BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2148—2151 (1973)

Polarographic Reductions of Some Alkali and Alkaline Earth Metal Ions in Dimethylacetamide. Effect of Cation of the Supporting Electrolyte

Kosuke IZUTSU,* Sachiko SAKURA, and Taitiro FUJINAGA

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

(Received February 19, 1973)

Polarographic reductions of lithium, barium, strontium, and calcium ions in dimethylacetamide (DMA) have been examined in the supporting electrolytes of various kinds of tetraalkylammonium perchlorates. As having been observed in hexamethylphosphoramide, the reductions of these metal ions in DMA are influenced significantly by the cation of the supporting electrolyte. When the cation of the supporting electrolyte is small in size and easily adsorbed onto the negatively charged electrode surface, as in the case in Et_4NClO_4, the reductions of these metal ions are difficult and they either do not occur at all until the reduction of the supporting electrolyte itself or, if they occur, the limiting currents are small and controlled by some preceding processes. With the increase of the cationic size of the supporting electrolyte, the reductions become much easier. Thus, in Bu_4NClO_4 and in Hex_4NClO_4, these metal ions are reduced almost reversibly. The effect of cation of the supporting electrolyte on the reduction of lithium ion has also been examined briefly in dimethylsulfoxide, dimethylformamide and propylenecarbonate.

In our recent papers,[1-3] we reported that the polarographic reductions of alkali and alkaline earth metal ions in hexamethylphosphoramide (HMPA) are strongly influenced by the cation of the supporting electrolyte. As an example, the behavior of sodium ion in various kinds of perchlorate solutions is shown in Fig. 1: In 0.05 M Et_4NClO_4, sodium ion is not reduced until the reduction of the supporting electrolyte. In 0.05 M Pr_4NClO_4 or in Bu_4NClO_4, however, a small sodium wave is observed and its limiting current is controlled kinetically. In 0.05 M Hex_4NClO_4, the sodium wave becomes much higher, but still partly controlled by the kinetic process. If 0.05 M $LiClO_4$ is used instead of tetraalkylammonium salts, the reduction of sodium ion becomes reversible and diffusion controlled. We showed that these effects are mainly due to the pheno-

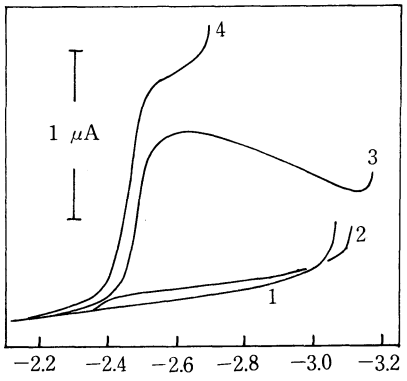

Fig. 1. Polarograms of 1 mM $NaClO_4$ in HMPA. Supporting electrolyte: curve 1, Et_4NClO_4; 2, Bu_4NClO_4; 3, Hex_4NClO_4; and 4, $LiClO_4$. Each in 0.05 M.

* Present Address: Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390.

1) K. Izutsu, S. Sakura, and T. Fujinaga, This Bulletin, **45**, 445 (1972).

2) K. Izutsu, S. Sakura, K. Kuroki, and T. Fujinaga, *J. Electroanal, Chem.*, **32**, A pp. 11—44 (1971).

3) K. Izutsu, S. Sakura, and T. Fujinaga, This Bulletin, **46**, 493 (1973).

mena occurring near the electrode double layer. At extremely negative potentials, smaller cations are preferentially attracted onto the electrode surface. Thus, Et_4N^+ ion, which is smallest of the cations used in Fig. 1, is most easily adsorbed and inhibits the reduction of heavily solvated sodium ion completely. The inhibition seems to be due mainly to electrostatic effect but steric effect may also be involved. In Pr_4NClO_4 or in Bu_4NClO_4, Bu_4N^+, or Pr_4N^+ ion is still adsorbed rather easily and the reduction of sodium ion must be preceded by a process, which may be considered to be either a (partial) desolvation of the sodium ion or its penetration through the layer of the adsorbed tetraalkylammonium ion, and the rate of the preceding process controls the limiting current of the sodium wave. In $LiClO_4$, on the contrary, sodium ion is more easily attracted onto the electrode surface than lithium ion and its reduction is not inhibited at all.

