Internal Cation Mobilities in the Molten Binary Systems (Li, Na)Cl and (Na, K)Cl

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Internal mobility ratios of the two cations in the molten binary systems (Li, Na)Cl and (Na, K)Cl have been measured with Klemm's column method. From these and available data on the densities and conductivities the internal mobilities b_{Li}, b_{Na} and b_K have been calculated. In (Li, Na)Cl, b_{Li} is smaller than b_{Na} in the investigated composition and temperature range, and in (Na, K)Cl, the Chemla effect occurs, that is a crossing of the isotherms is observed.

The internal cation mobilities b_M are well expressed by the empirical relation

$$b_M = [A/(V - V_0)] \exp(-E/RT),$$

where A, E and V_0 are constants depending on the cation M and V is the molar volume of the mixture.

Introduction

The ionic mobilities in mixtures of molten salts have been interpreted in terms of anion polarization [1] and complex formation [2]. The Chemla effect [3] refers to the phenomenon that in a charge symmetrical mixture with a common anion the mobility isotherms of the two cations cross at some concentration.

In all binary alkali nitrates systems except (Li, Na)NO$_3$, the Chemla effect has been observed [4]. Especially (Na, K)NO$_3$ shows the Chemla effect [5]. In (Li, Na)NO$_3$ the mobility of Na$^+$ is throughout larger than that of Li$^+$ [6].

In the molten alkali halide mixtures (Li, K)Cl [1, 2, 7, 8], (Li, K)Br [9], (Li, Rb)Cl [10], (Li, Cs)Cl [2, 11], (Na, K)Cl [2] and (Na, Cs)Cl [2] the internal cation mobilities have been measured. To our knowledge, the internal cation mobilities have not been measured in molten (Li, Na)Cl. For (Na, K)Cl, the internal mobilities were measured by the EMF method [2], which involves large errors in some cases [13, 14]. Therefore, in the present study the internal mobilities of the latter two binary alkali chloride systems have been measured by the Klemm method, which yields the

most accurate and precise data among the available methods.

Experimental

Reagent grade LiCl, NaCl and KCl were vacuum dried at 150 °C overnight and stored in a desiccator.

The setup for electromigration is quite similar to the one described in [8]. A mixture of the eutectic composition of (Li, Na, K)Cl (53.5, 8.6, 37.9 mol%) was used as a thermostat bath in the large cathode compartment.

The inner diameter of the separation tube of quartz was 4 mm. The tube was packed with alumina powder of 150 ∼ 180 μm, fixed with quartz wool at the bottom and top. The length of the diaphragm was about 20 cm.

A mixture of a chosen composition was melted in a quartz vessel and filled into the separation tube by pump suction. The tube was then transferred into the electromigration cell containing the ternary eutectic mixture mentioned above. Graphite rods of 3 mm ∅ were used as electrodes, and chlorine gas, which was dried by passing through concentrated sulfuric acid, was bubbled into the cathode compartment in order to convert the otherwise electrodeposition metal into the alkali chloride. The transported charge was measured with three copper coulometers connected in series. The temperature was kept at the desired one within ± 2 °C with a temperature controller.

