Internal Cation Mobilities and Their Isotope Effects in the Molten System (Li, K)NO_3

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Z. Naturforsch. **42 a,** 683–689 (1987); received January 21, 1987

With the Klemm method internal mobility ratios of the two cations have been measured for melts of the binary system (Li, K)NO_3 over a wide range of temperature and composition, and their isotope effects have been determined near the eutectic composition. The Chemla effect has been observed. With increasing temperature the Chemla crossing point shifts, as expected, toward higher concentrations of the smaller cation. At very high concentrations of $LiNO_3$ the mobility of K^+ tends to decrease, which is attributed to the free space effect. For both Li^+ and K^+ the isotope effect increases with temperature.

Introduction

Ratios of the internal mobilities of cations have been studied systematically for molten binary mixtures of alkali nitrates, see Table 1 of [1]. The present study concerns (Li, K)NO_3. The external mobilities of this system have been studied previously by Lantelme and Chemla [2], and the Chemla effect had been observed, i.e. in a certain range of temperature and concentration the mobility of the large cation is greater than that of the small cation. Their experiment will be referred to as exp. A in the following. More accurate information on cation mobilities should be obtainable with the Klemm method, which gives internal transport numbers instead of external ones.

Also the isotope effect of cation migration has been measured near the eutectic composition (mole fraction of $LiNO_3$: $x_{Li} = 0.412$), mainly for determining the temperature dependence.

Experimental

The chemicals $LiNO_3$ and KNO_3 were of reagent grade. The salts were dried at 120 °C overnight, mixed in a chosen ratio and melted.

Two types of electromigration cells were used. For both of them the amount of salt on the anode side of the separation tube was small, and a platinum wire served as the anode. For the measurements of the Li to K mobility ratio the cell described in [3] was used: The cathode compartment contained molten NH_4NO_3, and an intermediate compartment (separated from both electrode compartments by tubes packed with some powder) contained a nearly eutectic mixture of (Li, Na, K)NO_3. If also the isotope effect was studied, the cell was similar to the one described in [4]: A dried mixture of NO_2 and O_2 gas was introduced through an aluminium tube into the cathode compartment, which contained an (Li, K)NO_3 mixture of the composition that was to be studied. The temperature was kept within ± 1 °C in the former cell and ± 4 °C in most runs with the latter cell.

In both cases the separation tube was 15–20 cm long. The powder in the separation tube was silica (100–150 mesh in the isotope experiments and 80–100 mesh in the others). A portion of the melt was stored in a small vessel, from which it was filled into the separation tube before each run. The separation tube was then inserted into the large (intermediate or cathode) compartment. The difference between the two types of cells should not affect the results. All other experimental procedures are similar to those described in papers such as [5, 6].

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Table 1. Experimental conditions and relative differences in internal cation mobilities, ε_c, and isotope mobilities, ε_{Li} and ε_K. x_K is the mole fraction of K^+, Q the transported charge, and t the duration.

