Polarography of Some Metal Ions in Fused LiCl-KCl-AlCl₃ System with a Dropping Mercury Electrode

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Polarography of Some Metal Ions in Fused LiCl-KCl-AlCl₃ System with a Dropping Mercury Electrode*

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Synopsis

Preparation and purification of fused LiCl-KCl-AlCl₃ system (m.p. 120°C) and polarographic behaviors of Pb(II), Cd(II), and Zn(II) ions in the fused salt at 160°C were studied by using a dropping mercury electrode as an indicator electrode. All the current-voltage curves of these metal ions were reproducible and the electrode reactions were reversible. Each of log(iliq-1) vs. E plots gave a straight line with a slope of 43~45 mV, which agreed well with the theoretical value of 43 mV for two electron discharge at 160°C. The heights of the polarographic waves of Cd(II) and Zn(II) ions were proportional to their concentrations, and the diffusion current constants of Cd(II) and Zn(II) ions were 2.610±0.008 and 0.507±0.001, respectively.

I. Introduction

The polarography has been applied comparatively in recent years for the studies on the behaviors of metal ions in the fused salt media. Lyalikov and others⁴ obtained the polarographic current-voltage curve of a metal ion by using solid platinum as an indicator electrode. They found linear relationships between the concentrations and the heights of polarographic waves of some metal ions.

Polarographic studies of metal ions with a dropping mercury electrode as an indicator electrode in the fused salt having low melting point were carried out first by Nachtrieb and others⁵. They dissolved nickel salt in fused lithium nitrate, ammonium nitrate and ammonium chloride system and obtained a good polarographic wave. Consequently, it was found that the reduction wave of nickel ion followed the Ilkovic equation. However, it was unstable fused salt and after the salts of nickel, lead, cadmium and zinc were dissolved in the eutectic nitrate of lithium, sodium and potassium (m.p. 120°C) as the fused solvent of the low melting point, polarographic waves were obtained by using a dropping mercury electrode⁶. Then, the relation between concentrations of reducible ions and wave heights, and the current-voltage curves were examined and also potentials of the amalgam

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(1) Yu. S. Lyalikov and V.I. Karmazin, Zavodskaya Lab., 14 (1948), 144.
(3) N.H. Nachtrieb and M. Steinberg, ibid., 72 (1950), 3858.
electrode of these metals were measured. Colichman\(^{(4)}\) measured the decomposition potentials of various metal ions in fused ammonium formate using a dropping mercury electrode. Gut\(^{(5)}\) made an experiment on chloride fused salt of sodium, potassium and aluminium as the supporting electrolyte of low melting point, using solid platinum microelectrode to obtain the polarographic waves of niobium and tantalum. He succeeded in finding the separated wave of niobium and tantalum. In the present experiment, the polarography of fused salt was also studied with the purpose to make clear the electrochemical behavior of metal ions in fused salt. First, the low melting fused salt of a ternary system of lithium chloride, potassium chloride and aluminium chloride was tried to use and the preparation and the purification of this fused salt was examined. Then, oxides of cadmium, lead and zinc were dissolved in the purified eutectic solution and the polarographic studies of these metal ions were made with a dropping mercury electrode.

II. Apparatus and reagents

1. Polarograph apparatus

   The polarograph used was the Yanagimoto's pen-recording DC polarograph and its polarization rate was 3.2 mV/sec at 0~2.0V.

2. Cell for preparation of fused salt and for polarography

   The fused salt was prepared with a porcelain crucible or with a hard glass cell. The cell used for the polarography was made of borosilicate glass. As shown in Fig. 1, it was 35 mm in diameter and 150 mm in depth. At the bottom of the cell a hollow

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place, 15 mm in diameter and 3.0 mm in depth was prepared for the mercury pool as an anode.

3. Dropping mercury electrode and reference electrode

The dropping mercury electrode used was 2~5 sec/drop at about 30~60 cmHg in fused salt solution at 160°C. The reference electrode proposed by Nachtrieb(3) was used. As shown in Fig. 2, it was a test tube, 10 mm in diameter and 150 mm in depth, made of borosilicate glass, in which a branch tube of 2 mm in diameter was fixed. Mercury was put in the bottom of the test tube. Mercurous chloride and mercury were mixed well muddily, and then well-dried potassium chloride were added to it. This tube was immersed in the fused salt solution at 160°C and the fused salt was put into the branch tube. Then, it was kept to stand for about one or two days and made the potential stable. The polarograms of some metal ions were taken and the stability of this reference electrode was found by examining the variation of those half-wave potentials. With the above-mentioned procedure, the saturated calomel electrode was stabilized enough and though it became hard with cooling, it could be used again if it was heated.