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Fig. 1. Isotherms of the internal cation mobilities in the binary system (Li, Na)Cl. − − −: at 600 °C, − · − · −: at 700 °C, ——: at 800 °C. $\square$: b_{Li}, $\bigcirc$: b_{Na}. $\bullet$: b_{Na} for pure NaCl at 600 °C and 700 °C, as extrapolated below the melting point (801 °C). $\blacksquare$ and $\bullet$: extrapolated values for mixtures.
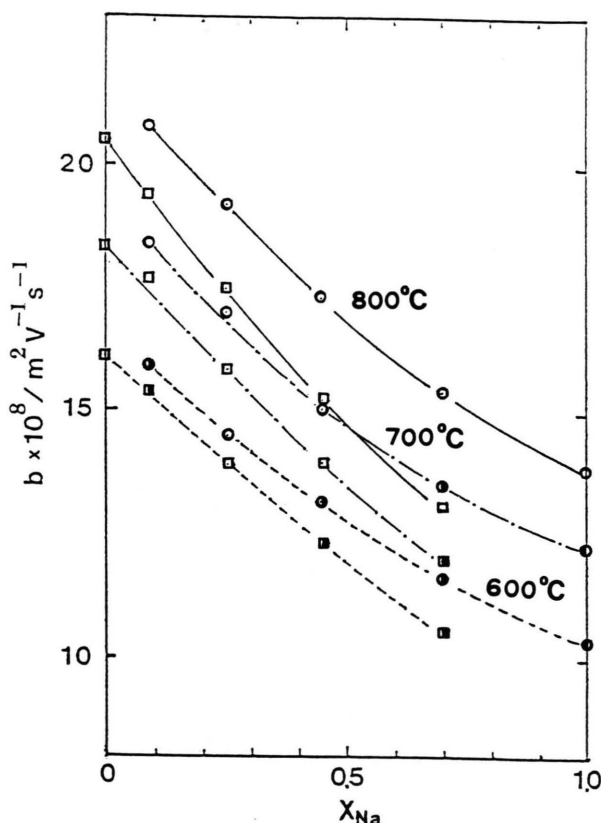
Fig. 2. Isotherms of the internal cation mobilities in the binary system (Na, K)Cl. − − −: at 600 °C, − · − · −: at 700 °C, ——: at 800 °C. $\bigcirc$: b_{Na}, $\blacktriangle$: b_K. $\bullet$ and $\blacktriangle$: b_{Na} and b_K for pure NaCl and KCl, respectively, as extrapolated below the melting point. $\bullet$ and $\blacktriangle$: extrapolated values for mixtures.

After electromigration for a few hours, the separation tube was taken out, cleaned on the outside and cut into pieces of ca. 10 mm length. The salt in each fraction was dissolved in pure water, and the contents of the cations were determined by atomic absorption spectrophotometry.

Results

The main experimental conditions and the obtained relative differences in the internal mobilities of the two cations, ε_{12}, for the systems (Li, Na)Cl and (Na, K)Cl are given in Tables 1 and 2, respectively. The ε_{12} values were calculated from the change of the concentration of the cationic species in the separation tube after electromigration and the transported charge by use of the equations presented in [12].
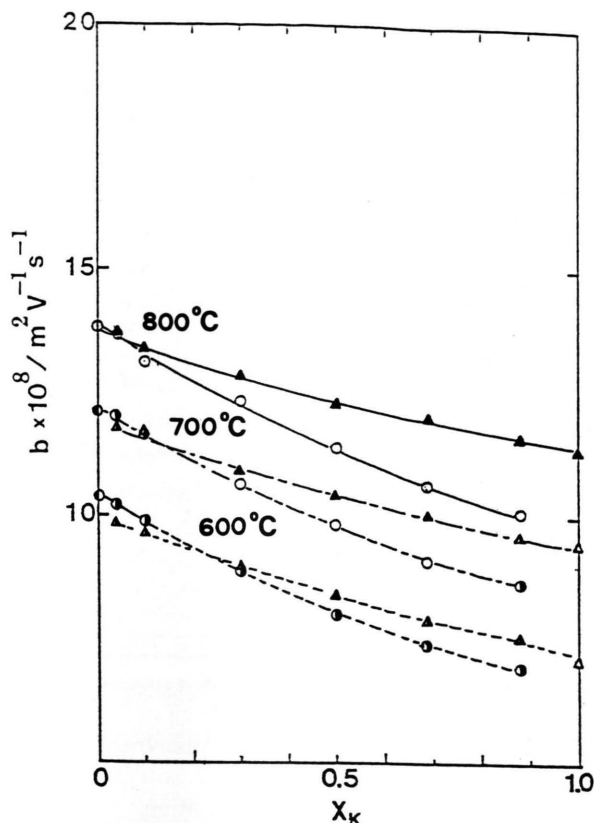
Table 1. Experimental conditions and results for the system (Li, Na)Cl.

