The Internal Mobilities of the Molten Binary System $(Rb-Cs)NO_3$

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Internal mobility ratios in the molten binary system $(Rb-Cs)NO_3$ have been measured with the Klemm method. From these and the available data on the densities and conductivities, the internal mobilities of Rb^+ and Cs^+ have been calculated. Above (below) 420 °C, Cs^+ is found to be more (less) mobile than Rb^+. The internal mobilities of these ions in various binary alkali nitrates are compared.

1. Introduction

In a series of investigations we have studied ratios of the internal mobilities of the two cations in molten binary alkali nitrates with a countercurrent electromigration method, i.e. the Klemm method [1] (see Table 1). In all the systems except $(K-Rb)NO_3$, the Chemla effect ([9, 10]) has been observed, i.e. the phenomenon that the mobility of the larger cation is greater than that of the smaller one in a certain range of temperature and concentration. When the difference in the size of the two cations is small, the Chemla effect occurs only at high concentrations of the larger cation at relatively high temperatures, as exemplified by the case of $(Na-K)NO_3$ [7]. In the present work we explore whether the Chemla effect occurs in the system $(Rb-Cs)NO_3$.

In a study using radioactive tracers in a Hittorf-type cell, Shvedov and Ivanov have found that the mobilities of Rb^+ and Cs^+ in $(Rb-Cs)NO_3$ are nearly equal at 693 K in the whole concentration range [11].

We have employed the Klemm method for the determination of the internal mobility ratio of Rb^+ and Cs^+ because this method seems to be the most accurate one in case of cations with nearly equal mobilities.

From the mobility ratios and the available data on the densities and conductivities the internal mobilities of Rb^+ and Cs^+ have been calculated.

2. Experimental

$RbNO_3$ and $CsNO_3$ of better than 99% purity, produced by Soekawa Chem. Co. in Tokyo, were used without further purification since the Klemm method is relatively insensitive to small amounts of impurity. Possible moisture was removed with the procedure previously described [4].

The electromigration cell is shown in Figure 1. In the large compartment, $(Li-Na-K)NO_3$ of the eutectic composition (37.5–18–44.5 mol%) was used. The method of filling the cathode compartment with NH_4NO_3, which had been used in some of our previous experiments, has not been employed in the present study because it was necessary to go to rather high temperatures where NH_4NO_3 decomposes too quickly.

Therefore the classical way of bubbling a mixture of NO_2 and O_2 at the cathode to regenerate otherwise electrodeposited metal into the original nitrate [12, 13] was employed. The aluminium wire used as the cathode was gradually corroded, probably by

Table 1. Binary alkali nitrate systems $(M_1-M_2)NO_3$ whose internal cationic mobility ratios have been measured with the Klemm method [1].

M_1 \ M_2	Na	K	Rb	Cs
Li	[5]	[8]	[4]	[4]
Na	–	[2 a, 7]	[6]	[5]
K	–	–	[3]	[7]
Rb	–	–	–	this work

a Measured at an $NaNO_3$ concentration of 91.8 mol% at 649 K.

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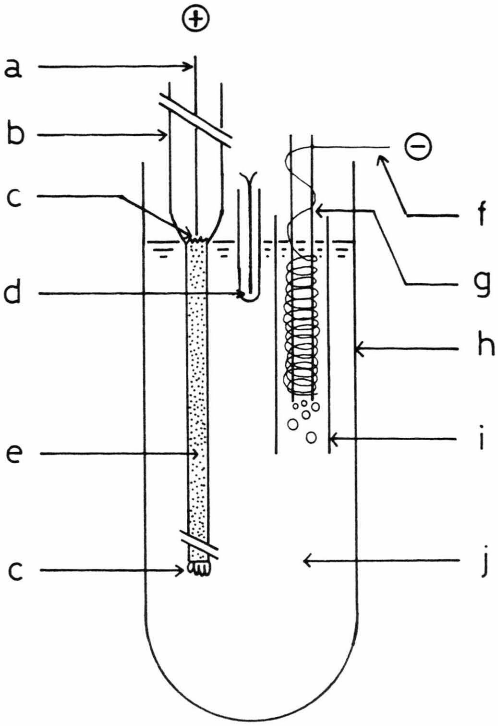

