BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 493—495 (1973)

Polarographic Reductions of Alkaline Earth Metal Ions in Hexamethylphosphoramide. 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

(Received July 17, 1972)

Polarographic reductions of barium, strontium and calcium ions in hexamethylphosphoramide (HMPA) have been investigated in the supporting electrolytes of various perchlorates. The reduction of these alkaline earth metal ions are strongly influenced by the cation of the supporting electrolyte. When the size of the cation of the supporting electrolyte is small and easily adsorbed on the negatively charged electrode surface as in the cases of Me_4N^+ and Et_4N^+ ions, the reduction of the metal ions does not occur until that of the supporting electrolyte. The reduction becomes easier with the increase of cationic size. Thus, in Hex_4NClO_4 or $LiClO_4$, these metal ions are reduced almost reversibly. These effects of the cation of the supporting electrolyte can be explained as electrode surface phenomena as in the reduction of alkali metal ions.

In a previous paper,[1] we reported on the polarographic reduction of alkali metal ions in hexamethylphosphoramide (HMPA). We observed a significant influence of the cation of the supporting electrolyte on reduction: Sodium ion in 0.05 M Et_4NClO_4, for example, is not reduced until the reduction of the supporting electrolyte takes place. In 0.05 M Pr_4NClO_4 and 0.05 M Bu_4NClO_4 solutions, however, it gives a small reduction wave, the limiting current of which is controlled by the rate of the preceding process. With 0.05 M $LiClO_4$ as a supporting electrolyte, a reversible, diffusion-controlled sodium wave is obtained at −2.47 V *vs.* Ag/0.1 M $AgClO_4$ (HMPA). We attributed these effects to the change of the double-layer properties with the species of the cation of the supporting electrolyte.

We have investigated the polarographic behavior of the calcium, strontium and barium ions in HMPA by use of various perchlorates as supporting electrolytes. A significant effect of the cation of the supporting electrolyte was also observed as in the reduction of alkali metal ions. The reduction of magnesium ion was not studied, because in the solution of magnesium perchlorate an unexpected wave was observed which might be due to some decomposition product of HMPA.

Apparatus and Reagents

Apparatus. The AC polarograms were recorded with a Yanagimoto polarograph, Type P8-AC. The dropping mercury electrode had the following characteristics in 0.05 M Et_4NClO_4-HMPA and at $h=62$ cm: $m=1.88$ mg/sec with the circuit open and $t=1.39$ sec at −2.6 V *vs.* Ag/0.1 M $AgClO_4$ (HMPA) electrode. Other apparatus were the same as described previously.[1]. All experiments were carried out at 25±0.1°C.

Reagents. Tetra-*n*-hexylammonium perchlorate (Hex_4NClO_4) was prepared from $AgClO_4$ and Hex_4NI (product of the Eastman Kodak Co.) in ethanol, and recrystallized three times from ethanol. It was air dried. Other tetraalkylammonium perchlorates and lithium perchlorate were prepared and dried following the previous procedures.[1] The calcium and strontium perchlorates were prepared by neutralizing the reagent grade calcium and strontium hydroxides, respectively, with perchloric acid. The barium perchlorate was obtained commercially. These alkaline earth perchlorates were dried in a vacuum at 200°C. HMPA was purified following the method in the previous report.[1]

Experimental

The polarographic behavior of the calcium, strontium and barium ions in HMPA was examined by use of Me_4NClO_4, Et_4NClO_4, Pr_4NClO_4, Bu_4NClO_4, Hex_4NClO_4, and

---

* Electrochemical Studies in Hexamethylphosphoramide. II. For Part I, see Ref. 1).