![Fig. 2. Saturated calomel electrode](image)

1) Mercury
2) Mercurous chloride
3) KCl crystal
4) Fused salt
5) Pt wire sealed with lead glass
6) Salt bridge
7) Cork stopper

4. Heat and temperature control

A vertical type electric furnace, that was wound with iron-chromium wire of 1.2 mm in diameter on a tubular Alundum refractory, was used for preparing the fused salt. Paraffin bath stirred well with a stirrer was used for heating the polarographic cell. The paraffin was not decomposed even at 200°C, but when it was used for a long time its color gradually became dark brown. Then, it could not be used for the observation of the electrode, and it was necessary to change it for a new one.
5. Reagents
The reagents used were of the first grade or of the special grade. Metal oxide was prepared from each metal salt by the usual method.

III. Preparation and purification of fused salt

1. Preparation
Well-dried lithium chloride and potassium chloride were mixed with the molar ratio of 21.1 to 19.7. It was put into the porcelain crucible and heated to melt at 700°C in the electric furnace. In this case it was unnecessary to fuse it in nitrogen atmosphere, but the lid of the crucible should be closed tightly, not to absorb any moisture. The melting point of the eutectic salt was about 400°C. After fusion it was cooled in a desiccator, put into a hard glass beaker and heated to melt slowly in the electric furnace. Then, aluminium chloride was added little by little and dissolved more than the calculated value. As white fumes of aluminium chloride evolved very much, it was necessary to lower the temperature under 200°C. When the fusion was continued at the temperature below 200°C, excess of aluminium chloride evaporated gradually and the eutectic composition became constant and stable. There was almost no evaporation of aluminium chloride afterwards. The fused salt prepared by the above-described method contained a large amount of impurities (mainly iron and water) and was transparent and of yellowish brown color.

2. Purification
The purification of this raw fused salt was made as follows: The fused salt containing impurities was put into a hard glass tube, 30 mm in diameter and 250 mm in depth. It was heated gradually to melt at about 200°C in the electric furnace and aluminium pieces (99.99 per cent purity) were added to it at the ratio of about 5~6 g to 100 g of the fused salt. At first it boiled extremely, but the white fume of aluminium chloride did not evolve. This state stopped after 5~10 minutes and afterwards a quiet convection took place. The fused salt changed its color into black and then formed black granules by degrees. Soon, they gathered, became a large lump and continued the convection. When it was heated for a day, the black grains stuck to the aluminium pieces, and colorless and transparent fused salt was obtained.

3. Composition and melting point of purified fused salt
The analytical result of the composition of purified fused salt is shown in

<table>
<thead>
<tr>
<th></th>
<th>Weight %</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>8.7</td>
<td>21.1</td>
</tr>
<tr>
<td>KCl</td>
<td>14.4</td>
<td>19.7</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>78.9</td>
<td>59.2</td>
</tr>
</tbody>
</table>
Table 2. Result of melting point measurement of the fused salt.

<table>
<thead>
<tr>
<th></th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. at which melting begins</td>
<td>95</td>
</tr>
<tr>
<td>Temp. at which solution becomes clear</td>
<td>110~125</td>
</tr>
<tr>
<td>Temp. at which first crystal begins to</td>
<td>120</td>
</tr>
<tr>
<td>deposit from clear solution</td>
<td></td>
</tr>
</tbody>
</table>

Table 1, and the measurement of the melting point is tabulated in Table 2.

IV. Result of the polarographic experiment and the consideration

The polarograms of lead, cadmium and zinc ions and also that of the mixed ions of cadmium and zinc are shown in Figs. 3(a) and (b). The polarographic waves of every metal ion obtained in the present experiments were similar to those in the aqueous solution by using the dropping mercury electrode, and all of them showed their figures like S type. In the mixed solution of lead and cadmium the separated polarographic waves could not be obtained because of the approach of their half-wave potentials. However, in the mixed solution of cadmium and zinc ions, separated and good polarographic waves were obtained as shown in Fig. 3(b).