Fig. 1. Electromigration cell. a: Pt anode, b: separation column (quartz), c: quartz wool, d: CA-thermocouple, e: quartz powder (80 – 100 mesh), f: Al cathode, g: quartz tube, h: quartz vessel, i: quartz tube, j: salt bath ($LiNO_3$–$NaNO_3$–KNO_3 of the eutectic composition).

making an alloy with Li metal, but this did not disturb the separation process on the anode side, The content of Rb^+ and Cs^+ in the samples from the separation tubes was determined with flame spectrophotometry; 1000 ppm of Na^+ were added to each aqueous solution containing several 10 ppm of Rb^+ and Cs^+ in order to depress too easy ionization of the corresponding salts.

The other experimental procedures were similar to those previously employed ([4–7]).

3. Results

Table 2 gives the main experimental conditions and the obtained relative differences in the internal mobilities

$$\varepsilon_{12} = (b_{Rb} - b_{Cs})/(p_{Rb}\, b_{Rb} + p_{Cs}\, b_{Cs}) \,, \tag{1}$$

where b and p are the internal mobility and the mole fraction of the ion specified by the subscript, respectively; $p_{Rb} + p_{Cs} = 1$. The internal cationic mobilities result from the equations

Table 2. Experimental conditions and results. Q is the transported charge.

Run	p_{Cs}	T/K	Q/C	ε_{12}
1	0.1160 ± 0.0009	659	2326	0.0103 ± 0.0028
2		684	2268	0.0132 ± 0.0066
3		733	1989	− 0.0093 ± 0.0057
4		771	2016	− 0.0077 ± 0.0027
5	0.4214 ± 0.0015	635	2733	− 0.0030 ± 0.0030
6		716	2813	− 0.0043 ± 0.0010
7	0.5186 ± 0.0015	723	2250	− 0.0081 ± 0.0030
8		785	2328	− 0.0047 ± 0.0026
9	0.7964 ± 0.0012	776	2089	− 0.0138 ± 0.0025
10		778	2155	− 0.0136 ± 0.0023
11		806	1995	− 0.0207 ± 0.0026
12		823	2286	− 0.0216 ± 0.0023

$$b_{Rb} = (\Lambda/F)\,(1 + p_{Cs}\,\varepsilon_{12}) \,, \tag{2}$$

$$b_{Cs} = (\Lambda/F)\,(1 - p_{Rb}\,\varepsilon_{12}) \,, \tag{3}$$

where Λ is the molar conductivity of the mixture calculated from the data on the densities [14] and conductivities [15]; F is the Faraday constant. Our obtained internal cation mobilities vs. p_{Cs} are shown in Fig. 2 together with those obtained by Shvedov and Ivanov [11]. As these authors have used different conductivity data, their internal mobilities at 693 K, which we have estimated by reading the external mobilities from their drawing, appear to be considerably lower than ours; their data are, however, in good agreement with ours in that the mobilities of Rb^+ and Cs^+ are nearly equal in the whole concentration range.

4. Discussion

We have found from MD simulation of some molten alkali chlorides [10] that the internal mobilities are paralleled by the separating motion of neighbouring unlike ions. Three main factors affecting the separating motion have been taken into consideration [4–7]: Coulombic attraction between unlike ions, agitation of the ions, and free space.

Figure 2 shows that the Chemla effect occurs at the high temperature. With an increase in temperature the number density of the anions becomes smaller; therefore it becomes less favourable for the (smaller) cations than for the larger ones to leave a nearest neighbouring anion toward another anion, the process essential in ionic mobility.