x_K	T/K	Q/C	t/hr	ε_c	ε_{Li}	ε_K
0.01	573	7399	21.0	0.305 ± 0.004		
	623	6916	19.4	0.134 ± 0.004		
	673	8670	24.1	0.074 ± 0.003		
0.05	573	7084	20.1	0.068 ± 0.002		
	623	5850	18.0	0.049 ± 0.002		
0.10	553	9551	27.3	0.104 ± 0.003		
	573	8440	25.0	0.045 ± 0.002		
	623	8155	24.2	0.026 ± 0.002		
	673	2028	6.2	-0.012 ± 0.003		
0.20	573	6404	5.7	0.046 ± 0.002		
0.573	653	6876	15.5	-0.108 ± 0.003	0.0083 ± 0.0011	0.0024 ± 0.0002
	746	6245	13.9	-0.131 ± 0.004	0.0100 ± 0.0009	0.0033 ± 0.0004
0.59	452	3453	30.1	0.069 ± 0.002	0.0059 ± 0.0002	0.0012 ± 0.0005
	454	2440	18.2	0.078 ± 0.002	0.0066 ± 0.0005	0.0021 ± 0.0009
	[a] 463	6823	27.7	0.059 ± 0.001	0.0060 ± 0.0002	0.0009 ± 0.0003
	474	6298	25.2	0.063 ± 0.003	0.0069 ± 0.0002	0.0010 ± 0.0004
	513	8830	24.2	0.013 ± 0.001	0.0061 ± 0.0002	0.0020 ± 0.0003
	517	9027	24.0	0.009 ± 0.001	0.0049 ± 0.0002	0.0011 ± 0.0001
	521	8615	24.0	-0.002 ± 0.001	0.0059 ± 0.0003	0.0014 ± 0.0001
	533	5297	27.1	-0.018 ± 0.003	0.0061 ± 0.0004	0.0012 ± 0.0002
	575	8718	24.0	-0.049 ± 0.002	0.0087 ± 0.0004	0.0018 ± 0.0002
	576	9221	24.0	-0.049 ± 0.001	0.0046 ± 0.0004	0.0015 ± 0.0001
	578	9047	24.0	-0.052 ± 0.002	0.0087 ± 0.0004	0.0015 ± 0.0001
	614	8837	24.0	-0.076 ± 0.003	0.0099 ± 0.0006	0.0021 ± 0.0002
	622	8851	24.0	-0.083 ± 0.003	0.0108 ± 0.0004	0.0018 ± 0.0003
	648	8804	24.0	-0.118 ± 0.003	0.0110 ± 0.0005	0.0019 ± 0.0002
	672	9418	24.0	-0.108 ± 0.003	0.0111 ± 0.0005	0.0019 ± 0.0001
	687	10600	24.0	-0.127 ± 0.004	0.0100 ± 0.0007	0.0029 ± 0.0002
0.90	623	8350	27.6	-0.095 ± 0.002		
	673	8107	23.9	-0.191 ± 0.002		
0.95	623	2129	6.0	-0.101 ± 0.003		
	673	1784	5.1	-0.179 ± 0.003		
0.98	623	2033	6.1	-0.117 ± 0.004		
	673	2240	6.4	-0.166 ± 0.003		
0.99	623	8136	23.8	-0.105 ± 0.004		
	673	7027	19.7	-0.110 ± 0.004		

[a] For this run, the chemical and isotope distribution in the separation tube is given in Table 2 of [7]; the values of $\varepsilon_c(0.0025 \pm 0.0004)$ and $\varepsilon_K(0.00011 \pm 0.00015)$ in the footnote of that table should be corrected as given here.

Results

The main experimental conditions and the results are given in Table 1. ε_c, ε_{Li} and ε_K are defined as

$$\varepsilon_c = (b_{Li} - b_K)/\bar{b}\,, \tag{1}$$

$$\varepsilon_{Li} = (b_6 - b_7)/b_{Li}\,, \tag{2a}$$

$$\varepsilon_K = (b_{39} - b_{41})/b_K\,, \tag{2b}$$

where b: internal mobility; $\bar{b} = x_{Li} b_{Li} + x_K b_K$, $b_{Li} = y_6 b_6 + y_7 b_7$ and $b_K = y_{39} b_{39} + y_{41} b_{41}$ (y: abundance of isotope; $y_6 + y_7 = 1$ and $y_{39} + y_{41} \fallingdotseq 1$); the suffixes 6, 7, 39, and 41 refer to $^6Li^+$, $^7Li^+$, $^{39}K^+$, and $^{41}K^+$, respectively. These values were calculated as described in [7].

The values of b_{Li} and b_K are calculated from the obtained ε_c and available data on the density [8, 9] and conductivity [9] (cf. Table 2).

Figure 1 shows ε_c values vs. temperature.

Figure 2 shows the isotherms of b_{Li} and b_K at 573 K, 623 K, and 673 K together with those calculated from the sum of the external mobilities of the respective cations [2] and NO_3^- [10], which were measured by Lantelme and Chemla with the asbestos strip method; for the calculation of these external mobilities other data [11] on density and conductivity were used by them.

In Fig. 3 the ε_{Li} and ε_K values near the eutectic compositions are plotted against temperature.

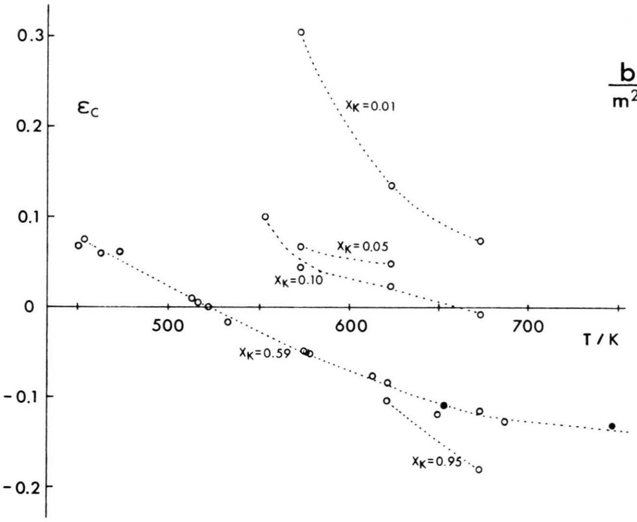

Fig. 1. Relative difference in internal cation mobilities, ε_c, vs. temperature in the system (Li, K)NO_3 for various mole fractions, x_K. Two points at $x_K = 0.573$ (●) are included in the curve for $x_K = 0.59$.