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

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

TABLE 1. RESULTS OF POLAROGRAPHIC REDUCTIONS OF ALKALINE EARTH METAL IONS IN HMPA a)

Supporting electrolyte	Ba^{2+}			Sr^{2+}			Ca^{2+}		
	$E_{1/2}$	i_1/C	$i_p/2i_1\tau^{1/2}$	$E_{1/2}$	i_1/C	$i_p/2i_1\tau^{1/2}$	$E_{1/2}$	i_1/C	$i_p/2i_1\tau^{1/2}$
Me_4NClO_4	not reduced			not reduced			not reduced		
Et_4NClO_4	not reduced			not reduced			not reduced		
Pr_4NClO_4	-2.42 b)	0.1_9 b)	—	not reduced			not reduced		
Bu_4NClO_4	-2.45 b)	1.3_0 b)	$8._0$ b)	-2.70 b)	0.9_4 b)	—	-2.82 b)	0.9_4 b)	$6._1$ b)
Hex_4NClO_4	(-2.41) c)	1.9_4 c)	$19._4$ c)	(-2.61) c)	1.5_8 c)	$23._5$ c)	(-2.76) c)	1.7_4 c)	$15._6$ c)
$LiClO_4$	(-2.40) c)	2.4_1 c)	$13._6$ c)	—	—	—	—	—	—

a) The concentration of the supporting electrolyte is 0.05 M in each case.
$E_{1/2}$: half-wave potential in V *vs.* Ag/0.1 M $AgClO_4$, i_1: limiting current in μA, i_p: AC peak height in μmho, C: concentration of the depolarizer in mM, and τ: drop_time at the peak potential in sec.

b) Kinetic controlled, irreversible wave.

c) Diffusion controlled, reversible wave, but with a polarographic maximum.

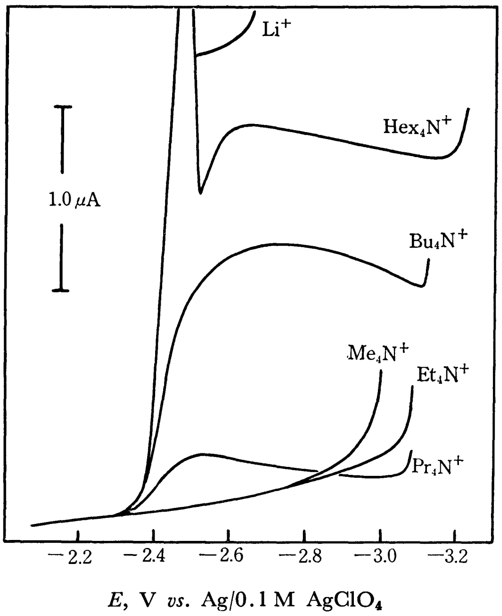

Fig. 1. Polarograms of 1.05 mM $Ba(ClO_4)_2$ in HMPA. 0.05 M solutions of various perchlorates are used as the supporting electrolytes. Cation of the supporting electrolyte is shown on each curve.

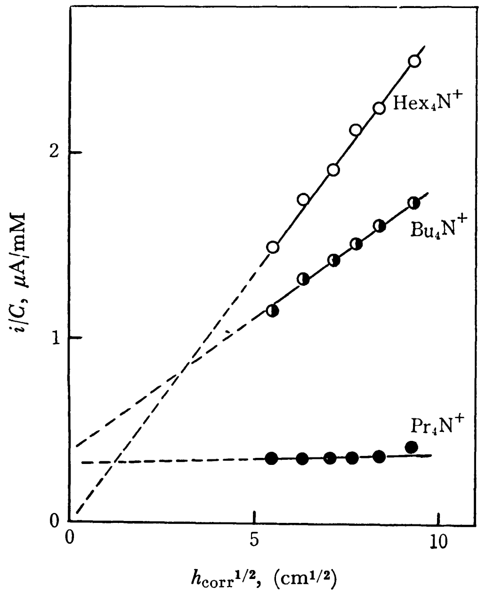

Fig. 2. Effect of the height of the mercury column on the limiting current of barium wave in HMPA. Cations of the supporting electrolytes of 0.05 M perchlorates are shown on the curves.

$LiClO_4$ as supporting electrolytes. The results are summarized in Figs. 1, 4, and 5 and in Table 1.

