Internal Cation Mobilities in Molten (Ca, Ba) Cl_2

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Internal cation mobility ratios in molten (Ca, Ba) Cl_2 have been measured by the Klemm method for x_{Ba} (mole fraction of barium chloride) = 0.25 – 0.51 at 973 K and $x_{Ba} = 0 - 0.61$ at 1073 K. From these and available data on the densities and conductivities the internal cation mobilities b have been calculated, assuming additivity of the molar volume. Although b_{Ca} in pure $CaCl_2$ is greater than b_{Ba} in pure $BaCl_2$, b_{Ca} is smaller than b_{Ba} in all the investigated mixtures at the respective temperatures. With increasing molar volume at constant temperature both b_{Ca} and b_{Ba} decrease. Since the profile of the isotherms is similar to that for the binary monovalent chloride systems so far studied, monoatomic ionic species are assumed to carry the current also in the alkaline earth chloride melts.

Introduction

We have studied internal mobilities of various monovalent cations in binary molten systems with a common anion by Klemm's countercurrent electromigration method; the results are summarized in [1]. We have found that, when the Coulombic attraction between cation and anion is expected to be the dominant factor for the electrical conductance, the internal mobilities are well expressed by

$$b = [A/(V - V_0)] \exp(-E/RT), \tag{1}$$

were V is the molar volume and A, E, and V_0 are parameters characteristic of the considered cation and nearly independent of the cocation. Equation (1) holds, for instance, for the molten binary chlorides (Li, M)Cl (M = Na [2], K [3], Rb [3], and Cs [3]) and (Na, K)Cl [2]. In the binary monovalent cation systems the Chemla effect usually occurs [1], which has been interpreted in terms of the self-exchange velocity [4].

To our knowledge, mobilities have not been measured in additive binary divalent cation systems, while internal mobilities have been studied in binary alkali-alkaline earth nitrates [5–7] and halides [8, 9]. Thus, the main aim of the present work was to measure the internal cation mobilities in the binary divalent cation system (Ca, Ba) Cl_2 and to obtain insight into the electrical conductance in divalent cation chloride melts.

The structure of the pure melts of $CaCl_2$ and $BaCl_2$ has been previously studied by neutron diffraction [10, 11], X-ray diffraction [12, 13] and Raman spectroscopy [14]. Based on the hole model, Bockris et al. assumed that the main positively charged entities in alkaline earth chloride melts would be MCl^+ complexes [15]. This assumption was, however, doubted later [16]. It has been argued [11] that even for $ZnCl_2$ melts there appears to be no need to involve special effects associated with covalency or to introduce into the discussion chemical species like $ZnCl^+$ or $ZnCl_3^-$.

We expected that the data of the internal mobilities would yield a hint about the current-carrying species in melts consisting of divalent cations.

Experimental

$CaCl_2$ and $BaCl_2$ (Kanto Chemical Co. Inc.) of reagent grade were used without further purification. The salts were vacuum dried at ca. 450 K overnight. For the experiments, the concentrations and temperatures shown in Fig. 1 were chosen in view of the phase diagram [17]. After sufficient mixing at a desired composition, the mixture was melted in a small quartz vessel. The electromigration cell was the same as that used previously (see Fig. 1 a in [18]); The diameter of diaphragm part of the separation tube was 4 mm. With a temperature controller, the temperature was kept within ±2 K during electromigration. After several hours of electromigration with constant electric current of ca. 100 mA, the separation tube was taken out, cleaned on the outside wall and cut into several pieces of 5–6 mm length. Each fraction was kept in a diluted hydrochloric solution for several hours to dis-

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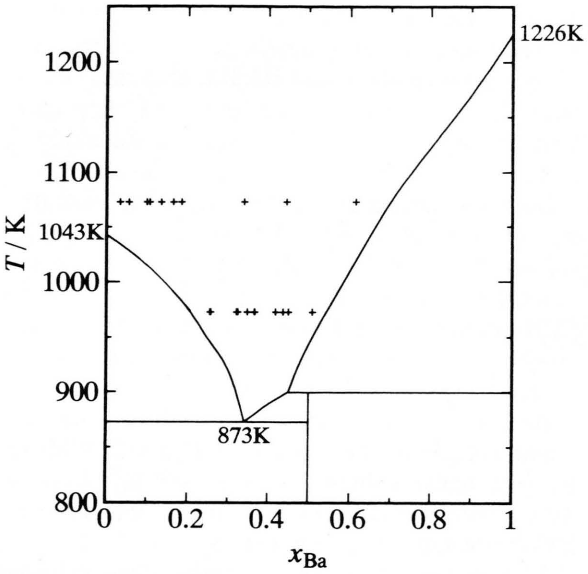

Fig. 1. Concentration and temperature ranges of the measurements of ε for the system (Ca, Ba)Cl_2 [17]. +: measured points.

solve the salt completely. The contents of Ca and Ba were determined by an ion chromatographic analyzer (IC 500 Yokogawa Hokushin Electric. Co, Ltd.).

