CHEMICAL EQUILIBRIUM IN MOLten SALT SOLutionS

Yuri K. Delimarsky

Institute of General and Inorganic Chemistry, Ukrainian SSR Academy of Sciences, Kiev, USSR

Abstract — The paper discusses two types of chemical equilibrium reactions (complex formation and acid-base reactions) in molten salt solutions. The thermodynamic and electrochemical methods for the study of complex formation in molten salt media are also discussed. Two types of acid-base equilibrium in ionic melts containing oxygen ions are considered.

INTRODUCTION

In molten salt solutions, two types of chemical equilibrium reactions are of greatest interest: 1) complex formation reactions; 2) acid-base reactions. Many methods have been developed for the study of complex formation in molten salt systems. They may be divided into three groups: 1) thermodynamic methods; 2) electrochemical methods; 3) physicochemical nonequilibrium methods (Ref. 1-6). In this paper, thermodynamic and electrochemical methods are considered.

THERMODYNAMICS

To thermodynamically characterize the complex formation in salt melts, we have proposed (Ref. 7) to use excessive thermodynamic functions. They are differences between the experimental and "ideal" values of the corresponding thermodynamic quantities

\[ \Delta \tilde{G}^E = \tilde{G} - \tilde{G}^i \]  
\[ \Delta \tilde{S}^E = \tilde{S} - \tilde{S}^i \]  
\[ \Delta \tilde{H}^E = \tilde{H} - \tilde{H}^i \]

\( \tilde{G}^E, \tilde{S}^E \) and \( \tilde{H}^E \) are the excessive functions, \( \tilde{G}^i, \tilde{S}^i \) and \( \tilde{H}^i \) the "ideal" values. The "ideal" values for molten salt systems can be calculated using Temkin's equation. For example, for \( \tilde{G}^i \) we have

\[ \Delta \tilde{G}^i = RT(N_A \ln N_A + N_B \ln N_B + N_C \ln N_C + N_D \ln N_D) \]

where \( N_A, N_B, N_C \) and \( N_D \) are the mole fractions of the molten salt system components. If we plot the excessive function against mole fraction, we obtain curves like those in Fig. 1.

The experimental values of thermodynamic functions are determined from emf measurements on appropriate chemical galvanic cells. By using this method, we have studied complex formation in many chloride systems. Some results of these studies are listed in Table 1. These data show that the most stable compounds are \( \text{Na}_2\text{BeCl}_4 \), \( \text{RbMgCl}_4 \) and \( \text{RbPbCl}_4 \). The composition of the most stable compounds can be established from the position of the minimum on \( \tilde{G}^E = N \) curves. After we had developed a platinum-oxygen reference electrode for ionic melts (Ref. 8), we studied the complex formation in molten oxide-salt systems. To this end, emf's of the chemical cells

\[ \text{Me} \mid \text{Me}_m\text{O}_n \text{ - salt} \mid \text{Pt}, \text{O}_2 \]

were measured. Sodium metaphosphate and borax were investigated as molten
Fig. 1. The change in excessive partial isobaric potential as a function of the composition of molten lithium, sodium, potassium and rubidium chlorides containing magnesium chloride at 718 °C