Barium Ion. The barium ion in HMPA is irreducible when 0.05 M Me_4NClO_4 or 0.05 M Et_4NClO_4 is used as the supporting electrolyte (Fig. 1). In 0.05 M Pr_4NClO_4, however, a small wave appears at around −2.4 V and the limiting current is controlled by the rate of a preceding process, as judged from its dependence on the square root of the height of the mercury column (Fig. 2). In 0.05 M Br_4NClO_4, the barium wave is fairly well-defined but the i_1–$h^{1/2}$ relation in Fig. 2 shows that the limiting current is still not entirely diffusion-controlled. With 0.05 M Hex_4NClO_4 as the supporting electrolyte, a big maximum of the first kind is observed in the DC wave, but from the i_1–$h^{1/2}$ relation (Fig. 2) and from the high AC wave (Table 1) the reduction seems to be reversible and diffusion-controlled. The big limiting current observed in 0.05 M $LiClO_4$ is probably due to the maximum of the second kind.1)

Figure 3 shows the effect of Et_4NClO_4 on the barium wave in 0.05 M Hex_4NClO_4. It is noted that the addition of a very small amount of Et_4NClO_4 completely interferes with the reduction of the barium ion.

Strontium Ion. The strontium ion is irreducible in 0.05 M Me_4NClO_4, 0.05 M Et_4NClO_4, 0.05 M Pr_4NClO_4 (Fig. 4). With 0.05 M Bu_4NClO_4 as a supporting electrolyte, an irreversible wave is observed and the limiting current is controlled partly by diffusion and partly by the rate of a preceding process. In 0.05 M Hex_4NClO_4, a diffusion-controlled wave is obtained with the half-wave potential at about −2.61V, though the value is somewhat inaccurate due to the maximum of the first kind. The reduction in this supporting electrolyte seems to be reversible judging from the height of the AC polarographic wave (Table 1).

Calcium Ion. The calcium ion is irreducible in 0.05 M Me_4NClO_4, 0.05 M Et_4NClO_4, and 0.05 M Pr_4NClO_4 solutions (Fig. 5). In 0.05 M Bu_4NClO_4, an irreversible wave is observed, but the reduction is also controlled by the rate of a precedig process and then wave height is only half that of the diffusion wave. In 0.05 M Hex_4NClO_4 solution, the reduction of calcium ion preceeds reversibly, though an abnormal small maximum (or decrease of the base current) appears about 0.2V in advance to the main wave at $E_{1/2}=-2.76$ V, which also is accompanied by a small maximum (Fig. 5).

The calcium perchlorate salt is hygroscopic and the small amount of water from the salt makes the height of both

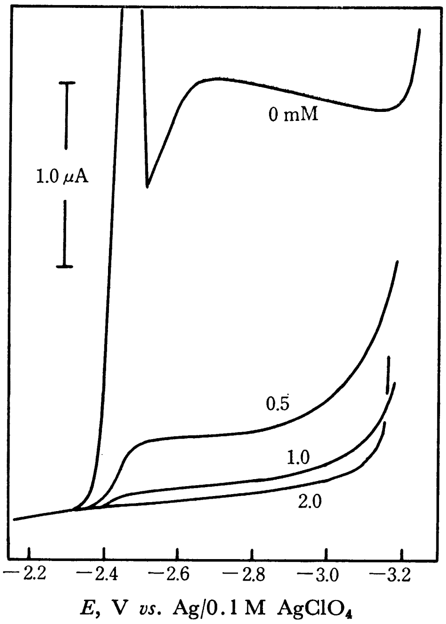

Fig. 3. Effect of the addition of the Et_4N^+ ion on the reduction wave of 1.07 mM barium ion in 0.05 M Hex_4NClO_4-HMPA.
Concentration of Et_4N^+ ion in mM is shown on each curve.