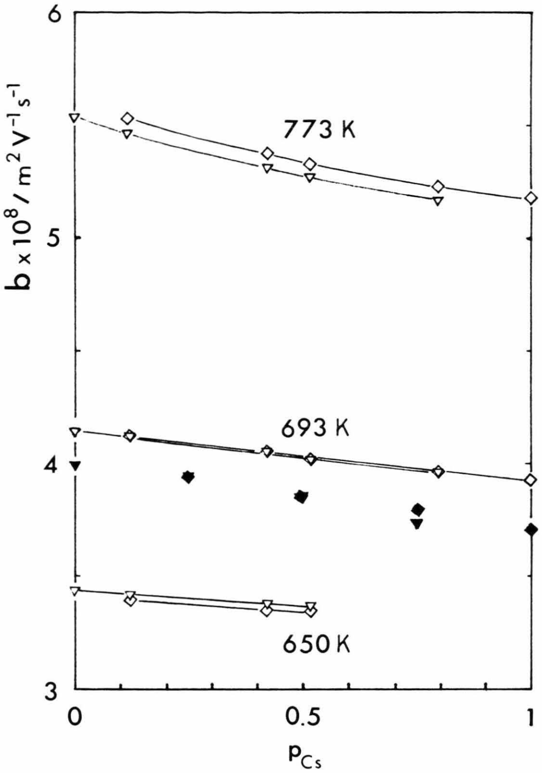

Fig. 2. Internal cation mobilities vs. mole fraction of $CsNO_3$. ▽: b_{Rb}; ◇: b_{Cs}; ▼: b_{Rb}; ◆: b_{Cs}; as evaluated from the external mobilities at 693 K given in [11].

The concentration dependence of ε_{12} is small in the present system. This may be mainly due to the small relative variation in molar volume V from $RbNO_3$ to $CsNO_3$; viz. $V = 64.7$ and $72.6\ cm^3\ mol^{-1}$ for $RbNO_3$ and $CsNO_3$, respectively, at 800 K, while for $NaNO_3$ and KNO_3, where the concentration dependence of ε_{12} is greater, $V = 45.6$ and $54.6\ cm^3\ mol^{-1}$, respectively, at 650 K [16]. Also the variation of the free space and agitation effects over the concentration range would be small in $RbNO_3$–$CsNO_3$ mixtures.

A survey of the reciprocals of the internal mobilities of Rb^+ and Cs^+ in mixtures with other alkalinitrates in their dependence on the molar volume of the mixtures is given in Figures 3 and 4.

We have found [4–7] that the mobilities of small cations, and to some extent also of large ones, in binary alkali nitrates are well expressed by the equation

$$b = \{A/(V - V^0)\} \exp(-E/RT)\,. \qquad (4)$$

Here, A and E are constants depending on the cation of interest and V^0 is a constant nearly independent of temperature. In a limited concentration region near pure $RbNO_3$ and $CsNO_3$, b_{Rb} and b_{Cs} respectively might be expressed by (4). From the data of pure $RbNO_3$ and $CsNO_3$ recommended in [16], the parameter values of (4) have been calculated as given in Table 3.

In Figs. 5 and 6, b_{Rb} and b_{Cs} in several molten binary alkali nitrates are plotted against p_{Rb} and p_{Cs}. At a given concentration, b_{Rb} and b_{Cs} become generally greater with decreasing radius of the

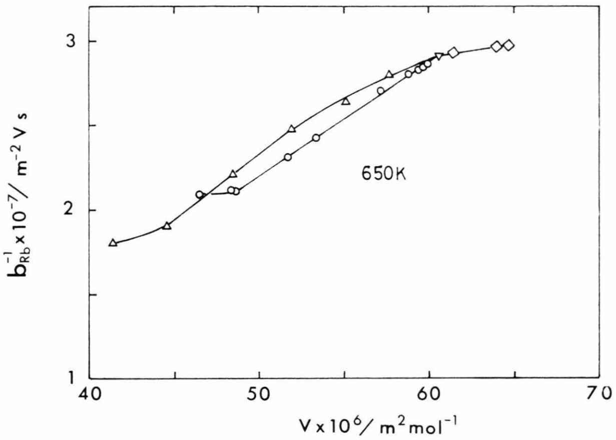

Fig. 3. Reciprocal of the internal mobilities of Rb^+ vs. molar volume in (M–Rb)NO_3. △: M = Li [4]; ○: Na [6]; ▽: pure $RbNO_3$ [16]; ◇: Cs.

