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:

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

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.

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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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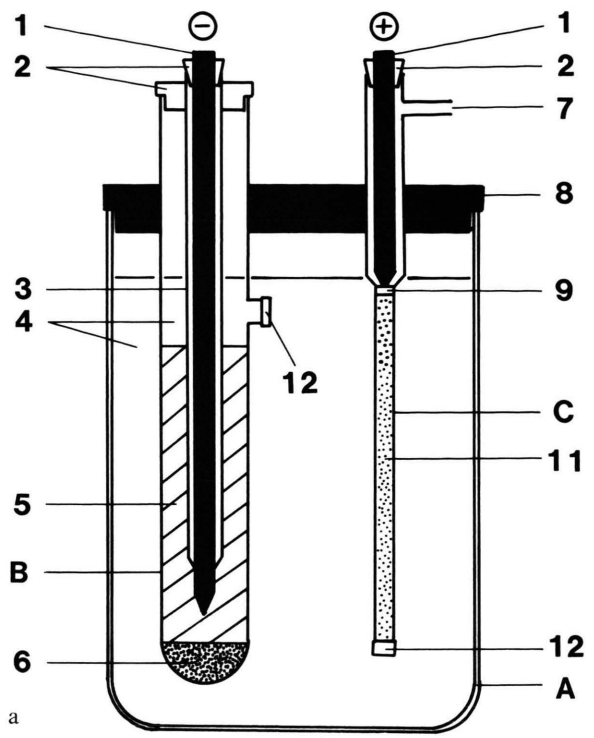

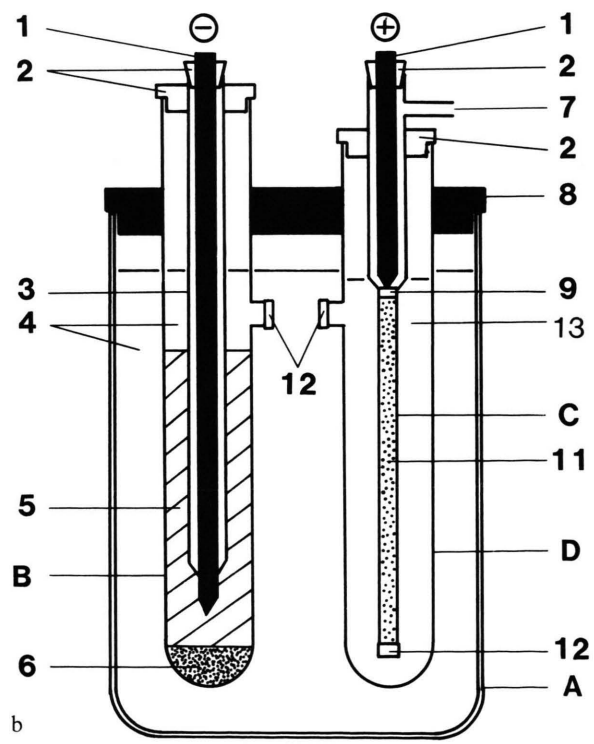

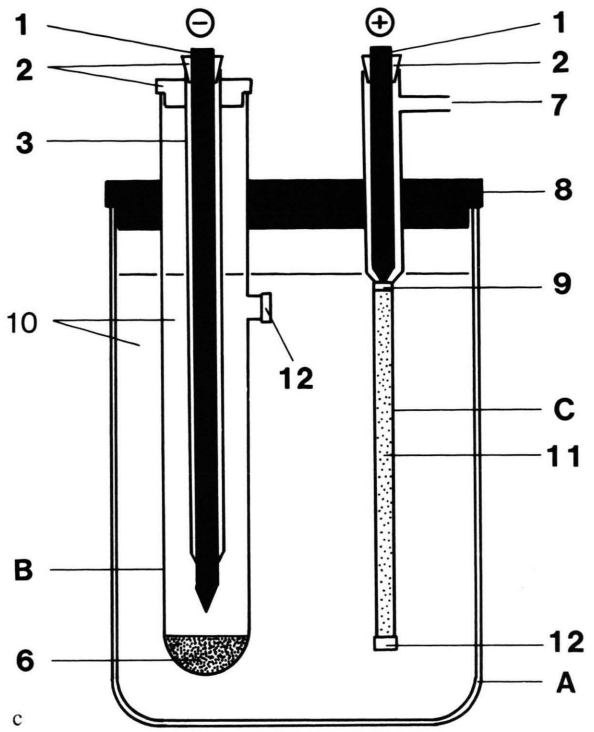

Fig. 1. Electromigration cells (types a, b, and c). A: Large container (alumina), B: cathode compartment (silica), C: separation tube (Vycor), D: compartment (silica). **1**: Graphite electrode, **2**: Silicon-Teflon stopper, **3**: Vycor sheath for the cathode, **4**: molten (Li, K)Cl at about the eutectic composition, **5**: molten $PbCl_2$, **6**: molten Pb metal, **7**: Cl_2 gas outlet, **8**: carbon cover, **9**: quartz wool, **10**: molten (Li, Pb(II))Cl at about eutectic composition, **11**: alumina powder (100–150 μm), **12**: quartz filter, **13**: the same mixture as in the separation tube.