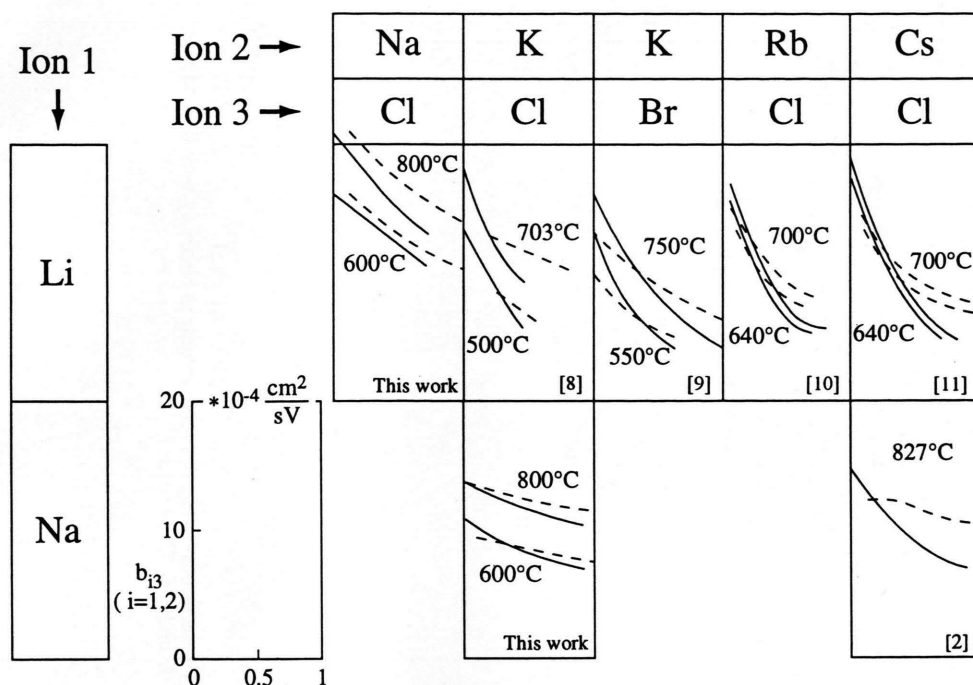| Run no.	x_{Na}	$T/°C$	Q/C	ε_{12}
1	0.70	750	3080	−0.1429
2	0.70	800	3052	−0.1625
3	0.45	650	3089	−0.0826
4	0.45	650	3147	−0.0982
5	0.45	750	3019	−0.1095
6	0.45	800	3007	−0.1257
7	0.25	600	3186	−0.0496
8	0.25	650	3109	−0.0600
9	0.25	700	3280	−0.0758
10	0.25	750	3283	−0.0589
11	0.25	800	3271	−0.1003
12	0.09	700	3102	−0.0461
13	0.09	750	3071	−0.0586
14	0.09	800	3052	−0.0714

Fig. 3. The isotherms of the internal mobilities b_{13} and b_{23} in binary alkali halides. With the exception of (Li, K)Br (disc method) and (Na, Cs)Cl (emf A method), they were measured with the Klemm method. Solid lines: b_{13}, broken lines: b_{23}.

Table 2. Experimental conditions and results for the system (Na, K)Cl.