Polarographic reductions of alkali and alkaline earth metal ions in dimethylacetamide (DMA) have already been studied by Gutmann *et al.*[4,5] and by Broadhead and Elving,[6] but they used only tetraethylammonium salt as the supporting electrolyte. In the present paper, the reductions of these metal ions in DMA and in several other dipolar aprotic solvents have been examined by using various kinds of tetraalkylammonium perchlorates as the supporting electrolytes.

Apparatus and Reagents

Most of the apparatus are the same as those used in the previous reports.[1,3] Except the measurement of Fig. 8, the dropping mercury electrode had the following characteristics in 0.05 M Et_4NClO_4–DMA and at $h=62$ cm; $m=1.88$ mg/sec with the circuit open and $t=1.31$ sec at -3.1 V *vs.* Ag/0.1 M $AgClO_4$ (DMA) reference electrode. The DME for Fig. 8 had $m=1.62$ mg/sec at $h=62$ cm and with the circuit open.

DMA was distilled following the method of Gutmann *et al.*[4] All perchlorates used in this experiment are the same as those in the previous reports[1,3] and were dried before use. Measurements were carried out at 25 ± 0.1 °C.

Results and Discussion

Alkali Metal Ions in DMA: Gutmann *et al.*[4] have shown that lithium ion is irreducible in truly anhydrous DMA by using 0.1 M Et_4NClO_4 as the supporting electrolyte.

Figure 2 shows the effect of the cation of the supporting electrolyte on the lithium wave. In accordance with the Gutmann's results, lithium ion is irreducible in 0.1 and 0.05 M Et_4NClO_4 untill the reduction of the supporting electrolyte, though a very small wave becomes to be observed in 0.02 M Et_4NClO_4. In 0.05 M Bu_4NClO_4 and Hex_4NClO_4, the lithium wave is AC polarographically reversible and the DC limiting current is diffusion controlled, though a big polarographic

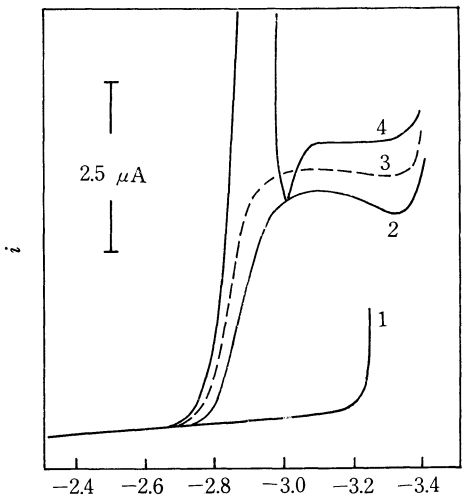

Fig. 2. Polarograms of 1.9 mM Li^+ in DMA.
Supporting electrolyte: curve 1, Et_4NClO_4; 2, Pr_4NClO_4; 3, Bu_4NClO_4; and 4, Hex_4NClO_4. Each in 0.05 M.

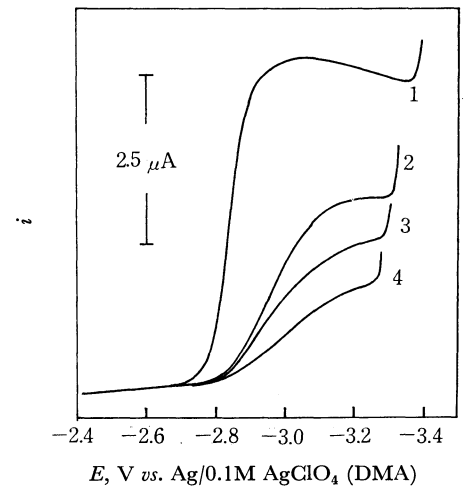

Fig. 3. Effect of Et_4NClO_4 on the reduction wave of 2.1 mM Li^+ in 0.05 M Bu_4NClO_4–DMA.
Concn. of Et_4NClO_4: curve 1, 0 mM; 2, 2 mM; 3, 4 mM; and 4, 10 mM.