Results

The relative difference in the internal mobilities of Ca and Ba is defined as

$$\varepsilon = (b_{Ca} - b_{Ba})/b_c, \tag{2}$$

where b_c is the average cationic mobility of the mixture; b_c is related with the conductivity $\varkappa$ and the molar volume V of the mixture by

$$b_c = \varkappa V/F. \tag{3}$$

Here $M_{0.5}Cl$, i.e. the equivalent unit, is regarded as the molar unit (SI unit).

The ε values were calculated by the equation based on the material balance [19, 20]:

$$\varepsilon = (F/Q)\,(N_{Ba}/x_{Ba} - N_{Ca}/x_{Ca}), \tag{4}$$

where N_M is the number of moles, of M toward the anode in the separation tube where the chemical composition has changed during electromigration, Q is the transported charge and x_M the mole fraction of MCl_2.

Table 1. Experimental conditions and ε in the molten system (Ca, Ba)Cl_2 at 973 K (1 a) and 1073 K (1 b).

Exp. No.	x_{Ba}	Q (C)	ε
(1 a)			
1	0.255 ± 0.001	1124.1	−0.029 ± 0.005
2	0.257 ± 0.001	920.4	−0.034 ± 0.004
3	0.320 ± 0.002	2602.2	−0.034 ± 0.002
4	0.323 ± 0.001	1533.3	−0.035 ± 0.004
5	0.347 ± 0.000	1310.0	−0.042 ± 0.008
6	0.365 ± 0.001	1806.9	−0.044 ± 0.005
7	0.366 ± 0.000	1311.4	−0.025 ± 0.000
8	0.418 ± 0.001	2576.3	−0.035 ± 0.001
9	0.437 ± 0.001	2258.1	−0.035 ± 0.001
10	0.450 ± 0.001	1111.1	−0.060 ± 0.008
11	0.509 ± 0.002	1382.3	−0.044 ± 0.002
(1 b)			
1	0.033 ± 0.001	2231.8	−0.041 ± 0.003
2	0.033 ± 0.002	1530.6	−0.050 ± 0.002
3	0.055 ± 0.001	2213.8	−0.037 ± 0.001
4	0.099 ± 0.000	1337.3	−0.045 ± 0.002
5	0.106 ± 0.001	1555.2	−0.043 ± 0.001
6	0.134 ± 0.001	2033.4	−0.047 ± 0.002
7	0.164 ± 0.001	2203.6	−0.051 ± 0.003
8	0.184 ± 0.001	803.9	−0.046 ± 0.003
9	0.339 ± 0.000	1602.8	−0.055 ± 0.002
10	0.445 ± 0.000	1158.0	−0.051 ± 0.001
11	0.614 ± 0.001	1010.3	−0.053 ± 0.002

The ε values are given in Table 1 together with the main experimental conditions.

The internal mobilities of these cations were obtained by

$$b_{Ca} = (\varkappa V/F)\,(1 + \varepsilon x_{Ba}) \tag{5}$$

$$b_{Ba} = (\varkappa V/F)\,(1 - \varepsilon x_{Ca}). \tag{6}$$

As density data of the present mixtures are not available, these were interpolated from those of the pure melts [17] by assuming additivity for the molar volumes.

In Table 2 the calculated b_{Ca} and b_{Ba} are given together with the molar volume (i.e. the equivalent volume) and the conductivity [21]. The isotherms of b_{Ca} and b_{Ba} are shown in Figure 2.

Discussion

Figure 2 shows that, although b_{Ca} in pure $CaCl_2$ is greater than b_{Ba} in pure $BaCl_2$; b_{Ca} is smaller than b_{Ba} in all the investigated conditions. However, it is conjectured from the isotherms in Fig. 2 that at sufficiently low x_{Ba} particularly at low temperature (below the melting point) the smaller cation would be more mobile than the larger one. These features resemble

Table 2. Internal mobilities of Ca^{2+} and Ba^{2+} in the molten system (Ca, Ba)Cl_2 at 973 K (2a) and 1073 K (2b).

