The Internal Mobilities of the Molten Binary System (Rb—Cs)NO₃

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Internal mobility ratios in the molten binary system (Rb—Cs)NO₃ have been measured with the Klemm method. From these and the available data on the densities and conductivities, the internal mobilities of Rb⁺ and Cs⁺ have been calculated. Above (below) 420 °C, Cs⁺ is found to be more (less) mobile than Rb⁺. The internal mobilities of these ions in various binary alkali nitrates are compared.

1. Introduction

In a series of investigations we have studied ratios of the internal mobilities of the two cations in molten binary alkali nitrates with a countercurrent electromigration method, i.e. the Klemm method [1] (see Table 1). In all the systems except (K—Rb)NO₃, the Chemla effect ([9, 10]) has been observed, i.e. the phenomenon that the mobility of the larger cation is greater than that of the smaller one in a certain range of temperature and concentration. When the difference in the size of the two cations is small, the Chemla effect occurs only at high concentrations of the larger cation at relatively high temperatures, as exemplified by the case of (Na—K)NO₃ [7]. In the present work we explore whether the Chemla effect occurs in the system (Rb—Cs)NO₃.

In a study using radioactive tracers in a Hittorf-type cell, Shvedov and Ivanov have found that the mobilities of Rb⁺ and Cs⁺ in (Rb—Cs)NO₃ are nearly equal at 693 K in the whole concentration range [11].

We have employed the Klemm method for the determination of the internal mobility ratio of Rb⁺ and Cs⁺ because this method seems to be the most accurate one in case of cations with nearly equal mobilities.

From the mobility ratios and the available data on the densities and conductivities the internal mobilities of Rb⁺ and Cs⁺ have been calculated.

2. Experimental

RbNO₃ and CsNO₃ of better than 99% purity, produced by Soekawa Chem. Co. in Tokyo, were used without further purification since the Klemm method is relatively insensitive to small amounts of impurity. Possible moisture was removed with the procedure previously described [4].

The electromigration cell is shown in Figure 1. In the large compartment, (Li—Na—K)NO₃ of the eutectic composition (37.5—18—44.5 mol%) was used. The method of filling the cathode compartment with NH₄NO₃, which had been used in some of our previous experiments, has not been employed in the present study because it was necessary to go to rather high temperatures where NH₄NO₃ decomposes too quickly.

Therefore the classical way of bubbling a mixture of NO₂ and O₂ at the cathode to regenerate otherwise electrodeposited metal into the original nitrate [12, 13] was employed. The aluminium wire used as the cathode was gradually corroded, probably by

Table 1. Binary alkali nitrate systems (M₁—M₂)NO₃ whose internal cationic mobility ratios have been measured with the Klemm method [1].

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁</td>
<td></td>
<td>[5]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₂</td>
<td></td>
<td>[8], [5]</td>
<td>[6]</td>
<td></td>
<td>[4]</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td></td>
<td></td>
<td>[3]</td>
<td>[7]</td>
</tr>
<tr>
<td>Rb</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>this work</td>
</tr>
</tbody>
</table>

*Measured at an NaNO₃ concentration of 91.8 mol% at 649 K.
making an alloy with Li metal, but this did not disturb the separation process on the anode side. The content of Rb+ and Cs+ in the samples from the separation tubes was determined with flame spectrophotometry; 1000 ppm of Na+ were added to each aqueous solution containing several 10 ppm of Rb+ and Cs+ in order to depress too easy ionization of the corresponding salts.

The other experimental procedures were similar to those previously employed ([4–7]).

3. Results

Table 2 gives the main experimental conditions and the obtained relative differences in the internal mobilities

\[ \varepsilon_{12} = \left( b_{\text{Rb}} - b_{\text{Cs}} \right) / \left( \rho_{\text{Rb}} b_{\text{Rb}} + \rho_{\text{Cs}} b_{\text{Cs}} \right), \]

where \( b \) and \( \rho \) are the internal mobility and the mole fraction of the ion specified by the subscript, respectively; \( \rho_{\text{Rb}} + \rho_{\text{Cs}} = 1 \). The internal cationic mobilities result from the equations

\[ b_{\text{Rb}} = \left( \Lambda / F \right) \left( 1 + \rho_{\text{Cs}} \varepsilon_{12} \right), \]

\[ b_{\text{Cs}} = \left( \Lambda / F \right) \left( 1 - \rho_{\text{Rb}} \varepsilon_{12} \right), \]

where \( \Lambda \) is the molar conductivity of the mixture calculated from the data on the densities [14] and conductivities [15]; \( F \) is the Faraday constant. Our obtained internal cation mobilities vs. \( \rho_{\text{Cs}} \) are shown in Fig. 2 together with those obtained by Shvedov and Ivanov [11]. As these authors have used different conductivity data, their internal mobilities at 693 K, which we have estimated by reading the external mobilities from their drawing, appear to be considerably lower than ours; their data are, however, in good agreement with ours in that the mobilities of Rb+ and Cs+ are nearly equal in the whole concentration range.