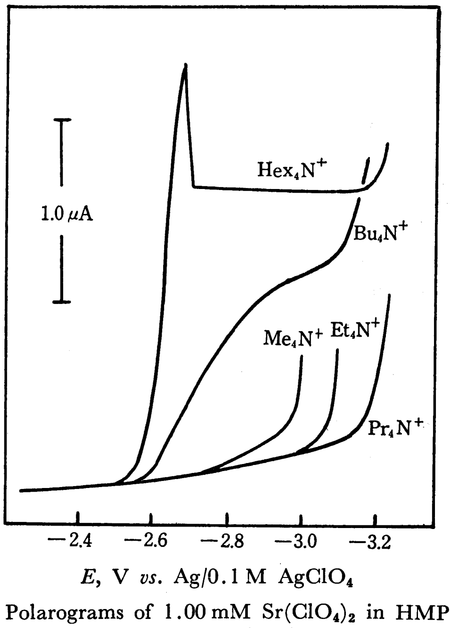

Fig. 4. Polarograms of 1.00 mM $Sr(ClO_4)_2$ in HMPA.
Cation of the supporting electrolyte is shown on each curve.

maxima increase. However, the reason for the appearance of the abnormal maximum, change of height and the shift of the potential of the abnormal maximum by the addition of water has not been elucidated yet.

Discussion

As in the case of alkali metal ions,[1] the reduction of alkaline earth metal ions in HMPA is strongly influenced by the cation of the supporting electrolyte. The effect is closely related to the size of the solvated cation of the supporting electrolyte. If the size of the solvated cation of the supporting electrolyte is small as in the cases of Et_4NClO_4 and Me_4NClO_4, the reduction of all alkaline earth metal ions is made irreducible. The reduction becomes easier with the increase in size. In Hex_4NClO_4 solutions, the reduction of all alkaline earth metal ions proceeds reversibly and is diffusion-controlled. When the size is in between these two extremes, reduction is irreversible and the limiting current is kinetically controlled.

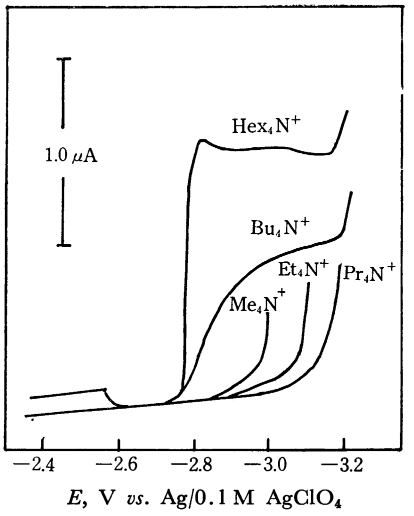

Fig. 5. Polarograms of 0.81 mM $Ca(ClO_4)_2$ in HMPA.
Cation of the supporting electrolyte is shown on each curve.

The adsorption of monovalent cation on the charged electrode surface at highly negative potential becomes easier with the decrease of the size of the solvated cation and, in the presence of two kinds of monovalent cations, a preferential adsorption of the smaller cation takes place.[1]

In the supporting electrolyte with small cation, the approach of heavily solvated alkali metal ions to the electrode surface is difficult and a preceding process is necessary in advance to the reduction of these ions. We considered this preceding process to be either a (partial) desolvation of the depolarizing cation or the penetration of the depolarizing ion through the adsorbed layer of the cation of the supporting electrolyte.

In HMPA, alkaline earth metal ions are heavily solvated and the Stokes law radii of the solvated ions 5.8—6.0Å for barium, strontium and calcium ions.[2] These values are much larger than 2.7Å for Et_4N^+, 3.2Å for MeN^+ and 3.7Å for Pr_4N^+, somewhat larger than 4.3Å for Bu_4N^+ and 4.9Å for Li^+, and approximately the same as 5.7Å for Hex_4N^+. Similar to the case of alkali metal ions, the reduction of alkaline earth metal ions in the supporting electrolyte with relatively small cation also seems to be difficult.

Gutmann *et al.*[3] reported that alkaline earth metal ions in dimethylacetoamide (DMA) are irreducible unless a small amount of water is introduced into the electrolytic solutions. They used Et_4NClO_4 as the supporting electrolyte. Alkaline earth metal ions in DMA also become reducible by using supporting electrolytes with larger cations.

---

[2] T. Fujinaga, K. Izutsu, and S. Sakura, *Nippon Kagaku Kaishi*, submitted to publication.

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