maximum of the first kind appears. In 0.05 M Pr_4NClO_4, the limiting current is still somewhat smaller than that expected for diffusion controlled process. In 0.05 M Bu_4NClO_4–DMA, $E_{1/2}$ is -2.8_5 V.

Figure 3 shows how the addition of Et_4NClO_4 affects the lithium wave in 0.05 M Bu_4NClO_4. The addition of as small as 2 mM Et_4N^+ ion decreases the limiting current to about a half of its original value.

Though the reduction wave of lithium ion in DMA is influenced by the cation of the supporting electrolyte, the reversible reduction wave of cesium, rubidium, potassium, and sodium ion is not influenced. For an example, the wave of cesium ion has $E_{1/2}$, -2.4_6 V in all the supporting electrolytes used.

Alkaline Earth Metal Ions in DMA:

Polarograms of barium, strontium and calcium ions are shown in Figs. 4, 5, and 6, respectively.

In 0.05 M Pr_4NClO_4 and Bu_4NClO_4, diffusion con-

4) V. Gutmann, M. Michlymayr, and G. Peychal-Heiling, *Anal. Chem.*, **40**, 619 (1968).

5) V. Gutmann, M. Michlmayr, and G. Peychal-Heiling, *J. Electroanal. Chem.*, **17**, 153 (1968).

6) J. Broadhead and P. J. Elving, *J. Electrochem. Soc.*, **118**, 63 (1971).

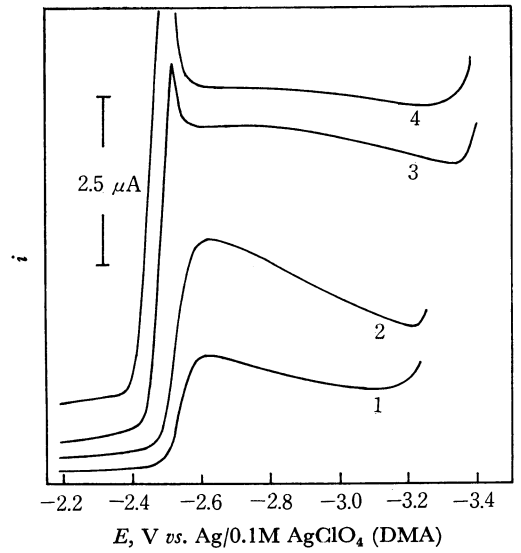

Fig. 4. Polarograms of 1.0 mM Ba^{2+} in DMA.
Supporting electrolyte: curve 1, 0.1 M Et_4NClO_4; 2, 0.05 M Et_4NClO_4; 3, 0.05 M Pr_4NClO_4; and 4, 0.05 M Bu_4NClO_4.

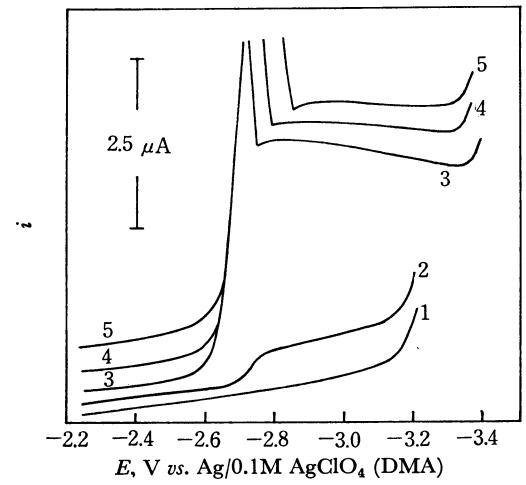

Fig. 5. Polarograms of 0.8 mM Sr^{2+} in DMA.
Supporting electrolyte: curve 1, 0.1 M Et_4NClO_4; 2, 0.05 M Et_4NClO_4; 3, 0.05 M Pr_4NClO_4; 4, 0.05 M Bu_4NClO_4; and 5, 0.05 M Hex_4NClO_4.