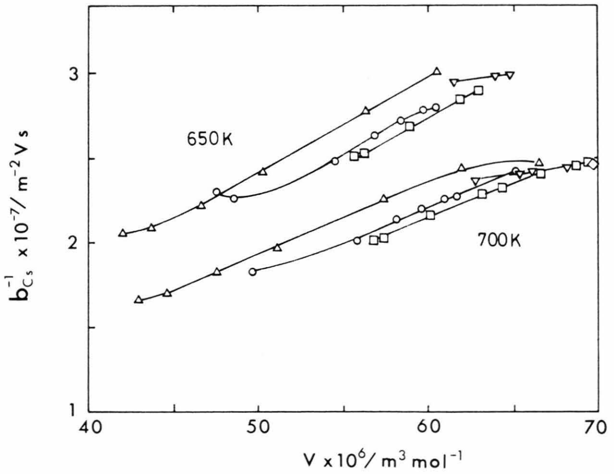

Fig. 4. Reciprocal of the internal mobilities of Cs^+ vs. molar volume in (M–Cs)NO_3. △: M = Li [4]; ○: Na [5]; □: K [7]; ▽: Rb; ◇: pure $CsNO_3$ [16].

coexisting cations. b_{Cs} in (Li–Cs)NO_3 is singularly small at high p_{Cs}. This seems to be the case also for b_{Rb} in (Li–Rb)NO_3, although b_{Rb} has not been measured at very high p_{Rb} (> 0.859). A similar trend is seen though not so clear, also for b_{Rb} in (Na–Rb)NO_3 in which b_{Rb} has been measured at rather high p_{Rb}. At a low density of the NO_3^- ions, every Li^+ ion will be strongly clustered with neighbouring NO_3^- ions, and therefore the agitation effect by the Li^+ ions upon the separating motion of the Cs^+ (or Rb^+) and NO_3^- ions will be small. This may be the reason for the singularly small b_{Cs} (or b_{Rb}). Very strong interaction of Li^+ ions with anions at a low density of the anions has also shown up in the MD simulation of molten (Li–K)Cl by Lantelme and Turq [17], in which the Li–Cl distance is 212 pm at $p_K = 0.90$ while 221 pm in pure LiCl.

Table 3. Parameter values of (4) in a limited concentration region near pure $RbNO_3$ and $CsNO_3$.

M	$A \times 10^{11}$ / $m^5\,V^{-1}\,s^{-1}\,mol^{-1}$	E / $kJ\,mol^{-1}$	$V^0 \times 10^6$ / $m^3\,mol^{-1}$
Rb	2.56	21.86	48.5
Cs	3.33	21.07	47.4

In conclusion, even the small difference in the coulombic force of Rb^+ and Cs^+ with NO_3^- causes the Chemla effect at high temperature. Thus, in all

