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# Polarographic Studies of Several Metal Ions in the Molten Salts of $KNO_3$–$LiNO_3$–$NaNO_3$

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**Synopsis.** The polarographic waves of Pb(II), Cd (II), Zn(II), and Tl(I) ions in molten salts of $KNO_3$–$LiNO_3$–$NaNO_3$ were measured by means of d.c. polarography, using an $Ag/AgNO_3$ reference electrode. The half-wave potential of metal ions was shifted toward more negative values in comparison with those in a nitrate melt containing no Li(I) ion.

The formation constants of several metal halide complexes in an alkali nitrate melt have been determined by means of d.c. polarography.[1-3] On the other hand, there have been only a few studies about the effect of the alkali metal ion as a component of the solvent on the half-wave potential of the reducible species. Kawamura[4-6] studied, by means of voltammetry and chronopotentiometry, the change in the diffusion coefficient of the Ag(I) ion over a wide composition range of molten salts of $KNO_3$–$NaNO_3$, $KNO_3$–$LiNO_3$, and $KNO_3$–$CsNO_3$. Francini and Martini reported that the peak potentials($E_p$) of the oscillopolarogram of some metal ions in molten salts of $KNO_3$–$NaNO_3$ were shifted toward more positive values by adding variable quantities of $LiNO_3$ to the melt.[3]

The present authors have studied the half-wave potential($E_{1/2}$) of the polarographic wave of several metal ions in the molten salts of $KNO_3$–$LiNO_3$–$NaNO_3$, using the $Ag/AgNO_3$ reference electrode, and compared the obtained half-wave potential with the data obtained by Swofford and Holified[7] and by Tridot *et al.*[8]

## Experimental

Reagent-grade chemicals were used in these experiments. The solvent used was the $KNO_3$–$LiNO_3$–$NaNO_3$(53 : 30 : 17 mol%, mp 120 °C) eutectic system. The eutectic materials were separately dried in a vacuum-oven at 100 °C for several days, and these mixed and gently fused in an argon gas atmosphere.

The metal salts used were $Pb(NO_3)_2$, $TlNO_3$, $Cd(NO_3)_2 \cdot 4H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$. The polarographic waves of the metal ions were not disturbed by the crystal water in metal salts. The concentration of the metal ions in a melt was determined by means of EDTA titration. The capillary used as the dropping mercury electrode(DME) was made of Pyrex glass. The drop time of the DME was about 3—5 s per drop at a height of 60—80 cmHg. The $Ag/AgNO_3$(0.05 mol/kg) electrode was used as the reference electode. Asbestos was used as a diaphragm between the reference electrode and the test solution. The temperature used in the experiments was 180 °C. The rest of the experimental procedure has been described elsewhere.[9]

## Results and Discussion

The polarographic waves of some metal ions at 180 °C are shown in Fig. 1, in which curve(a) is a typical residual current curve and in which the useful potential range available to obtain polarographic waves is from 0 to −1.4 V *vs.* the $Ag/AgNO_3$ reference electrode; the maximum current obtained in this range was about 2 μA at −1.4 V. However, the final ascendent potential in the residual current was shifted toward a positive potential and the useful potential range was diminished about 100 mV, when the solution stood for a day and night. Curves(b), (c), (d), and (e) in Fig. 1 are the polarographic waves of the Pb(II), Cd(II), Tl(I), and Zn(II) ions. The polarographic waves of these metal ions indicated S-shaped waves. The plots of $E$ *vs.* $\log[i/(i_d-i)]$ for polarographic waves are shown in Fig. 2, in which the plots give a straight line and the slope of the line was Pb(II): 45 mV, Cd(II): 41 mV, Tl(I): 80 mV, and Zn(II): 41 mV

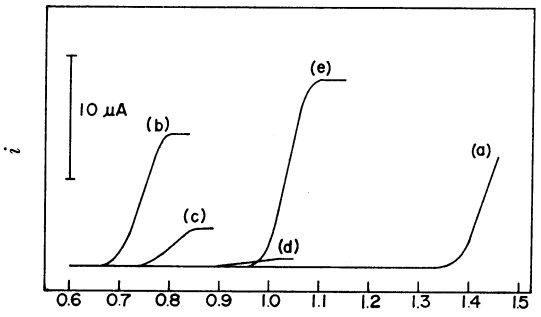


Fig. 1. Polarographic waves of some matel ions at 180 °C,
(a): Residual current curve of the molten salts of $KNO_3$–$LiNO_3$–$NaNO_3$, (b): Pb(II) ion, 2 mmol/kg, (c): Cd(II) ion, 1 mmol/kg, (d): Tl(I) ion, 0.2 mmol /kg, (e): Zn(II) ion, 3 mmol/kg.