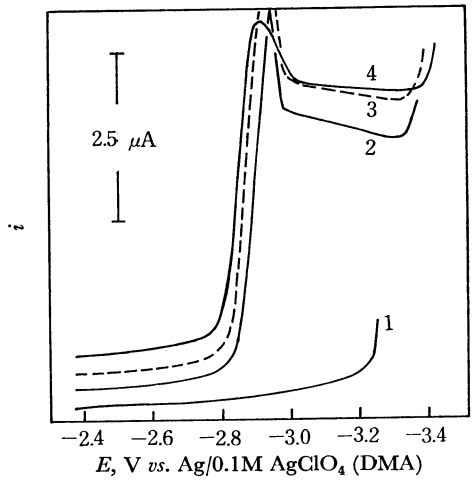

Fig. 6. Polarograms of 1.0 mM Ca^{2+} in DMA.
Supporting electrolyte: curve 1, Et_4NClO_4; 2, Pr_4NClO_4; 3, Bu_4NClO_4; and 4, Hex_4NClO_4. Each in 0.05 M.

trolled barium wave with $E_{1/2}$ of *ca.* -2.4_5 V is observed. AC polarographic measurement shows that the wave is reversible. The barium wave in 0.1 M and 0.05 M Et_4NClO_4, on the other hand, is partly controlled kinetically (Fig. 7) and its limiting current is smaller than that expected for the diffusion process.

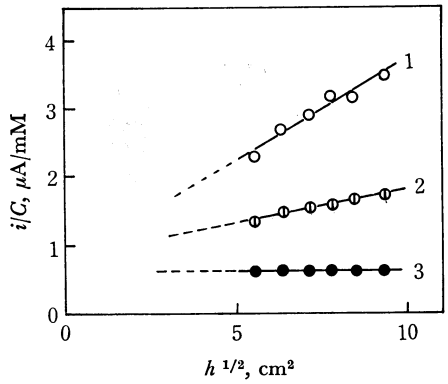

Fig. 7. Change of the limiting currents with the height of the mercury column.
Curve 1, 1.0 mM Ba^{2+} in 0.05 M Et_4NClO_4–DMA; 2, 1.0 mM Ba^{2+} in 0.1 M Et_4NClO_4–DMA; and 3, 0.9 mM Sr^{2+} in 0.05 M Et_4NClO_4–DMA.

Strontium ion is irreducible in 0.1 M Et_4NClO_4 but gives a small, kinetically controlled wave in 0.05 M Et_4NClO_4 (Fig. 7). In 0.05 M Pr_4NClO_4, Bu_4NClO_4, and Hex_4NClO_4, strontium wave is diffusion controlled with $E_{1/2}$ of *ca.* -2.6_8 V.

Calcium ion is irreducible in 0.05 M Et_4NClO_4, but in other supporting electrolytes, the wave is reversible and diffusion controlled with $E_{1/2}$ of *ca.* -2.8_5 V.