TABLE 1. Thermodynamic characterization of complex formation in molten chlorides

<table>
<thead>
<tr>
<th>Molten salt system</th>
<th>Temperature (°C)</th>
<th>Mole fraction</th>
<th>Thermodynamic excess quantities</th>
<th>( \Delta H^E ) (J/mol)</th>
<th>( \Delta G^E ) (J/mol)</th>
<th>( \Delta S^E ) (J/mol deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂-LiCl</td>
<td>718</td>
<td>0.33</td>
<td></td>
<td>-600000</td>
<td>+1975</td>
<td>21.7</td>
</tr>
<tr>
<td>MgCl₂-NaCl</td>
<td></td>
<td>0.33</td>
<td></td>
<td>-624000</td>
<td>-9450</td>
<td>21.6</td>
</tr>
<tr>
<td>MgCl₂-KCl</td>
<td></td>
<td>0.33</td>
<td></td>
<td>-624000</td>
<td>-29000</td>
<td>21.6</td>
</tr>
<tr>
<td>MgCl₂-RbCl</td>
<td></td>
<td>0.33</td>
<td></td>
<td>-</td>
<td>-41600</td>
<td>-</td>
</tr>
<tr>
<td>PbCl₂-LiCl</td>
<td>550</td>
<td>0.405</td>
<td></td>
<td>-335000</td>
<td>-175</td>
<td>4.05</td>
</tr>
<tr>
<td>PbCl₂-NaCl</td>
<td></td>
<td>0.551</td>
<td></td>
<td>-342000</td>
<td>-1890</td>
<td>1.07</td>
</tr>
<tr>
<td>PbCl₂-KCl</td>
<td></td>
<td>0.344</td>
<td></td>
<td>-351000</td>
<td>-9480</td>
<td>3.70</td>
</tr>
<tr>
<td>PbCl₂-RbCl</td>
<td></td>
<td>0.403</td>
<td></td>
<td>-354000</td>
<td>-10950</td>
<td>6.06</td>
</tr>
<tr>
<td>PbCl₂-NaCl-KCl</td>
<td>500</td>
<td>0.48</td>
<td></td>
<td>-330000</td>
<td>-5660</td>
<td>25.2</td>
</tr>
<tr>
<td>CuCl₂-PbCl₂-NaCl-KCl</td>
<td></td>
<td>0.40</td>
<td></td>
<td>-115800</td>
<td>-1590</td>
<td>16.6</td>
</tr>
<tr>
<td>AgCl₂-PbCl₂-NaCl-KCl</td>
<td></td>
<td>0.32</td>
<td></td>
<td>-3620</td>
<td>+2270</td>
<td>2.00</td>
</tr>
<tr>
<td>BiCl₃-PbCl₂-NaCl-KCl</td>
<td>430</td>
<td>0.30</td>
<td></td>
<td>-326000</td>
<td>-4680</td>
<td>18.8</td>
</tr>
<tr>
<td>BeCl₂-NaCl</td>
<td>500</td>
<td>0.32</td>
<td></td>
<td>-31300</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

salt ligands. Previous to that, the emf of the chemical cell

\[
\text{Me} | \text{Me}_m \text{O}_n | \text{Pt, O}_2
\]

had been studied. The results of these studies are given in Table 2. In five systems investigated, a noticeable chemical interaction takes place as evidenced by a great difference between concentrations and activities and by large values of excessive isobaric potentials. The strongest chemical interaction takes place in the systems: bismuth oxide-borax and bismuth oxide-sodium metaphosphate. The plot of Na\( \Delta \)G against N shows that in the
TABLE 2. Thermodynamic characterization of molten systems on the basis of emf measurements on galvanic cells

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Concentration (mole fraction)</th>
<th>Sodium metaphosphate</th>
<th>Borax</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Activity of the oxide</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Lead oxide</td>
<td>0.01</td>
<td>800</td>
<td>1.4x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>&quot;</td>
<td>8.2x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>&quot;</td>
<td>1.9x10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>&quot;</td>
<td>1.05x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>&quot;</td>
<td>8x10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>900</td>
<td>1.8x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>&quot;</td>
<td>0.8x10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>&quot;</td>
<td>7.8x10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>&quot;</td>
<td>3.3x10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>&quot;</td>
<td>2.3x10⁻⁴</td>
</tr>
<tr>
<td>Bismuth oxide</td>
<td>0.01</td>
<td>860</td>
<td>0.03x10⁻¹⁰</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>&quot;</td>
<td>0.3x10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>&quot;</td>
<td>0.12x10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>&quot;</td>
<td>0.3x10⁻⁶</td>
</tr>
<tr>
<td>Nickel oxide</td>
<td>0.05</td>
<td>900</td>
<td>0.21x10⁻²</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>&quot;</td>
<td>0.44x10⁻²</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>&quot;</td>
<td>0.72x10⁻²</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>&quot;</td>
<td>0.98x10⁻²</td>
</tr>
</tbody>
</table>

system lead oxide-sodium metaphosphate, the most stable complex corresponds to the composition PbO·6NaPO₃ (Fig. 2).

