Internal Cation Mobilities in the Molten Binary System 
(Ag, Tl)NO₃

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Internal mobility ratios in the molten binary system (Ag, Tl)NO₃ have been measured by Klemm's countercurrent electromigration method. In the usual way the internal cation mobilities have been calculated from these data and those available on the densities and conductivities. In the investigated region of temperature and composition $b_{Ag}$ is greater than $b_{Tl}$.

Introduction

Papers on the internal cation mobilities in molten (Ag, M)NO₃ and (Tl, M)NO₃ (M = alkali metal ion), as measured by Klemm's countercurrent electromigration method, are listed in Table 1. The system (Ag, Tl)NO₃ studied in the present paper is interesting when compared with the aforementioned systems. The melting points of the eutectic mixtures ($x_{Ag} = 0.486$ and 0.515) are at 81 °C [7], and also the melting points of AgNO₃ (212 °C) and TlNO₃ (206 °C) are considerably lower than those of the alkali nitrates.

Table 1. Molten binary systems (Ag, M)NO₃ and (Tl, M)NO₃ whose internal cation mobility ratios have so far been studied by Klemm's method.

<table>
<thead>
<tr>
<th>M</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺</td>
<td>[1]</td>
<td>[2]</td>
<td>[1]</td>
<td>[3]</td>
<td>[3]</td>
</tr>
</tbody>
</table>

Experimental

The chemicals AgNO₃ and TlNO₃ of reagent grade, made by Wako Chem. Co. Ltd. and Misawa Chem. Co. Ltd., Japan, respectively, were used without further purification. These salts were vacuum-dried at 180 °C for 48 hr and mixed at chosen ratios by weighing.

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For electromigrations above 220 °C, the cell was of the type described in [8]. Molten NH₄NO₃ was used as catholyte, and the large vessel in which the separation tube was set contained the eutectic mixture of (Li, Na, K)NO₃ (30, 17 and 53 mol%; mp.: 120 °C [7]).

For electromigrations below 170 °C a cell of the type shown in [9] was employed, which contained the eutectic mixture of (Li, NH₄)NO₃ (25.3 and 74.7 mol%; mp.: 120 °C [7]) in the large vessel.

A separation tube of Vycor of 4 mm inner diameter was filled with alumina powder (150–180 μm). The temperature of the separation tube was kept constant within ±2 °C by a controller. After electromigration at 90 mA for a few hours the separation tube was taken out, cleaned on the outside and cut into pieces of 6–7 mm length. Each fraction was dissolved in dilute nitric acid for several hours. The content of Ag and Tl atoms was determined by atomic absorption spectrophotometry and flame spectrophotometry, respectively.

The temperature was measured by an Alumel-Chromel thermocouple, which was located in the eutectic mixture at a distance of about 1.5 cm from the part of the separation tube where the initial concentration did not change. The temperature difference between the thermocouple and the inside of the separation tube was estimated according to [10] to be about 1 °C.

Results

The relative difference in the internal mobilities $b_{13}$ and $b_{23}$ ($1 = Ag$, 2 = Tl, 3 = NO₃⁻), defined by

$$e = (b_{13} - b_{23})/b_c,$$

(1)
was derived from an equation [11] which is based on the charge and material balances. Here, 

\[ b_\varepsilon = x_{13} b_{13} + x_{23} b_{23} = \kappa V_m/F, \]  

where \( x_{13} \) and \( x_{23} \) are the mole fractions of the salts, \( \kappa \) is the conductivity, \( V_m \) the molar volume of the mixture, and \( F \) the Faraday constant.

The obtained values of \( \varepsilon \) are given in Table 2 together with the main experimental conditions. The internal cation mobilities \( b_{13} \) and \( b_{23} \) were calculated from the \( \varepsilon \) values and the data [12] on the densities and conductivities. The calculated values are given in Table 3, and the corresponding isotherms are shown in Figs. 1a and 1b. Since at low temperatures the liquid range of the concentrations decreases, the region to be covered for the mobility isotherms \( b \) decreased as well.

### Discussion

It is usual to identify \( M_1 \) of a molten binary \((M_1, M_2)X\) (salt mole fractions \( x_{13} \) and \( x_{23} = 1 - x_{13} \) with the metal in which the pure salt has a greater internal mobility than \( M_2 \) in the pure salt \((b_{13}(0) > b_{23}(1))\). For \( M_1 = \text{Ag, } M_2 = \text{Li, Na, K, Rb or Cs,} \) and \( X = \text{NO}_3, b_{13}(x_{23}) \) was found to be greater than \( b_{23}(x_{23}) \) in the studied range of concentrations and
temperatures. Figure 1 shows that this is also true for 
\( M_1 = \text{Ag}, \ M_2 = \text{Tl} \) and \( X = \text{NO}_3 \).

Generally for such binaries, \( b_{13} \) and \( b_{23} \) decrease 
with increasing \( x_{23} \), the decrease of \( b_{13} \) being steeper 
than that of \( b_{23} \). Figure 1 shows that for \((\text{Ag, Tl})\text{NO}_3\) 
this holds generally, but that it does not hold at 120°C 
and 140°C in the range \( 0.4 < x_{23} < 0.6 \), and at 220°C, 
270°C and 350°C in the range \( 0 < x_{23} < 0.2 \).

In [6] we will report on the mobilities in \((\text{K, Tl})\text{NO}_3\) 
and \((\text{Cs, Tl})\text{NO}_3\), so that then all systems listed in 
Table 1 will have been studied. On this occasion we 
intend to discuss the observations, including 
\((\text{Ag, Tl})\text{NO}_3\), in a broader context and in more detail.

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