Internal Mobilities in Molten (Li, Pb(II))Cl as Remeasured by the Klemm Method

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Internal cation mobility ratios in molten (Li, Pb(II))Cl at 650 °C have been remeasured by Klemm’s column method. From these and available data on the densities and conductivities, the internal mobilities $b_{Li}$ and $b_{Pb}$ have been calculated. It was found that at low LiCl content $b_{Li}$ is surprisingly high, while at low PbCl$_2$ content $b_{Pb}$ is surprisingly low. The former trend agrees with that found by Klemm and Monse with the migrating boundary method and disagrees with that found by Behl and Egan with the EMF method. The latter trend agrees with that resulting from a neglected point given by Behl and Egan and disagrees with that tentatively reported by Klemm and Monse. The peculiar mobility behaviour of (Li, Pb(II))Cl is compared with that of similar Cd(II), Sr, and Ba systems.

Introduction

More than 30 years ago the interal mobilities $b_{Li}$ and $b_{Pb}$ in molten mixtures of LiCl and PbCl$_2$ were measured by Klemm and Monse with the migrating boundary method [1] and by Behl and Egan with the EMF method [2]. At high PbCl$_2$ concentrations, an unexpected increase of $b_{Li}$ with increasing PbCl$_2$ content was found in [1] while the expected continuation of the decrease of $b_{Li}$ was found in [2]. This discrepancy prompted us to remeasure the mobility ratio $b_{Li}/b_{Pb}$ with Klemm’s column method [3], which we believe is more reliable than the other methods. The system (Li, Pb(II))Cl is convenient for such measurements because the mixtures melt at temperatures below 610 °C and are chemically stable. Also, molten lead, electrodeposited at the cathode, is neither corrosive nor forms dendrites.

With 1, 2, and 3 corresponding to Li, Pb and Cl, respectively, one has the following relations between mole fractions $x$ and equivalent fractions $y$:  

\[
y_1 = x_1/(2 - x_1), \quad y_2 = 2x_2/(1 + x_2), \\
x_1 = 2y_1/(1 + y_1), \quad x_2 = y_2/(2 - y_2).
\]

According to recent IUPAC recommendations one could define moles of Pb$_{0.5}$Cl and consequently call the $y$-values mole fractions. In this paper we do not follow these recommendations because they cause confusions when discussing earlier publications.

Experimental

The enrichment of PbCl$_2$ in the anode compartment and the adjoining vertical separation tube caused by electromigration was to be measured. From experience we knew that a disturbing gravitational convection does not occur in our separation tube, though PbCl$_2$ is denser than LiCl. (The densities of LiCl and PbCl$_2$ at 650 °C are 1.485 and 4.728 g/cm$^3$, respectively.) The cells shown in Figs. 1a, 1b, and 1c were used for the composition ranges 0 < $y_2$ < 0.5, 0.5 < $y_2$ < 0.75 and 0.75 < $y_2$ < 1, respectively, in order to have the levels in the container A and the anode compartment at about equal altitude. The container A of the cells a and b was filled with the eutectic mixture of LiCl and KCl ($y_{Li} = 0.588$ [4]), while that of the cell c was filled with the heavier eutectic mixture of LiCl and PbCl$_2$ ($y_{Li} = 0.208$ [5]). In cell b, the separation tube was placed inside a compartment D containing the same mixture as in the separation tube because the above eutectic mixtures seemed to be somewhat too light and too heavy, respectively, compared with the mixture in the separation tube. The cathode compartment B contained PbCl$_2$ in cells a and b, and the eutectic mixture of LiCl and PbCl$_2$ in cell c.

Reagent grade lithium chloride and lead chloride were used. The salts were vacuum-dried at ca. 180 °C.

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overnight. After sufficient mixing at the desired composition, the mixture was melted in a small quartz vessel. The separation tube C of Vycor, densely packed with alumina powder of 100–150 μm, was put in the vessel. The internal diameter of the separation tube was 4 mm, and the length of its diaphragm part was ca. 20 cm. The molten mixture was raised up over the diaphragm part by pump suction. Then the tube was transferred into A or D, and electromigration was started. Both electrodes were graphite rods of 10 mm Ø. With a temperature controller, the temperature was kept at the desired one within ±2 °C during electromigration.