Run no.	x_{Na}	$T/°C$	Q/C	ε_{12}
1	0.88	760	6071	−0.1266
2	0.88	800	6328	−0.1355
3	0.69	720	6668	−0.1045
4	0.69	800	6524	−0.1170
5	0.50	680	2832	−0.0585
6	0.50	720	6581	−0.0692
7	0.50	760	6481	−0.0726
8	0.50	800	6527	−0.0730
9	0.30	720	4428	−0.0286
10	0.30	760	6539	−0.0328
11	0.30	800	6764	−0.0345
12	0.10	780	6987	−0.0181
13	0.10	800	6785	−0.0205
14	0.04	800	5197	−0.0017

The internal mobilities of the two cations were calculated from the values of ε_{12}, the conductivity $\varkappa$ and the density d by

$$b_1 = (\varkappa V/F)(1 + \varepsilon_{12} x_2), \tag{1}$$

$$b_2 = (\varkappa V/F)(1 - \varepsilon_{12} x_1), \tag{2}$$

where F is the Faraday constant, x the mole fraction of MCl and V the molar volume of the mixture ($V =$

$(x_1 w_1 + x_2 w_2)/d$, where w_i is the molecular weight of M_iCl).

The obtained mobilities in (Li, Na)Cl and (Na, K)Cl at 600, 700 and 800 °C are shown in Figs. 1 and 2, respectively.

Discussion

The profiles of the isotherms for (Li, Na)Cl are similar to those of (Li, Na)NO$_3$ [6] in that the larger cation is more mobile than the smaller one in the whole concentration and temperature range. The sharp increase in b_{Li} and b_{Na} with increasing concentration of LiCl is due to the sharp increase in the number density of the Cl$^-$ ions.