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 ∅. With a temperature controller, the temperature was kept at the desired one within $\pm 2\,^{\circ}C$ 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].

Table 1. Main experimental conditions and ε_{12} values at 650 °C. Q is the transported charge and t the duration. The errors given are those due to the chemical analysis only.

Run no.	y_{Pb}	Q (C)	t (hr)	ε_{12}
1	0.046	804.1	0.9	0.741 ± 0.007
2	0.076	903.0	0.9	0.577 ± 0.006
3	0.099	1029.8	1.0	0.514 ± 0.004
4	0.165	1110.3	1.1	0.408 ± 0.002
5	0.193	1075.4	1.0	0.389 ± 0.007
6	0.327	1200.5	1.0	0.328 ± 0.003
7	0.477	2015.6	2.1	0.318 ± 0.001
8	0.597	1005.7	1.2	0.388 ± 0.003
9	0.697	1095.4	1.0	0.462 ± 0.002
10	0.795	800.7	2.3	0.432 ± 0.006
11	0.854	1003.6	3.0	0.513 ± 0.004
12	0.901	500.0	1.4	0.577 ± 0.004
13	0.926	504.0	1.5	0.676 ± 0.008
14	0.930	1087.5	3.3	0.657 ± 0.009
15	0.952	500.5	1.4	1.387 ± 0.009
16	0.953	550.2	1.6	1.342 ± 0.011
17	0.956	500.0	1.4	1.127 ± 0.012
18	0.960	806.6	2.4	1.375 ± 0.009

Table 2. Conductivities, equivalent volumes and internal cation mobilities in the molten system (Li, Pb(II))Cl at 650 °C. The errors given are those due to ε_{12}.

Run no.	y_{Pb}	$\varkappa$ (10^2 S m^{-1})	V_e (10^{-6} m^3 mol^{-1})	b_{Li} (10^{-8} m^2 V^{-1} s^{-1})	b_{Pb}
	0	5.922	28.55	17.52	–
1	0.046	5.698	28.59	17.46 ± 0.01	4.95 ± 0.11
2	0.076	5.542	28.62	17.16 ± 0.01	7.69 ± 0.09
3	0.099	5.424	28.64	16.92 ± 0.01	8.64 ± 0.06
4	0.165	5.094	28.70	16.17 ± 0.01	9.99 ± 0.03
5	0.193	4.959	28.72	15.87 ± 0.02	10.13 ± 0.08
6	0.327	4.348	28.84	14.39 ± 0.01	10.13 ± 0.03
7	0.477	3.733	28.96	12.90 ± 0.01	9.34 ± 0.01
8	0.597	3.295	29.07	12.23 ± 0.02	8.38 ± 0.01
9	0.697	2.966	29.15	11.85 ± 0.01	7.71 ± 0.01
10	0.795	2.676	29.24	10.90 ± 0.04	7.39 ± 0.01
11	0.854	2.517	29.29	10.99 ± 0.03	7.07 ± 0.00
12	0.901	2.398	29.33	11.08 ± 0.03	6.87 ± 0.00
13	0.926	2.338	29.35	11.56 ± 0.05	6.76 ± 0.00
14	0.930	2.328	29.35	11.41 ± 0.06	6.76 ± 0.00
15	0.952	2.277	29.37	16.08 ± 0.06	6.47 ± 0.00
16	0.953	2.275	29.37	15.78 ± 0.07	6.49 ± 0.00
17	0.956	2.268	29.38	14.35 ± 0.08	6.56 ± 0.00
18	0.960	2.259	29.38	15.96 ± 0.06	6.50 ± 0.00
	1	2.137	29.41	–	6.51

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.