It should be noted, however, that the temperature in the separation tube might have been somewhat higher due to Ohmic heating, cf. [6].
After several hours of electromigration, the tube C was taken out, cleaned on the outside and cut into several pieces of 10–15 mm length. Each fraction was kept in hot water at 90 °C for several hours to dissolve the salt completely (0.99 g and 3.34 g of lead chloride are soluble in 100 cm$^3$ water at 20 and 100 °C, respectively [7]). Then, the solution was diluted to 200 cm$^3$ and a portion of definite volume was further diluted to 100 cm$^3$. The contents of the Li and Pb were determined by flame and atomic absorption spectrophotometry, respectively.

**Results**

The "relative difference" in the internal mobilities of Li$^+$ and Pb$^{2+}$, as defined in [8], is

\[
\varepsilon_{12} = \frac{(b_1 - b_2)}{\bar{b}}
\]

with

\[
\bar{b} = y_1 b_1 + y_2 b_2.
\]

We use this definition here, though the average of the mobilities is $x_1 b_1 + x_2 b_2$. From the measurements, the $\varepsilon_{12}$ values were calculated as described in [8]. The main experimental conditions and results are given in Table 1.
The internal mobilities were calculated from
\[ b_1 = (x V_x / F) (1 + y_2 e_1), \]
\[ b_2 = (x V_x / F) (1 - y_2 e_1), \]
where \( x \) is the conductivity (formerly called specific
conductivity), \( V_x \) the equivalent volume of the mixture
and \( F \) is the Faraday constant. Density data of this
system were not available; therefore we assumed addi-
tivity of the molar volumes of LiCl and PbCl\(_2\). The
conductivities were read from Fig. 8 in [1]. The result-
ning mobilities are given in Table 2.

**Discussion**

In Fig. 2 the \( b_{Li} (= b_1) \) and \( b_{pb} (= b_2) \) values as
obtained in the present work, in [1] and in [2] are
plotted against \( y_2 \). We have included a point which is
missing in Fig. 2 of [2] but can be calculated from the
internal transport number \( t_{12} = 0.897 \) for \( x_1 = 0.9 \)
given in Table II of [2]. This is the point at \( b_2 =
0.8 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1} \) for \( y_2 = 0.182 \).

Our data agree with both [1] and [2] for \( b_1 \) in the
range \( 0.2 < y_1 < 1 \) and \( b_2 \) in the range \( 0.2 < y_2 < 1 \).
For \( b_1 \) in the range \( 0 < y_1 < 0.2 \) they agree with [1] but
disagree with [2], while for \( b_2 \) in the range \( 0 < y_2 < 0.2 \)
they agree with [2] but disagree with [1]. As for
the latter disagreement, it was stated in [1] that the
 correctness of the three \( b_2 \)-values in the range
\( 0 < y_2 < 0.06 \) cannot be claimed with certainty be-
cause they stemmed from a single experiment whose
course was irregular. (Due to imperfect starting condi-
tions, there appeared four migrating boundaries in-
stead of the expected two boundaries, cf. [9].)

In Fig. 3 we compare our results on (Li, Pb(II))Cl
with those on (Li, Cd(II))Cl [10], (Li, Sr)Cl [11], and
(Li, Ba)Cl [12]. Since the equivalent volume and the
cationic radius of PbCl\(_2\) are in between those of SrCl\(_2\)
and BaCl\(_2\) (see Table 3), one would expect that the
mobility behaviour of the (Li, Pb)-system is similar to
that of the (Li, Sr)- and the (Li, Ba)-system. This, how-
ever, is not the case for the mobilities of the diluted
cations. Doubts arise if the rare-ion mobilities of Sr\(^{2+}\)
and Ba\(^{2+}\) are reported correctly, because those results
were obtained with the EMF method which is known
to be unreliable for the determination of the mobilities
of diluted ions. We feel that these results should be

![Fig. 3. Mobility isotherms of the systems (Li, Cd(II))Cl [10], (Li, Sr)Cl [11], (Li, Pb(II))Cl [this work], and (Li, Ba)Cl [12].](image-url)
checked with the more direct analytical or migrating boundary methods.

The mobility behaviour of the system (Li, Pb(II))Cl is unusual and opposite to what is observed in the case of the Chemla effect. It would be interesting to learn if molecular dynamics simulations can mimic this behaviour.

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