1. Current-voltage curves of polarographic waves

If the above electrode reactions of reducible species in this fused salt are reversible as in the aqueous solution using the dropping mercury electrode, the Heyrovsky-Ikovic equation (1) should be set up on the current-voltage curves.

\[ E = E_{1/2} - 2.3 \text{RT/nF} \cdot \log \left( i/i_0 - i \right) \]  \hspace{0.5cm} (1)

where, \( E \) is electrode potential (V), \( E_{1/2} \) half-wave potential, \( n \) number of electron discharge given by electrode reactions, \( R \) gas constant, \( T \) absolute tem-

![Polarograms of Pb²⁺, Cd²⁺ and Zn²⁺ ions](image)

Fig. 3a. Polarograms of Pb²⁺, Cd²⁺ and Zn²⁺ ions
Pb²⁺: 2.5 mmoles, Cd²⁺: 0.66 mmoles, Zn²⁺: 2.7 mmoles, Temperature: 160°C
Fig. 3b. Polarogram of Cd\textsuperscript{2+}+Zn\textsuperscript{2+} ions
Cd\textsuperscript{2+}: 1.7 mmoles, Zn\textsuperscript{2+}: 2.5 mmoles, Temperature: 160°C

Fig. 4a. Relationship between E and log (i/i_d−i)
(A): Pb\textsuperscript{2+} ion, (B): Cd\textsuperscript{2+} ion

Fig. 4b. Relationship between E and log (i/i_d−i)
(C): Zn\textsuperscript{2+} ion
perature and F Faraday constant. Accordingly, the relation between the electrode potential and \( \log(i/i_d-i) \) in the equation (1) gives a straight line and its slope has to be \( 2.3RT/nF \). When \( \log(i/i_d-i) \) is zero, \( E \) is to be equal to \( E_{1/2} \).

When \( n \) is 2 at 160°C, the theoretical value of \( 2.3RT/nF \) should be 0.043 V. The relation between the electrode potential of the polarogram of each metal ion and \( \log(i/i_d-i) \) obtained from Fig. 3 is shown in Figs. 4(a) and (b). From these results, it was found that a slope of the straight line is 0.043 V in the case of lead ion and 0.045V in both cases of cadmium and zinc ions. Then, half-wave potential obtained from the polarogram is –0.34V on lead ion, –0.37V on cadmium ion and –0.62V on zinc ion vs. the saturated calomel electrode. On the other hand, the half-wave potential obtained from the relation between the electrode potential and \( \log(i/i_d-i) \), that is, the voltage at the position of \( \log(i/i_d-i)=0 \), is –0.34\textsubscript{9}V on lead ion, –0.37\textsubscript{9}V on cadmium ion and –0.62\textsubscript{3}V on zinc ion. The difference is within ±0.005V except lead ion.

2. Relation between the concentration of reducible ion and the limiting current

Supposing that the behavior of the fused salt is the same as that of the electrolyte in the aqueous solution, the current is limited only to diffusion current on the polarogram, it is directly proportional to the concentration of the reducible substance in the solution, and it should follow the Ilkovic equation. From the result of the experiment in the cases of cadmium and zinc, it is recognized that the proportional relation is composed by passing through the original point on the graph between the concentration of reducible ion and the diffusion current. Table 3 shows the relations between the average weight (m) of a mercury drop of the dropping mercury electrode, dropping intervals (t) and the diffusion current \( i_d \) for cadmium chloride.

<table>
<thead>
<tr>
<th>Solution</th>
<th>( t ) (sec)</th>
<th>( m^{3/3}, \frac{t^{1/6}}{\text{max}} )</th>
<th>( i_d ) (μA)</th>
<th>( \frac{i_d}{m^{3/3}, \frac{t^{1/6}}{\text{max}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N-KCl aqueous soln.</td>
<td>4.10</td>
<td>1.288</td>
<td>11.73</td>
<td>9.11</td>
</tr>
<tr>
<td>Fused LiCl-KCl-AlCl\textsubscript{3} soln.</td>
<td>4.25</td>
<td>1.219</td>
<td>8.0</td>
<td>6.56</td>
</tr>
</tbody>
</table>

* Cd\textsuperscript{2+} ion: 2.5 mmoles.

Table 3. Comparison of \( i_d/m^{3/3}, \frac{t^{1/6}}{\text{max}} \) of Cd\textsuperscript{2+} ion* in 1N-KCl aqueous solution and fused LiCl–KCl–AlCl\textsubscript{3} solution

in both cases of aqueous solution and fused salt solution. The value of \( i_d/m^{3/3}, \frac{t^{1/6}}{\text{max}} \) in the case of fused salt solution is about 72 per cent of that in the case of aqueous solution. Because the fused salt solution has higher viscosity than the aqueous solution, the reducible ions could not diffuse in the fused salt media as rapid as in the aqueous solution. Next, the results of the diffusion current constants (I) of cadmium and zinc ions calculated by the equation (2) are shown in Tables 4 and 5.
Table 4. Diffusion current constant of Cd\(^{2+}\) ion in fused LiCl–KCl–AlCl\(_3\) solution.