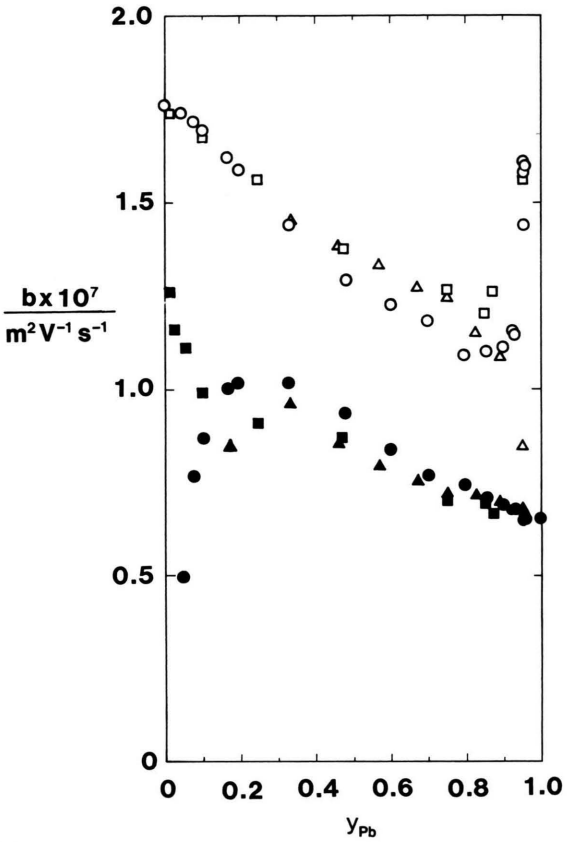

Fig. 2. Isotherms of internal cation mobilities in the system (Li, Pb(II))Cl at 650 °C. b_{Li}: ○ (this work), □ [1], △ [2]; b_{Pb}: ● (this work), ■ [1], ▲ [2].

Results

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

$$\varepsilon_{12} = (b_1 - b_2)/\bar{b} \quad (1)$$

with

$$\bar{b} = y_1 b_1 + y_2 b_2 . \quad (2)$$

We use this definition here, though the average of the mobilities is $x_1 b_1 + x_2 b_2$. From the measurements, the ε_{12} values were calculated as described in [8]. The main experimental conditions and results are given in Table 1.

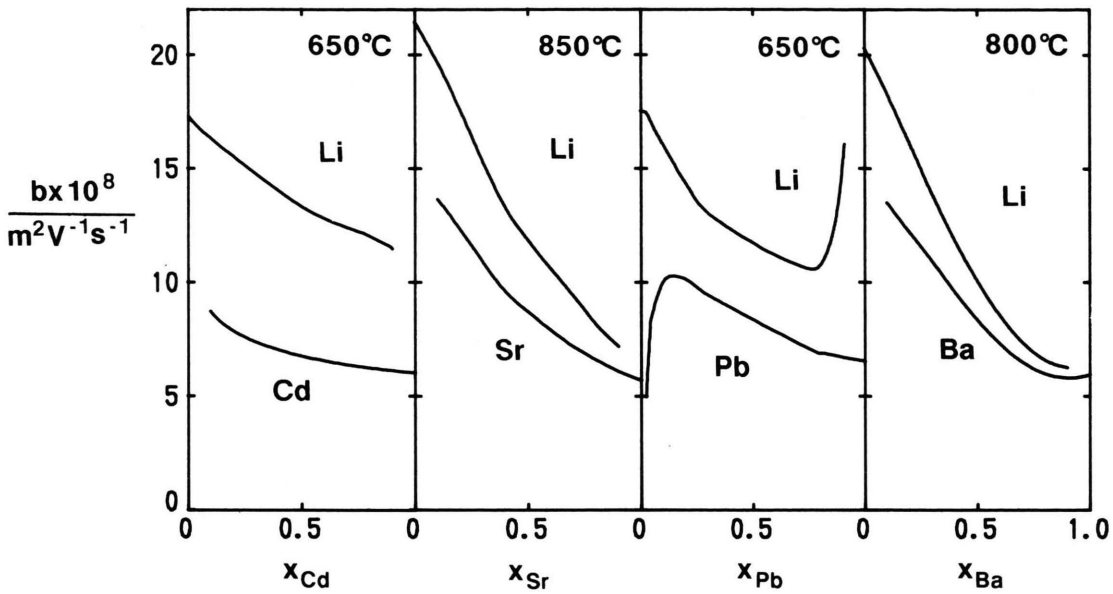

Fig. 3. Mobility isotherms of the systems (Li, Cd(II))Cl [10], (Li, Sr)Cl [11], (Li, Pb(II))Cl [this work], and (Li, Ba)Cl [12].

	V_e/cm^3 eq.$^{-1}$ [13]	r^+/Å [9]
LiCl	28.56	0.60
$CdCl_2$	27.60	0.97
$SrCl_2$	27.76	1.13
$PbCl_2$	29.42	1.21
$BaCl_2$	30.75	1.35

Table 3. Equivalent volumes of some molten chlorides at 650 °C, extrapolated for $SrCl_2$ and $BaCl_2$ on the assumption of linear temperature dependence, and the involved ionic radii.

The internal mobilities were calculated from

$$b_1 = (\varkappa V_e/F)(1 + y_2 \varepsilon_{12}), \quad (3a)$$

$$b_2 = (\varkappa V_e/F)(1 - y_1 \varepsilon_{12}), \quad (3b)$$

where $\varkappa$ is the conductivity (formerly called specific conductivity), V_e the equivalent volume of the mixture and F is the Faraday constant. Density data of this system were not available; therefore we assumed additivity of the molar volumes of LiCl and $PbCl_2$. The conductivities were read from Fig. 8 in [1]. The resulting 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 $t_{13} = 0.897$ for $x_1 = 0.9$ given in Table II of [2]. This is the point at $b_2 = 0.8 \times 10^{-7}$ m^2 V^{-1} 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 because they stemmed from a single experiment whose course was irregular. (Due to imperfect starting conditions, there appeared four migrating boundaries instead 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, however, 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

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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