Exp. No.	x_{Ba}	$\varkappa$ (S cm^{-1})	V (cm^3 · mol^{-1})	$b_{Ba} \cdot 10^8$ (m^2 V^{-1} · s^{-1})	$b_{Ca} \cdot 10^8$ (m^2 V^{-1} · s^{-1})
(2a)					
1	0.255	1.44	27.46	4.20 ± 0.08	4.08 ± 0.01
2	0.257	1.44	27.48	4.21 ± 0.07	4.09 ± 0.01
3	0.320	1.41	27.78	4.16 ± 0.04	4.02 ± 0.01
4	0.323	1.41	27.79	4.16 ± 0.06	4.02 ± 0.01
5	0.347	1.40	27.91	4.16 ± 0.08	3.99 ± 0.02
6	0.365	1.39	28.00	4.15 ± 0.07	3.98 ± 0.01
7	0.366	1.39	28.00	4.11 ± 0.02	4.00 ± 0.00
8	0.418	1.37	28.25	4.10 ± 0.03	3.96 ± 0.01
9	0.437	1.36	28.34	4.08 ± 0.02	3.95 ± 0.01
10	0.450	1.36	28.41	4.13 ± 0.07	3.89 ± 0.02
11	0.509	1.34	28.69	4.06 ± 0.03	3.89 ± 0.01
(2b)					
1	0.033	1.92	26.93	5.56 ± 0.08	5.34 ± 0.00
2	0.033	1.92	26.93	5.61 ± 0.08	5.34 ± 0.00
3	0.055	1.90	27.04	5.51 ± 0.07	5.32 ± 0.00
4	0.099	1.87	27.26	5.50 ± 0.08	5.27 ± 0.00
5	0.106	1.87	27.29	5.48 ± 0.06	5.26 ± 0.00
6	0.134	1.85	27.43	5.47 ± 0.08	5.23 ± 0.01
7	0.164	1.83	27.58	5.46 ± 0.08	5.19 ± 0.01
8	0.184	1.82	27.68	5.42 ± 0.08	5.18 ± 0.00
9	0.339	1.74	28.44	5.30 ± 0.05	5.02 ± 0.01
10	0.445	1.69	28.96	5.21 ± 0.04	4.95 ± 0.01
11	0.614	1.62	29.80	5.10 ± 0.03	4.84 ± 0.02

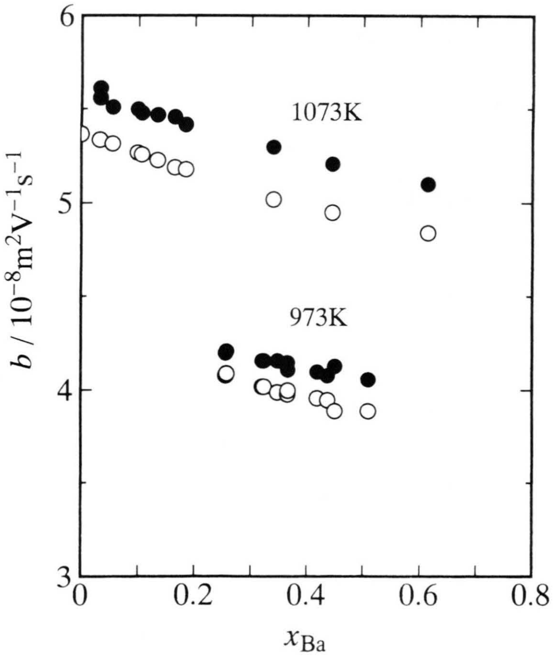

Fig. 2. Internal cation mobilities in the molten system (Ca, Ba)Cl_2 at 973 K and 1073 K. ○: b_{Ca}; ●: b_{Ba}.

those for the system (Li, Na)Cl [2]. This resemblance is presumably caused by the fact that among the interactions between alkali and chloride ions the ones between Li and Cl and between Na and Cl are particularly strong and that their relative difference is comparable to that for Ca and Cl vs. Ba and Cl.

Both mobilities decrease with increasing concentration of the larger cation. This decrease is steeper for the smaller cation. This rule for the present system is quite the same as that for the binary alkali halides [2, 3] and nitrates [1]. From Figs. 1 and 2 the Chemla crossing point is not expected to appear in the liquid state range of the present system.