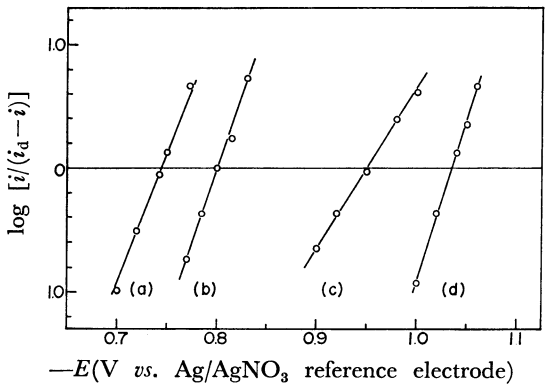


Fig. 2. Analyses of the polarographic waves of some metal ions at 180 °C. The slope of the line is 45, 41, 80, or 41 mV against $\log[i/(i_d-i)]$ for Pb(II), Cd(II), Tl(I), or Zn(II) ions.

Table 1. The half-wave potentials of some metal ions in molten alkali nitrates

| | $-E_{1/2}$ (V *vs.* $Ag/AgNO_3$) | | | | Ref. |
|---|---|---|---|---|---|
| | Pb(II) | Cd(II) | Tl(I) | Zn(II) | |
| Holifield and Swofford | — | 0.665 | 0.828 | — | (7) |
| Tridot *et al.* | 0.560 | 0.565 | 0.730 | 0.820 | (8) |
| Present authors | 0.744 | 0.800 | 0.949 | 1.034 | |

($2.303RT/F=90$ mV at 180 °C). These polarographic waves are reversible, and the electrode reactions of metal ions are the transfer of two electrons(one electron in the case of the Tl(I) ion). The half-wave potentials of the metal ions were determined from the logarithm plots; they are tabulated in Table 1. As is evident from Table 1, the half-wave potentials of metal ions had more negative values than that obtained in the solvent containing the Li(I) ion and the useful potential range is diminished as compared with those obtained in the molten salts of $KNO_3$–$NaNO_3$ by Swofford *et al.* and by Tridot *et al.* The half-wave potentials of the metal ions obtained by Swofford *et al.* also differed from those obtained by Tridot *et al.* It is considered that the discrepancy in the half-wave potentials in their data reflects the difference in the concentration of $AgNO_3$ in the reference electrode.

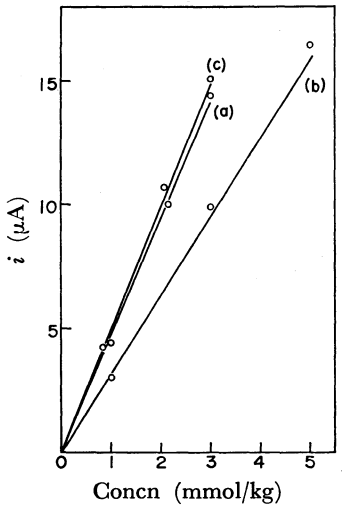


Fig. 3. Relationships between the limiting current and the concentrations of some metal ions at 180 °C.
(a): Pb(II) ion, (b): Cd(II) ion, (c): Zn(II) ion.

The linear dependence of the diffusion current on the metal ion concentration is shown in Fig. 3. The Ilkovic equation was applied in the ranges of 0.0—3.0 mmol/kg for Pb(II), 0.0—5.0 mmol/kg for Cd(II), and 0.0—3.0 mmol/kg for Zn(II). The diffusion current coefficients(I: $[\mu A]/[mg^{2/3}\,s^{-1/2}][mmol/kg]$) of the metal ions were Pb(II): 3.04, Cd(II): 3.11, Zn(II): 3.17. In the case of the Tl(I) ion, the maximum wave appeared in the concentration of the Tl(I) ion of more than 0.4 mmol/kg.

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