Fig. 2. A plot of $N \Delta G$ against $N$ for the system lead oxide-sodium metaphosphate: oo - 800 °C; xx - 900 °C

We studied the complex formation in the same molten systems by emf measurements on the concentration cells.
Complex formation in such systems can be inferred from the plots of $\gamma$ against $1/N_1$, where $\gamma$ is the emf and $N_1$ the mole fraction of the oxide. The bends on these plots correspond to the composition of complex compounds. In such a way, the complex compounds (Ref. 8-10): $\text{PbO} \cdot \text{NaPO}_3$; $\text{Bi}_2\text{O}_3 \cdot \text{NaPO}_3$ were determined. The formation of these compounds was confirmed by X-ray investigations (Ref. 11).
Chemical equilibrium in molten salt solutions

Fig. 3. Potentiodynamic curves: 1 — sodium chloride-potassium chloride melt (supporting electrolyte); 2 — supporting electrolyte + 4x10^{-3} mol of lead chloride; 3—6 — supporting electrolyte + 4x10^{-3} mol + 5x10^{-2}, 3x10^{-2}, 4x10^{-2} mol of potassium iodide respectively. These values are given for 1000 g of supporting electrolyte.

TABLE 3. Complex formation of the systems KCl-MeCl₂ (Me = Cd, Ni, Pb) in molten nitrates. Complexation of Pb²⁺ by the F⁻, I⁻ and CN⁻ ligands in molten chlorides

<table>
<thead>
<tr>
<th>Metal</th>
<th>Potentiometric method</th>
<th>Potentiodynamic method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ligand</td>
<td>solvent</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Cl⁻</td>
<td>NaNO₃-KNO₃</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Cl⁻</td>
<td>NaNO₃-KNO₃</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Cl⁻</td>
<td>NaNO₃-KNO₃</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>F⁻</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>I⁻</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>CN⁻</td>
<td>NaCl-KCl</td>
</tr>
</tbody>
</table>

Polarographic method

<table>
<thead>
<tr>
<th>Metal</th>
<th>ligand</th>
<th>solvent</th>
<th>β₁</th>
<th>β₂</th>
<th>β₃</th>
<th>β₄</th>
<th>n</th>
<th>β₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺</td>
<td>Cl⁻</td>
<td>NaNO₃-KNO₃</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Cl⁻</td>
<td>NaNO₃-KNO₃</td>
<td>5.5</td>
<td>6</td>
<td>15</td>
<td>14</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>Cl⁻</td>
<td>NaNO₃-KNO₃</td>
<td>21</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>

Interesting results were obtained when studying complex formation in the molten aluminium chloride-sodium chloride system. The concentration cells

\[
\begin{align*}
\text{Al} & \mid \text{AlCl}_3-\text{NaCl} \parallel \text{AlCl}_3-\text{NaCl} \mid \text{Al} \\
(\text{s}) & \parallel (\text{x})
\end{align*}
\]

have been investigated. In the left half-cell, there is a saturated sodium chloride solution and in the right one variable sodium chloride concentration (x).

In the melts under investigation, the most probable equilibria are

\[
\begin{align*}
\text{Al}_2\text{Cl}_6 + \text{Cl}^- & \rightleftharpoons \text{Al}_2\text{Cl}_7^\text{-} (K_1) \\
\text{Al}_2\text{Cl}_7^\text{-} & \rightleftharpoons \text{AlCl}_4^- + \text{AlCl}_3^- (K_2) \\
2\text{AlCl}_4^- & \rightleftharpoons \text{Al}_2\text{Cl}_7^\text{-} + \text{Cl}^- (K_3)
\end{align*}
\]
After the concentration of one of any species has been determined as a function of the melt composition, the concentrations of other species can be calculated from equations (10), (11) and (12). The equilibrium constants have the following values: $K_1 = (3 \pm 0.1) \times 10^8$; $K_2 = (2.6 \pm 0.1) \times 10^4$; $K_3 = (7.8 \pm 0.2) \times 10^4$.

In addition to potentiometric and potentiodynamic methods, we used polarography and chronopotentiometry for the study of complex formation in molten salt systems. With ionic melts, polarography is based on the application of solid electrodes. Therefore, we had to derive appropriate equations, which could permit the use of polarography with solid electrodes to study the complex formation in molten salt systems (Ref. 13). These equations are:

$$\varphi' - \varphi'' = \frac{nF}{RT} \ln \varphi - \frac{nF}{RT} \ln i_d/i_d$$

$$\varphi' - \varphi'' = \frac{nF}{RT} \ln \varphi$$

$$\varphi' - \varphi'' = \frac{nF}{RT} \ln \varphi - \frac{nF}{RT} \ln i_d/i_d$$

$$\varphi' - \varphi'' = \frac{nF}{RT} \ln \varphi - \frac{nF}{RT} \ln i_d/i_d$$

$$\varphi' - \varphi'' = \frac{nF}{RT} \ln \varphi - \frac{nF}{RT} \ln i_p/i_p$$

$$\varphi' - \varphi'' = \frac{nF}{RT} \ln \varphi - \frac{nF}{RT} \ln i_p/i_p$$

$\varphi$ is the complexity function, $i_d$ the limiting current, $i_p$ the peak current. A prime denotes the quantities that pertain to processes in the absence of ligand and a double prime in its presence. These equations permit determination of the function $\varphi$ by the shift of polarograms with adding a ligand.

Equations (13–18) describe different cases: reversible processes with and without depolarization, irreversible processes with and without depolarization. As is seen from Table 3, the agreement between the values obtained by potentiometric and polarographic methods is quite satisfactory. When studying the electrode kinetics in some ionic melts by chronopotentiometry, we detected kinetic currents, which indicate a chemical reaction, i.e., complex formation (Ref. 14). An example of such ionic melt is the system lithium chloride–potassium chloride–sodium tungstate. In this system exists the equilibrium

$$WO_4^{2-} \rightarrow WO_3 + O^{2-}$$

The species $WO_4^{2-}$ may be regarded as a complex ion, for which the stability constant may be given by the expression

$$K = \frac{[WO_3][O^{2-}]}{[WO_4^{2-}]}$$

To interpret the results of chronopotentiometric measurements, the following equations may be used:

$$i_k = nF \left\{ k_D \frac{[WO_3]}{K[O^{2-}]} \right\}^{1/2}$$

$$\mu = \left( \frac{D}{kK} \right)^{1/2}$$

$$\tau = \frac{K^2}{D}$$

$i_k$ is the kinetic current, $k$ the rate constant of electrode reaction, $D$ the diffusion coefficient, $K$ the equilibrium constant, and $\mu$ the reaction layer thickness. All these quantities can be determined from experimental data. The life time ($\tau$) of a complex species can be calculated from equation (23). For the $WO_4^{2-}$ and $CdBr_3^-$ species we found:
The complexity function is usually determined by the expression

$$\varphi = \frac{C}{[\text{Me}^{n+}]}$$

(24)

where $C$ is the total concentration, $[\text{Me}^{n+}]$ the concentration of "free" ions. Until recently, the discharge of a complex ion was considered to be preceded by its dissociation, e.g.,

$$\text{PbCl}_4^2- \rightarrow \text{Pb}^{2+} + 4\text{Cl}^-$$

(25)

$$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$$

(26)

In ionic melts, a direct discharge of complex species often takes place, e.g.

$$\text{SiF}_6^{2-} + 4e^- \rightarrow \text{Si} + 6\text{F}^-$$

(27)

In these cases, the expression (24) loses its physical meaning since there are no $\text{Me}^{n+}$ species in the ionic melt. Therefore, we proposed another expression for the complexity function in ionic melts:

$$\theta = \frac{[\text{MeX}_1]}{[\text{MeX}_m]}$$

(28)

where $[\text{MeX}_1]$ is the concentration of the total number of species containing $\text{Me}$, $[\text{MeX}_m]$ the concentration of electrochemically active species. On the basis of chronopotentiometric measurements, we have established a relation between the function $\theta$ and the electrode overpotential $\eta$ (Ref. 15):

$$\eta = \frac{t - \alpha}{\zeta} \frac{R}{2F} \ln \theta$$

(29)

Electrochemical methods give the most comprehensive information on the complex formation in ionic melts.

**ACID-BASE EQUILIBRIUM**

Interesting chemical interactions in ionic melts are acid–base equilibria. This type of equilibria was first studied by H. Lux (Ref. 16). Later on, such equilibria were studied by many investigators (Ref. 17, 18). We have studied acid–base equilibria of two types:

$$\text{MO}_{n/2} \rightleftharpoons \text{Me}^{n+} + n/2 \text{O}_2^-$$

(30)

$$\text{MO}_{n/2+1} \rightleftharpoons \text{MO}_{n/2} + \text{O}_2^-$$

(31)