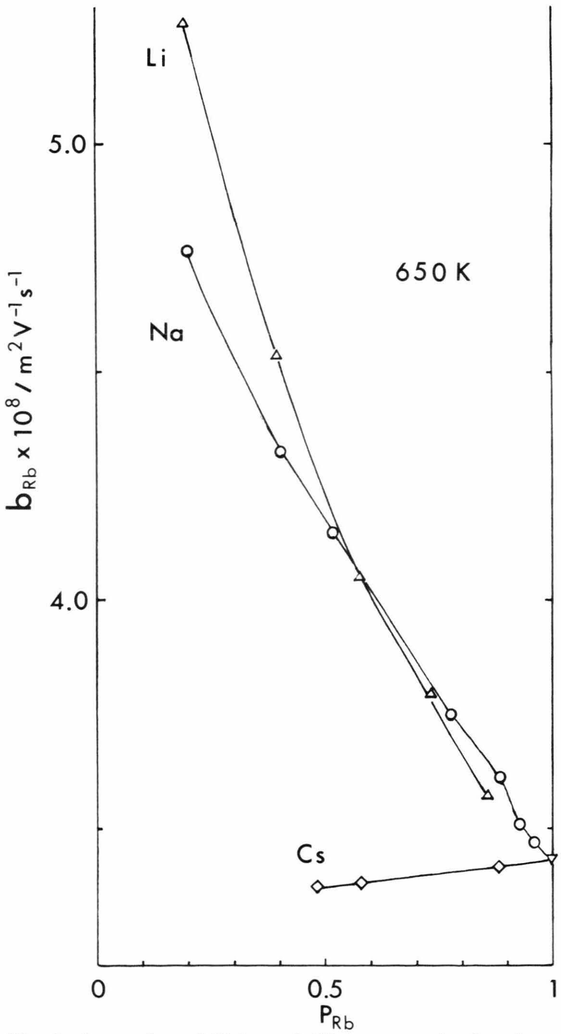

Fig. 5. Internal mobilities of Rb^+ vs. mole fraction in (M–Rb)NO_3. As for the symbols, see the legend to Figure 3.

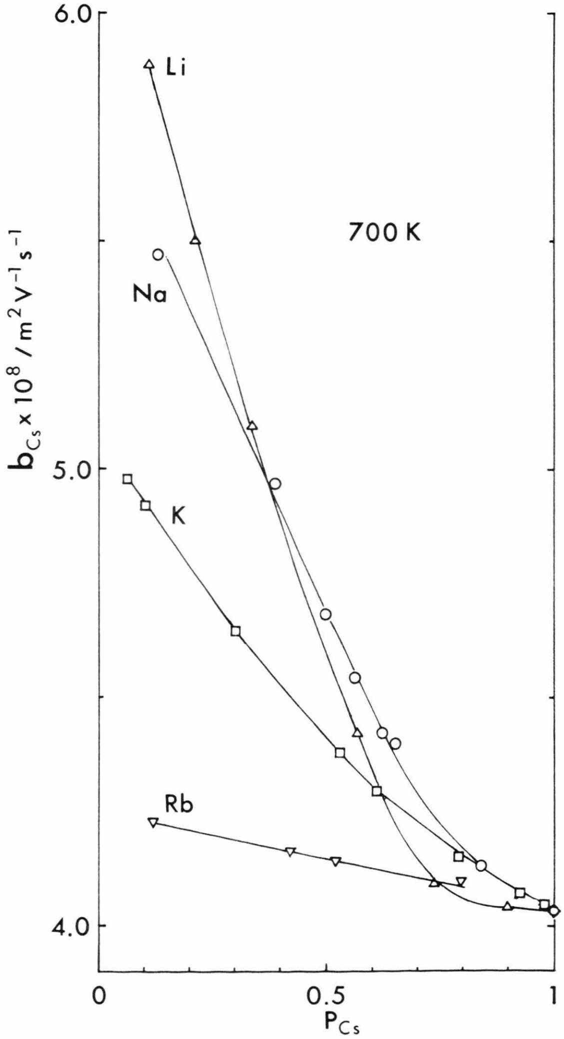

Fig. 6. Internal mobilities of Cs^+ vs. mole fraction in (M–Cs)NO_3. As for the symbols, see the legend to Figure 4.

molten binary alkali nitrates except (K–Rb)NO_3, the Chemla effect has been observed; also in (K–Rb)NO_3 the Chemla effect could be expected to occur at high temperature.

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