In the (Na, K)Cl system, the relative difference in the radii of the two cations is smaller, and therefore the difference in internal cation mobilities between the two cations is rather small. Similar isotherms with Chemla crossing points were seen for (Na, K)NO$_3$ [5], (K, Rb)NO$_3$ [15] and (Rb, Cs)NO$_3$ [16]. b_{Na} and b_K obtained in the present study are in satisfactory agreement with those obtained at 827 °C by the EMF method [2], in which the Chemla crossing point ap-
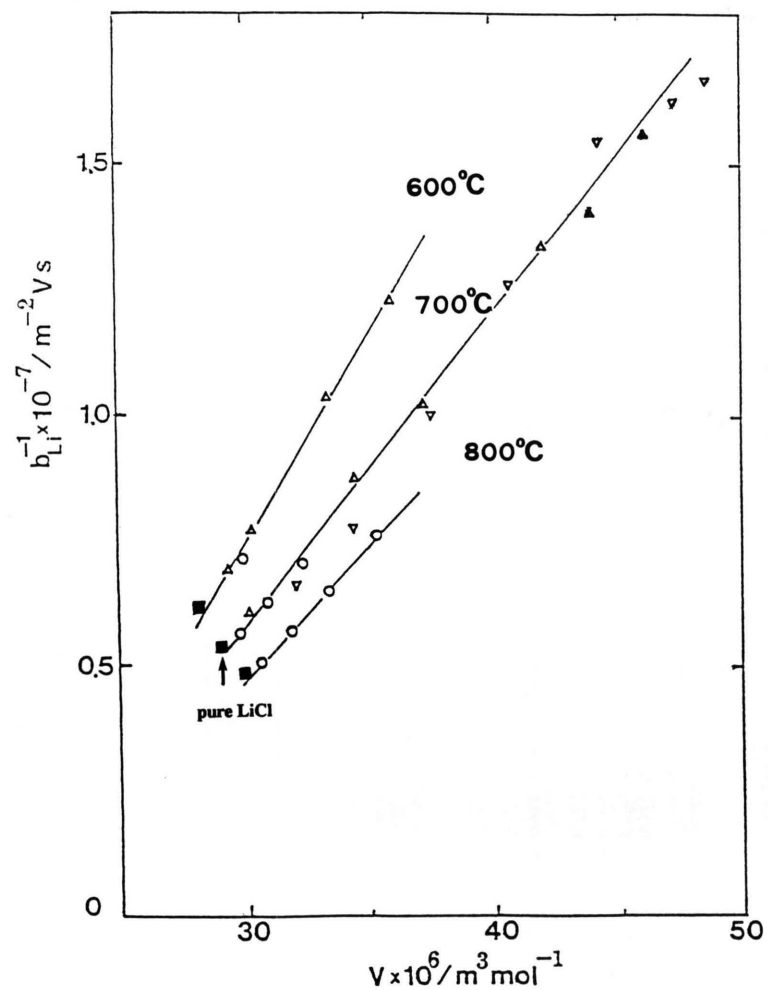
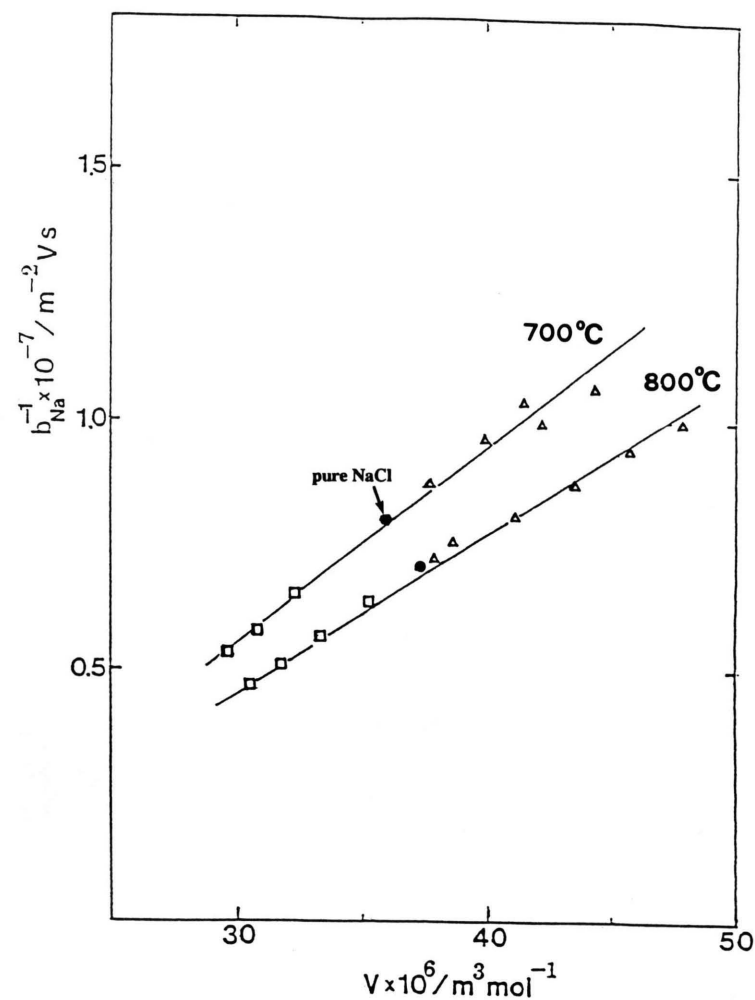Fig. 4. The reciprocal of b_{Li} vs. molar volume in binary systems (Li, M)Cl, at 600 °C, 700 °C and 800 °C. M = Na: $\bigcirc$, K: $\triangle$, Rb: $\triangledown$, Cs: $\blacktriangle$ [7].

