solution, the reduction process of the ammonium ion was diffusion-controlled. On the other hand, in the 0.05 M Et_4NClO_4 solution the value of i_l was proportional to $h^{1/2}$, but the line did not pass through the point of origin. In this case, therefore, the limiting current of the ammonium ion was not fully diffusion-controlled.

Benzyldimethyl(tetradecyl)ammonium (BDT^+) Ion: In the Et_4NClO_4 solution, the log-plot analysis of the

Electrochemical Studies in Hexamethylphosphoric Triamide, IX: For VIII: S. Sakura, *Bunseki Kagaku*, **28, 274 (1979).

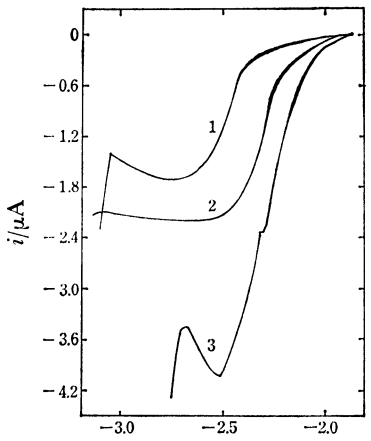

Fig. 1. Polarograms of 1.960 mM NH_4ClO_4 in HMPA solution.
Supporting electrolyte: Curve 1, Et_4N^+; Curve 2, Bu_4N^+; and Curve 3, Li^+. All are in 0.05 M.

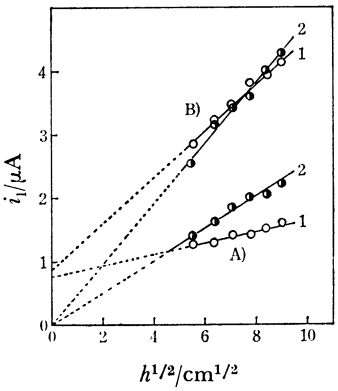

Fig. 2. Relationship between the limiting current (i_l) and square root of mercury height ($h^{1/2}$).
A) NH_4^+ and B) BDT^+.
Supporting electrolyte: Curve 1, Et_4N^+ and Curve 2, Bu_4N^+.

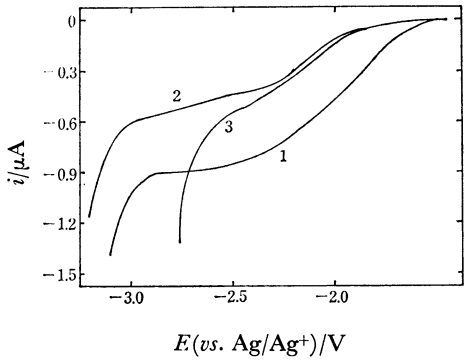

Fig. 3. Polarograms of 1.004 mM Dec_4NClO_4 in HMPA solution.
Supporting electrolyte: Curve 1, Et_4N^+; Curve 2, Bu_4N^+; and Curve 3, Li^+. All are in 0.05 M.

Table 1. Polarographic data of various ammonium cations in HMPA (25.0 °C)

	Et_4N^+(4.0)		Bu_4N^+(4.9)		Li^+(5.1)	
	$E_{1/2}$/V vs. Ag/Ag+	log-plot mV	$E_{1/2}$/V vs. Ag/Ag+	log-plot mV	$E_{1/2}$/V vs. Ag/Ag+	log-plot mV
Dec_4N^+ (4.94)	−1.98	338	−2.24	330	*ca.* −2.25	280
Dod_4N^+ (4.34)	−2.03	280	−2.23	250	−2.10	180
BDT^+ (5.07)	−2.57	87	−2.45	77	*ca.* −2.50	—
NH_4^+ (4.86)	−2.48	106	−2.31	150	*ca.* −2.26	—

The values in parentheses show the solvated radii in HMPA (Ref. 3).

reduction wave of BDT^+ ion showed 87 mV. This means that the BDT^+ ion was reduced irreversibly. When Bu_4N^+ or Li^+ was used as the supporting electrolyte cation, the reduction potential of the BDT^+ ion was shifted toward a positive value. In the $LiClO_4$ solution, its reduction wave was accompanied by a large maximum, as is shown in the case of NH_4^+. The measurement of the limiting current was impossible. From the relationship between $h^{1/2}$ and i_l shown in Fig. 2, the reduction current of BDT^+ in the Et_4NClO_4 solution was found to be partly controlled by a kinetic process. On the other hand, in the Bu_4NClO_4 solution its reduction process was completely diffusion-controlled and the log-plot showed 77 mV.

Tetradecylammonium (Dec_4N^+) Ion: The polarographic reduction of Dec_4N^+ in HMPA is shown in Fig. 3. The slope of the reduction wave in any supporting electrolyte examined was very gentle, showing the process to be fairly irreversible. The values of the log-plot were 280 mV, 330 mV, and 338 mV in $LiClO_4$, Bu_4NClO_4, and Et_4NClO_4 respectively. The reduction process in $LiClO_4$ was most reversible among these three solutions, judging from the values of the log-plot. However, the values of the half-wave potential showed that Dec_4N^+ was reduced at a more positive potential in the Et_4N^+ than in the Bu_4N^+ and Li^+ solutions. In this sense, the effect of size of the supporting electrolyte cation was not the same as with ammonium or BDT^+ ion.

Tetradodecylammonium (Dod_4N^+) Ion: The polarographic behavior of Dod_4N^+ resembled that of the Dec_4N^+ ion. The reduction was most reversible in $LiClO_4$ among the three solutions, judging from the values of the log-plot of the wave analysis. The values of the half-wave potential showed that Dod_4N^+ was reduced at a more positive potential in the Et_4N^+ than in the Bu_4N^+ and Li^+ solutions. In this case, the effect of the size of the supporting electrolyte cation was the same as that for Dec_4N^+.

The relationship between the size of the supporting electrolyte cation and that of the depolarizing ion could be generally the same as in the case of the reductions of metal ions. Especially in the case of the ammonium and BDT^+ ions, the potentials of reduction shifted in the positive direction, and the process of the reduction was more reversible, when the larger cation of the supporting electrolyte was used. However, in the cases of Dod_4N^+ and Dec_4N^+, the effect of the supporting electrolyte cation was different: in Et_4N^+, the potential of $E_{1/2}$ was the most positive, though the reduction process was very irreversible. The reductions of these two cations occurred at around −2.0 V, though other normal tetraalkylammonium ions, such as the tetramethylammonium, Et_4N^+, tetrapropylammonium, Bu_4N^+, tetrahexylammonium, and tetraheptylammonium ions, were reduced at around −3.0 V.[3] Therefore, the reductions of the higher tetraalkylammonium ions, such as Dec_4N^+ and Dod_4N^+, seem to be different from those of ammonium, BDT^+, and metal ions.

References

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