Both b_{Ca} and b_{Ba} are plotted for 1073 K against the molar volume of the mixture in Figure 3. With increasing molar volume, both b_{Ca} and b_{Ba} decrease. This tendency is also the same as that found for the alkali chlorides and nitrates [1–3].

We have conjectured that in molten alkali chlorides the current-carrying species are monoatomic alkali and chloride ions [22] because (i) the internal mobilities in (Li, Cs)Cl calculated based on the linear response theory [23] for the MD trajectories are strictly proportional to the self-exchange velocities, that is the separating velocity of neighbouring cation-anion pairs, and (ii) the free space effect [1], which is usually found for systems containing polyatomic species,

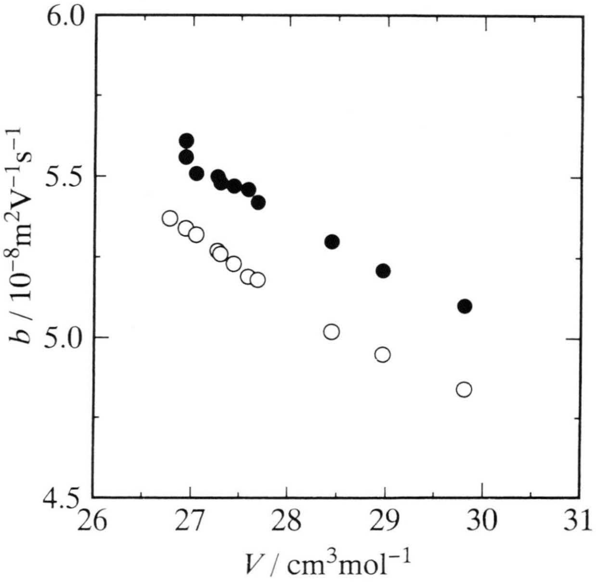

Fig. 3. $b_{Ca}$and b_{Ba} at 1073 K vs. molar volume. ○: b_{Ca}; ●: b_{Ba}.

is not found experimentally for such systems as (Li, Cs)Cl.

In the present system, b_{Ba} smoothly increases with increasing concentration of $CaCl_2$ also in its high concentration range. This indicates that the free space effect does not occur, which suggests that polyatomic species are not involved as the current-carrying species. Thus, since the above-mentioned general rules for the mobility isotherms in alkali chlorides hold also for the present system, one is lead to believe that the current-carrying species in the alkaline-earth chlorides are also monoatomic.

The reciprocal of b_{Ca} and b_{Ba} is plotted against the molar volume in Figure 4. These lines seem to lie on straight lines, as expected from (1). The parameters for (1) are given in Table 3. Figure 4 also suggests that the Chemla crossing point would shift toward higher concentrations of the smaller cations with increasing temperature. This trend is similar to that in alkali chlorides and nitrates [1–3].

Table 3. Parameters for b in (1) in the molten (Ca, Ba)$_{0.5}$Cl.

Cation	A (10^{-12} m^5 V^{-1} · s^{-1} mol^{-1})	E (kJ mol^{-1})	V_0 (cm^3 mol^{-1})
Ca	1.22	19.1	−0.961 (973 K) −0.837 (1073 K)
Ba	1.36	18.4	−5.769 (973 K) −4.121 (1073 K)

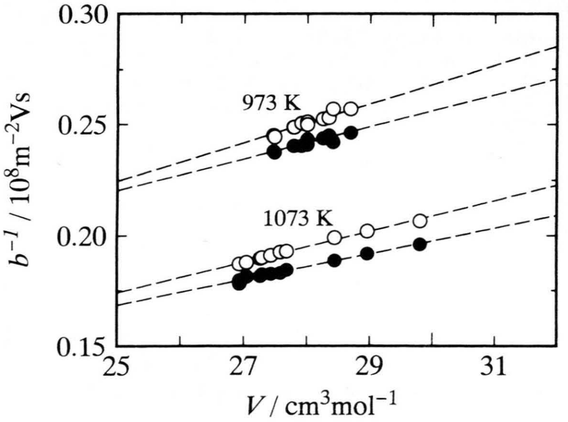

Fig. 4. The reciprocal of mobilities in the molten system (Ca, Ba)$_{0.5}$Cl at 973 K and 1073 K. ○: b_{Ca}^{-1}; ●: b_{Ba}^{-1}. The dashed lines are drawn according to (1) with the parameters in Table 3.