These studies may be divided into two groups: a) study of complex formation in acid–base equilibria; b) study of the effect of acid–base equilibria on electrochemical kinetics. The former problem was partly considered above. Besides this, using potentiometric method, the equilibria

$$\text{CO}_3^{2-} \rightleftharpoons \text{CO}_2 + \text{O}_2^-$$

(32)

$$\text{P}_2\text{O}_7^{4-} \rightleftharpoons 2\text{PO}_3^- + \text{O}_2^-$$

(33)

$$\text{PO}_4^{3-} \rightleftharpoons \text{PO}_3^- + \text{O}_2^-$$

(34)

in different supporting electrolytes have been studied. A platinum–oxygen electrode was used as the indicator electrode and emf's of galvanic cells of the type

$$\text{Pt} | \text{MO}_{n/2+1}^{2-} - \text{NaCl-KCl} || \text{NaCl-KCl-PbCl}_2 | \text{Pb}$$
were measured. The concentration of oxygen ions was determined using the equation

\[ E = \text{const} + \frac{R T}{n F} \ln [O^{2-}] \]  

(35)

In these experiments, sodium hydroxide was used as the oxygen ion donor. On the basis of experimental data, the plots

\[ \varphi - [O^{2-}]; \varphi - [CO_3^{2-}]; \varphi - [P_2O_7^{4-}]; \varphi - [PO_4^{3-}] \]

were made. These are straight lines with different slopes. All of them are shifted relative to the reactions (32), (33) and (34) towards more positive potential values by the addition of oxygen ion donor. The chemical activity of the anion increases in the order

\[
\text{CO}_3^{2-} < \text{PO}_4^{3-} < \text{PO}_3^{2-} < \text{PO}_4^{3-}
\]

As a result of potentiometric measurements, titration curves are obtained when adding oxygen ions to the starting melts containing metaphosphate or pyrophosphate ions. The first curve bend indicates that the reaction proceeds by the mechanism (33). A further addition of oxygen ions leads to equation (34). When the oxygen ions are in large excess, one more weak bend is observed, which is due to the reaction

\[
\text{PO}_3^{2-} + 2O^{2-} \rightleftharpoons \text{PO}_3^{2-} \cdot 2O^{2-}
\]

(36)

The corresponding potentiometric titration curves are shown in Fig. 4. The results of the determination of the constants for some acid-base equilibria are given in Table 4.

Fig. 4. Potentiometric titration curves:
\( a - 0.25 \text{ mol\% } \text{PO}_3^{2-} + O^{2-} \); \( b - 0.15 \text{ mol\% } P_2O_7^{4-} + O^{2-} \);
\( c - 0.25 \text{ mol\% } P_3O_5^{3-} + CO^{2-} \)

Using potentiometric titration, the acidic properties of magnesium, strontium, zinc and nickel ions in the molten sodium chloride-potassium chloride eutectic at 700 °C have been studied. A zirconium oxygen electrode was employed in these measurements. The stoichiometry of acid-base reaction was determined from the relation

\[
\tilde{n} = \left[ O^{2-} \right] \left[ O^{2-} \right] / [\text{Me}^{2+}]
\]

(37)

where \( [O^{2-}] \) and \( [O^{2-}] \) are the overall and equilibrium concentrations of oxygen ions. The concentration constants calculated from the equation

\[
K_n = \tilde{n} / [O^{2-}] (1 - \tilde{n})
\]

(38)
TABLE 4. Acid-base equilibrium constants for carbonate and phosphate ions in the NaCl-KCl melt at 700 °C