4. Discussion

We have found from MD simulation of some molten alkali chlorides [10] that the internal mobilities are paralleled by the separating motion of neighbouring unlike ions. Three main factors affecting the separating motion have been taken into consideration [4–7]: Coulombic attraction between unlike ions, agitation of the ions, and free space.

Figure 2 shows that the Chemla effect occurs at the high temperature. With an increase in temperature the number density of the anions becomes smaller; therefore it becomes less favourable for the (smaller) cations than for the larger ones to leave a nearest neighbouring anion toward another anion, the process essential in ionic mobility.
The concentration dependence of $\varepsilon_{12}$ is small in the present system. This may be mainly due to the small relative variation in molar volume $V$ from RbNO$_3$ to CsNO$_3$, viz. $V = 64.7$ and $72.6$ cm$^3$ mol$^{-1}$ for RbNO$_3$ and CsNO$_3$, respectively, at 800 K, while for NaN$_3$ and KN$_3$, where the concentration dependence of $\varepsilon_{12}$ is greater, $V = 45.6$ and $54.6$ cm$^3$ mol$^{-1}$, respectively, at 650 K [16]. Also the variation of the free space and agitation effects over the concentration range would be small in RbNO$_3$-CsNO$_3$ mixtures.

A survey of the reciprocals of the internal mobilities of Rb$^+$ and Cs$^+$ in mixtures with other alkali nitrates in their dependence on the molar volume of the mixtures is given in Figures 3 and 4.

We have found [4–7] that the mobilities of small cations, and to some extent also of large ones, in binary alkali nitrates are well expressed by the equation

$$b = \frac{A}{(V - V^0)} \exp (-E/RT). \tag{4}$$

Here, $A$ and $E$ are constants depending on the cation of interest and $V^0$ is a constant nearly independent of temperature. In a limited concentration region near pure RbNO$_3$ and CsNO$_3$, $b_{\text{Rb}}$ and $b_{\text{Cs}}$ respectively might be expressed by (4). From the data of pure RbNO$_3$ and CsNO$_3$ recommended in [16], the parameter values of (4) have been calculated as given in Table 3.

In Figs. 5 and 6, $b_{\text{Rb}}$ and $b_{\text{Cs}}$ in several molten binary alkali nitrates are plotted against $p_{\text{Rb}}$ and $p_{\text{Cs}}$. At a given concentration, $b_{\text{Rb}}$ and $b_{\text{Cs}}$ become generally greater with decreasing radius of the
coexisting cations. \( b_{\text{Cs}} \) in (Li–Cs)NO\(_3\) is singularly small at high \( p_{\text{Cs}} \). This seems to be the case also for \( b_{\text{Rb}} \) in (Li–Rb)NO\(_3\), although \( b_{\text{Rb}} \) has not been measured at very high \( p_{\text{Rb}} \ (> 0.859) \). A similar trend is seen though not so clear, also for \( b_{\text{Rb}} \) in (Na–Rb)NO\(_3\) in which \( b_{\text{Rb}} \) has been measured at rather high \( p_{\text{Rb}} \). At a low density of the NO\(_3^-\) ions, every Li\(^+\) ion will be strongly clustered with neighbouring NO\(_3^-\) ions, and therefore the agitation effect by the Li\(^+\) ions upon the separating motion of the Cs\(^+\) (or Rb\(^+\)) and NO\(_3^-\) ions will be small. This may be the reason for the singularly small \( b_{\text{Cs}} \) (or \( b_{\text{Rb}} \)).

Very strong interaction of Li\(^+\) ions with anions at a low density of the anions has also shown up in the MD simulation of molten (Li–K)Cl by Lantelme and Turq [17], in which the Li–Cl distance is 212 pm at \( p_{\text{K}} = 0.90 \) while 221 pm in pure LiCl.

In conclusion, even the small difference in the coulombic force of Rb\(^+\) and Cs\(^+\) with NO\(_3^-\) causes the Chemla effect at high temperature. Thus, in all

Table 3. Parameter values of (4) in a limited concentration region near pure RbNO\(_3\) and CsNO\(_3\).

<table>
<thead>
<tr>
<th>M</th>
<th>( A \times 10^{11} ) m(^5) V(^{-1}) s(^{-1}) mol(^{-1})</th>
<th>( E ) kJ mol(^{-1})</th>
<th>( V_0 \times 10^6) m(^3) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>2.56</td>
<td>21.86</td>
<td>48.5</td>
</tr>
<tr>
<td>Cs</td>
<td>3.33</td>
<td>21.07</td>
<td>47.4</td>
</tr>
</tbody>
</table>

Fig. 5. Internal mobilities of Rb\(^+\) vs. mole fraction in (M–Rb)NO\(_3\). As for the symbols, see the legend to Figure 3.

Fig. 6. Internal mobilities of Cs\(^+\) vs. mole fraction in (M–Cs)NO\(_3\). As for the symbols, see the legend to Figure 4.
molten binary alkali nitrates except (K–Rb)NO₃, the Chemla effect has been observed; also in
(K–Rb)NO₃ the Chemla effect could be expected to occur at high temperature.