<table>
<thead>
<tr>
<th>(C_s) (mmoles/1000 g)</th>
<th>(m) (mg/sec)</th>
<th>(t) (sec/drop)</th>
<th>(i_d) (μA)</th>
<th>(m^{2/3}t_{\text{max}}^{1/6})</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66</td>
<td>0.941</td>
<td>4.25</td>
<td>2.1</td>
<td>1.2192</td>
<td>2.607</td>
</tr>
<tr>
<td>1.00</td>
<td>0.941</td>
<td>4.25</td>
<td>3.2</td>
<td>1.2192</td>
<td>2.607</td>
</tr>
<tr>
<td>1.45</td>
<td>0.941</td>
<td>4.25</td>
<td>4.6</td>
<td>1.2192</td>
<td>2.607</td>
</tr>
<tr>
<td>1.74</td>
<td>0.941</td>
<td>4.25</td>
<td>5.5</td>
<td>1.2192</td>
<td>2.592</td>
</tr>
<tr>
<td>2.50</td>
<td>0.941</td>
<td>4.25</td>
<td>8.0</td>
<td>1.2192</td>
<td>2.607</td>
</tr>
</tbody>
</table>

Table 5. Diffusion current constant of Zn\(^{2+}\) ion in fused LiCl–KCl–AlCl\(_3\) solution.

<table>
<thead>
<tr>
<th>(C_s) (mmoles/1000 g)</th>
<th>(m) (mg/sec)</th>
<th>(t) (sec/drop)</th>
<th>(i_d) (μA)</th>
<th>(m^{2/3}t_{\text{max}}^{1/6})</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8</td>
<td>0.932</td>
<td>4.0</td>
<td>3.60</td>
<td>1.219</td>
<td>0.507</td>
</tr>
<tr>
<td>7.8</td>
<td>0.932</td>
<td>4.0</td>
<td>4.82</td>
<td>1.219</td>
<td>0.507</td>
</tr>
<tr>
<td>9.2</td>
<td>0.932</td>
<td>4.0</td>
<td>5.67</td>
<td>1.219</td>
<td>0.506</td>
</tr>
<tr>
<td>11.5</td>
<td>0.932</td>
<td>4.0</td>
<td>7.12</td>
<td>1.219</td>
<td>0.508</td>
</tr>
</tbody>
</table>

\[
I = \frac{i_d}{C_s \cdot m^{2/3} \cdot t_{\text{max}}^{1/6}}.
\] (2)

where, \(C_s\) expresses the concentration of the reducible ion.

The average value of the diffusion current constant in the case of cadmium is 2.60±0.01 at the concentration of 0.66—2.50 mmoles, and that in the case of zinc is 0.507±0.001 at the concentration of 5.8—9.2 mmoles.

3. Comparison of the half-wave potentials of lead, cadmium and zinc ions in various fused solvents by using a dropping mercury electrode

Table 6 was made for the comparison of half-wave potentials of various ions obtained by the present authors and other investigators. As will be seen in Table 6, it may be not proper to compare them with one another because the value of Colichman’s experiment of using fused ammonium formate is the potential against platinum anode and not the one against the saturated calomel reference electrode. But others are the values referred with the saturated calomel electrode.

Table 6. Comparison of half-wave potential of Pb\(^{2+}\), Cd\(^{2+}\) and Zn\(^{2+}\) in various fused salt solutions.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Fused LiNO(_3)-KNO(_3)-NaNO(_2)</th>
<th>Fused ammonium formate</th>
<th>Fused LiCl-KCl-AlCl(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V)</td>
<td>(V)*</td>
<td>(V)</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>-0.474</td>
<td>-0.12</td>
<td>-0.35</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>-0.554</td>
<td>-0.26</td>
<td>-0.37</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>-0.875</td>
<td>-0.70</td>
<td>-0.62</td>
</tr>
</tbody>
</table>

* vs. Pt anode
Cadmium and zinc ions in this fused salt are reduced at more positive potentials than those in the other media.

V. Conclusion

Studies on the polarographic waves of cadmium, lead and zinc ions with a dropping mercury electrode were carried out by using fused LiCl–KCl–AlCl₃ system as a solvent and an electrolyte. In consequence it was found that the polarographic waves of these metal ions were composed of the relation of \( E = E_{\text{dil}} - 2.3RT/nF \cdot \log(i/i_{\text{dil}}) \) and that of \( i = i_{\text{dil}}/C_{\text{dil}} \cdot m^{2/3} \cdot t_{\text{max}}^{1/4} \cdot \text{constant} \). However, when the fused salt was used as a solvent, the potential range obtained was 0~1.1 V vs. S.C.E. and confined within narrow limits as shown in the residual current. This is the same as the experiments of Nachtrieb and others, and of Colichman. Therefore, it is inconvenient that the metals, from which the good polarographic waves can be obtained, are limited to use.