<table>
<thead>
<tr>
<th>Acid-base reaction</th>
<th>Equilibrium constant values from experimental data</th>
<th>Equilibrium constant values from relations between constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 + \text{O}^{2-} \rightleftharpoons \text{CO}_3^{2-} )</td>
<td>( 2.5 \pm 0.5 )</td>
<td></td>
</tr>
<tr>
<td>( 2\text{PO}_3^{4-} + \text{O}^{2-} \rightleftharpoons \text{P}_2\text{O}_7^{4-} )</td>
<td>((2.9 \pm 1.2) \times 10^3)</td>
<td></td>
</tr>
<tr>
<td>( \text{PO}_4^{3-} + \text{O}^{2-} \rightleftharpoons 2\text{PO}_3^{4-} )</td>
<td>((2.5 \pm 1.4) \times 10^3)</td>
<td></td>
</tr>
<tr>
<td>( \text{PO}_3^{4-} + \text{P}_2\text{O}_7^{4-} \rightleftharpoons \text{PO}_4^{3-} )</td>
<td>((5.6 \pm 2.7) \times 10^2)</td>
<td>((2.7 \pm 2.5) \times 10^2)</td>
</tr>
<tr>
<td>( \text{PO}_3^{4-} + 2\text{O}^{2-} \rightleftharpoons \text{PO}_3^{2-} + 2\text{O}_2 )</td>
<td>(7.98 \times 10^4)</td>
<td></td>
</tr>
<tr>
<td>( \text{PO}_4^{3-} + \text{CO}_2^{2-} \rightleftharpoons \text{PO}_4^{2-} + \text{CO}_2 )</td>
<td>((0.5 \pm 0.1) \times 10^2)</td>
<td>((1.1 \pm 1.2) \times 10^2)</td>
</tr>
</tbody>
</table>

and from the equilibrium ratio

\[ K = \frac{[\text{MeO}]}{[\text{Me}^2+][\text{O}^{2-}]} \]  

are close to each other. On the basis of the studies of the equilibria

\[ \text{Me}^{2+} + \text{O}^{2-} \rightleftharpoons \text{MeO} \quad (\text{Me} = \text{Mg, Sr, Zn, Ni}) \]  

the acidic properties of cations were found to decrease in the order (Ref. 19):

\[ \text{Mg}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Sr}^{2+} \]

To elucidate the effect of acid-base reaction on the electrochemical kinetics in ionic melts, we have carried out chronopotentiometric and polarographic investigations. In particular, the reduction of carbonate ion in sodium chloride-potassium chloride eutectic as supporting electrolyte has been studied. In this melt, the equilibrium (40) exists. A two-step reduction of carbonate ion was established. To judge by the transition time ratio, the reduction of carbonate oxide agrees well with the following mechanism

\[ \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_2^{2-} \]  

(41)

\[ \text{CO}_2^{2-} + 2\text{e}^- \rightarrow \text{C} + 2\text{O}_2 \]  

(42)

Using the well-known equation

\[ \frac{1}{2} \gamma = \frac{1}{2} \mu^{1/2} \frac{1}{2} \text{PO}_3^{1/2} \frac{1}{2} \text{O}_2^{1/2} \frac{1}{2} \text{D}^{1/2} \frac{1}{2} \text{ki} \]  

(43)

and chronopotentiometric data, plots of \( \frac{1}{2} \gamma \) against \( i \) and \( \frac{1}{2} \gamma \) against \( \frac{1}{2} \gamma \) were made, which are shown in Fig. 5. The first plot (a) has a bend, the second plot is a straight line with a negative intercept. These two facts indicate a kinetic process besides electrode reactions. This kinetic process is an acid-base reaction. To calculate the electrochemical kinetic parameters, the chronopotentiometric equation

\[ \varphi = 0.193/\alpha n_a \lg(nkC/i) + 0.193/\alpha n_a \lg 1 - (t/\tau)^{1/2} \]  

(44)

was used. For the electrochemical characteristics of carbonate anion we found: \( \alpha = 0.5 \); \( n_a = 1 \); \( k = (6.7 \pm 0.5) \times 10^{-3} \) cm/s (Ref. 20 & 21).

The equilibrium

\[ \text{PbO} \rightleftharpoons \text{Pb}^{2+} + \text{O}^{2-} \quad (K_1) \]  

(45)
in the lithium chloride-potassium chloride system has been studied by the polarographic method. In an alkaline melt, such equilibria as

$$\text{PbO}_2^2- \rightarrow \text{PbO} + 0^2- \rightarrow \text{Pb}^{2+} + 20^2- \quad (K_2)$$

also occur. In this case, the equation

$$\phi_{1/2} = \frac{RT}{a} nF \ln K_2 - \frac{RT}{a} nF \ln K_1 - \frac{RT}{a} nF pO - \frac{RT}{a} nF \ln d i$$  \hspace{1cm} (47)

is valid (Ref. 22). Equation (47) permits calculation of some electrochemical kinetic parameters as well. Besides, it indicates an effect of acid-base equilibria on electrochemical kinetics. Thus, chronopotentiometric and polarographic methods can be successfully used for the study of acid-base reactions in ionic melts.

REFERENCES