These effects of cation of the supporting electrolyte can be explained almost in the same way as in the case in HMPA. Figure 8 shows the drop-time potential curves. The drop-time at extremely negative potentials differs considerably by the cation of the supporting

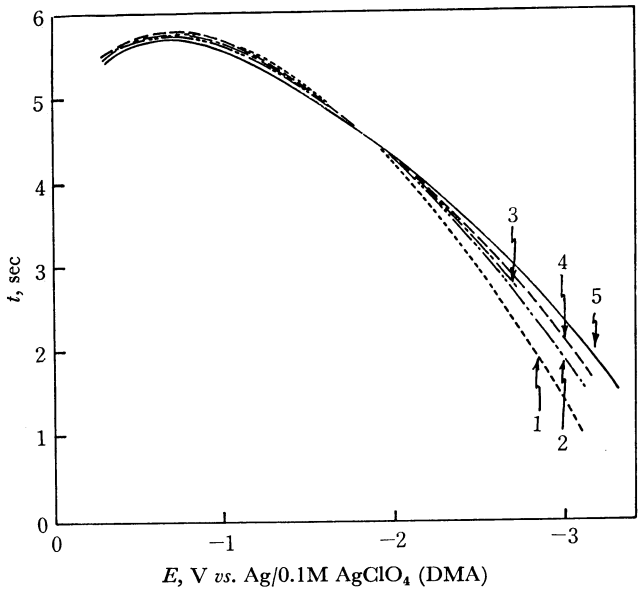

Fig. 8. Drop time—potential curves in 0.05 M perchlorates in DMA.
Curve 1, Et_4NClO_4; 2, Pr_4NClO_4; 3, $LiClO_4$; 4, Bu_4NClO_4; and 5, Hex_4NClO_4.

electrolyte. For tetraalkylammonium ions, it increases in the order $Et_4N^+ < Pr_4N^+ < Bu_4N^+ < Hex_4N^+$ and the drop time in 0.05 M $LiClO_4$ is approximately the same as that in 0.05 M Bu_4NClO_4. From these results, it is apparent that Et_4N^+ ion is preferentially adsorbed onto the electrode surface in the presence of other cations. Thus, for the metal ions to be reduced in Et_4NClO_4 solutions, they must approach to the electrode surface through the layer of adsorbed Et_4N^+ ions. If metal ions are lightly solvated and with moderate sizes, this process will be relatively easy. But, for heavily solvated, bulky metal ions, the process must be difficult, from both electrostatical and sterical points of view. The reduction either does not occur at all or, even if it occurs, it may take place at the rate controlled by the preceding process of the approach of solvated forms or somewhat desolvated forms of metal ions to the electrode surface.

Lithium Ions in DMF, DMSO, and PC: The reductions of lithium ion in Et_4NClO_4–DMSO and Et_4NClO_4–DMF have been reported to be irreversible.[6] Figure 9 shows the effect of supporting electrolytes on the lithium wave in DMF. In 0.05 M Me_4NClO_4 and Et_4NClO_4, lithium wave is irreversible as having been reported in literatures. But in solutions with larger tetraalkylammonium ions, the reduction of lithium ion becomes much more reversible. Similar increase of reversibility of lithium wave by the increase

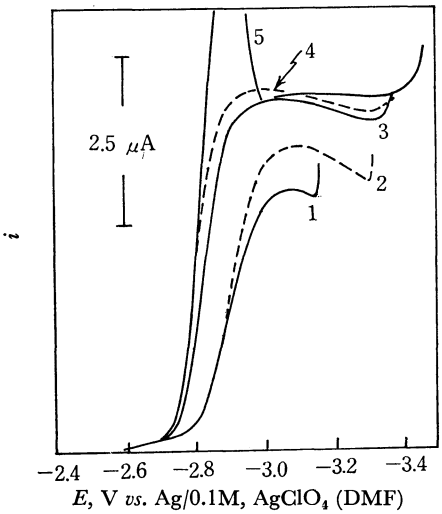

Fig. 9. Polarograms of 2.0 mM Li^+ in DMF.
Supporting electrolyte: curve 1, Me_4NClO_4; 2, Et_4NClO_4; 3, Pr_4NClO_4; 4, Bu_4NClO_4; and 5, Hex_4NClO_4. Each in 0.05 M.

of the size of the cation of the supporting electrolyte is observed also in DMSO.

In propylenecarbonate, in which the solvation of lithium ion is considered to be moderate, the lithium wave keeps almost reversible in all the tetraalkylammonium perchlorates solutions used.