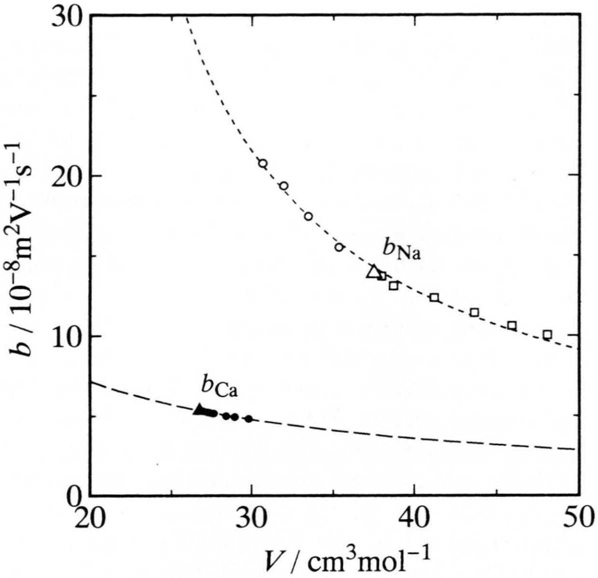

Fig. 5. Internal cation mobilities of Na^+ and Ca^{2+} at 1073 K vs. molar volume. ●: b_{Ca} (this work); ▲: pure b_{Ca}; ○, □: b_{Na} in the system (M, Na)Cl (M = Li and K) [2]; △: pure b_{Na}. The dotted lines are drawn by a least squares fit of the form of (1). As for the dashed line, see the legend of Figure 4.

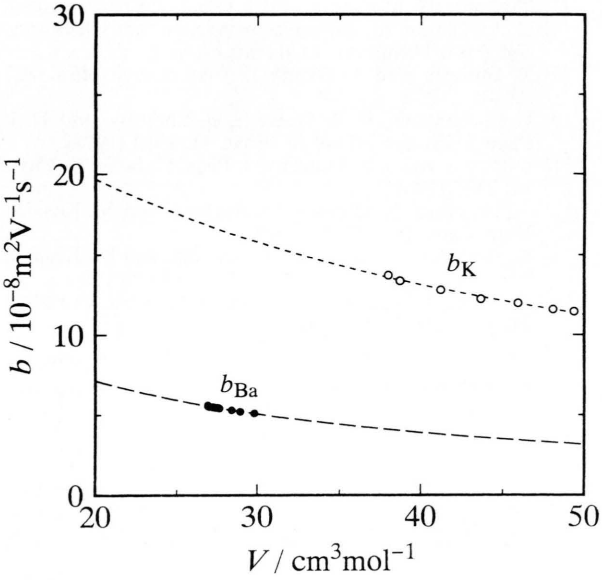

Fig. 6. Internal cation mobilities of K^+ and Ba^{2+} at 1073 K vs. molar volume. ●: b_{Ba} (this work); ○: b_K in the system (Na, K)Cl [2]. As for the dotted and dashed lines, see the legend of Figure 5.

b_{Ca} and b_{Ba} are compared with b_{Na} and b_K [2] at 1073 K in Figs. 5 and 6, respectively. The ionic radii of Ca^{2+} and Ba^{2+} are similar to those of Na^+ and K^+, respectively; the ionic radii of the 6-coordination state are 100 pm for Ca^{2+}, 102 pm for Na^+, 135 pm for Ba^{2+} and 138 pm for K^+ [24]. The mobilities of the divalent cations are considerably smaller than those of the monovalent cations. This can be interpreted qualitatively in terms of the cation-anion interactions. Since the coulombic interaction of the divalent cation with Cl^- is considerably stronger than that of the monovalent cation with Cl^-, it is less favourable for divalent cations to leave a neighbouring Cl^- than for monovalent cations. Although the self-exchange velocities have not been computed for the alkaline-earth chloride systems, one can assume that the self-exchange velocities for the alkaline-earth ions are by about factor of 3 smaller than those for the alkali ions of smaller sizes. This also suggests that current-carrying species are the monoatomic ions in the present system. The fact that the isotope effect on the internal mobilities of pure $CaCl_2$ and $BaCl_2$ [25] is not extremely small compared to that of alkali halides also supports this assumption.

In summary, the profiles of the isotherms of the internal cation mobilities in the present system are quite the same as those in alkali chlorides, although the values of b_{Ca} and b_{Ba} are smaller than those of b_{Na} and b_K, respectively, by a factor of 2–3. The present results suggest that the general rules so far found for the internal mobilities in the binary alkali chlorides hold also for those for binary alkaline-earth chlorides. The main current-carrying species in alkaline earth melts are conjectured to be monoatomic ions.

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