Fig. 5. The reciprocal of b_{Na} vs. molar volume in binary systems (Na, M)Cl, at 700 °C and 800 °C. M = Li: $\square$, K: $\triangle$.
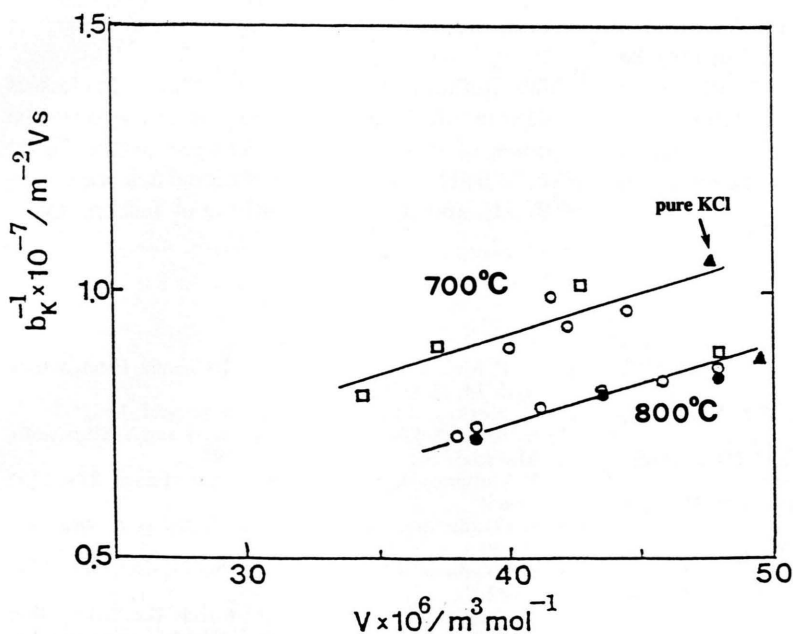
Fig. 6. The reciprocal of b_K vs. molar volume in binary systems (K, M)Cl, at 700 °C and 800 °C. M = Li: □, Na: ○, Na: ● [2].

pears at $x_K = 0.05 \sim 0.08$. As the temperature increases, the Chemla crossing points shifts towards higher concentrations of NaCl. Evidently, the higher the temperature, i.e. the larger the molar volume of the mixture, the more is the smaller cation able to associate anions, which reduces its mobility as compared to the bigger cation. Probably, at temperatures above 827 °C, K^+ is more mobile than Li^+ in the whole concentration range.

For binary alkali halide systems, the presently known isotherms of the cationic internal mobilities are shown in Fig. 3, which updates, as to the alkali halides, Fig. 19 in [17]. From Fig. 3, the following rules and conjectures for the cationic mobilities in binary alkali halide systems with a common anion can be deduced:

1. Among the two pure salts, the one with the smaller cation has the greater mobility.
2. Both mobilities decrease with increasing concentration of the bigger cation.
3. This decrease is steeper for the smaller cation.
4. At sufficiently low temperatures (especially below the melting point), the smaller cation is more mobile than the bigger one.
5. At sufficiently high temperatures, the bigger cation is more mobile than the smaller one.

6. Consequently, at temperatures between these two temperatures the two mobility isotherms must cross, the Chemla crossing point moving with increasing temperature to lower concentrations of the bigger cation.

We have found that, when the Coulombic force is the dominant factor influencing the internal mobilities in binary molten alkali nitrates, the internal mobilities b_M are well expressed by

$$b_M = [A/(V - V_0)] \exp[-E/RT], \tag{3}$$

where A, E, and V_0 are constants depending on the respective cation and V is the molar volume of the mixture. In order to see whether (3) holds, we plotted the reciprocals of b_{Li}, b_{Na}, b_K against the molar volume in Figs. 4, 5, and 6, respectively. As for the b_{Li}, b_{Na}, and b_K, the plots seem to lie on stright lines, and therefore the main factor dominating the mobility can be interpreted in terms of the Coulombic attraction effect.

In conclusion, the internal cation mobilities of Li^+, Na^+, and K^+ in the systems (Li, Na)Cl and (Na, K)Cl were determined over a wide range of concentration and temperature. The trend of the isotherms of the internal mobilities in the present binary systems is

interpreted in a similar way as in other systems such as alkali nitrates. The mobility of a cation may be expressed as a function of the number density of the common anion. When the Coulombic attraction plays a dominant role for the ionic motion, the internal cation mobilities are well expressed by the empirical equation (3).

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