Discussion

When $\varepsilon_c < 0$, i.e. $b_{Li} < b_K$, an anomalous distribution of the Li isotopes was observed along the separation tube. The region near the anode showed the expected enrichment of ^7Li but was followed by a region with an enrichment of ^6Li, while ^{41}K was enriched in both these regions. In the case $b_{Li} > b_K$ a corresponding anomalous distribution should instead be expected for the K isotopes, i.e. a first region with an enrichment of ^{41}K should be followed by one where ^{39}K is enriched. An example of this case is given in Table 2 of [7]. However, the anomaly is not as evident in this case, mainly because ε_K is rather small, but also because the accuracy of the mass spectrometer was not so good. The cause of the anomalous isotope distribution was discussed in detail in [7] and [7a].

Isotherms of the internal cation mobilities are shown in Fig. 2 for the present experiment as well as for exp. A. The agreement is as good as one can expect with the exception of the mobilities of very dilute potassium ions: The present study shows a strong decrease of b_K when x_K approaches zero while this was not observed in exp. A. It is, however, inevitable that the accuracy of external K^+ mobilities becomes particularly low when x_K approaches zero. The observed decrease of b_K at high x_{Li} might be due to the free space effect [5, 12], which has been observed in many other systems such as (Li, Rb)NO_3 and (Li, Cs)NO_3 [5]. It is quite reasonable that in the present case the free space effect is the greater the lower the temperature is. The Chemla crossing points are found at higher x_{Li} in our experiment than in exp. A.

For the experiments with the original composition $x_K = 0.59$, the final composition at the anode is plotted against temperature in Figure 4. Since this composition should approach that of the Chemla crossing point, the points of Fig. 4 should lie on a smooth curve. However, they seem to be more scattered than those of the corresponding experiment

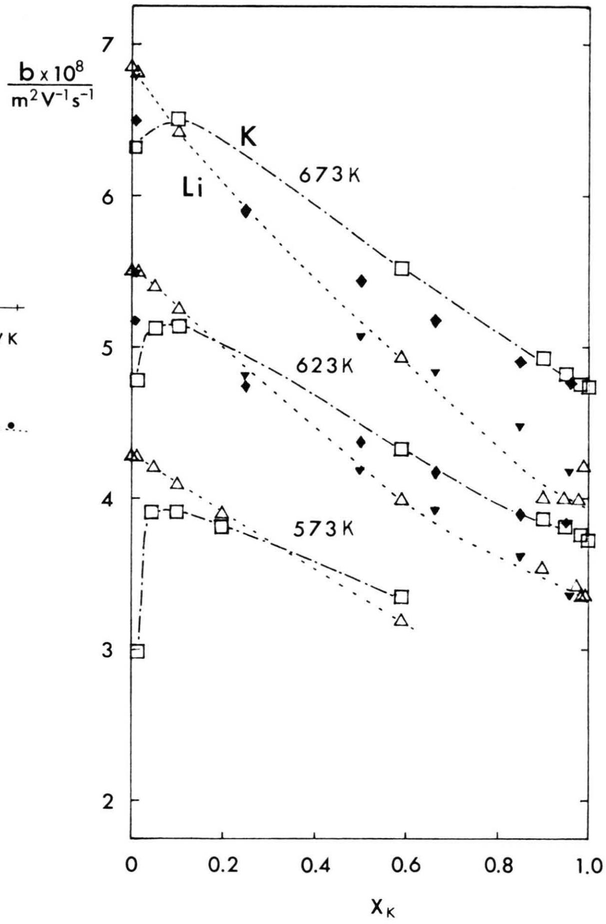

Fig. 2. Isotherms of the internal cation mobilities in the system (Li, K)NO_3. △: Li, □: K from the present ε_c measurements. ▲: Li and ◆: K calculated from external mobilities [2, 10].

Table 2. Internal mobilities of Li^+ and K^+ in (Li, K)NO_3 mixtures.

x_K	T/K	$\varkappa$/S cm^{-1}	V/cm^3 mol^{-1} [a]	$b_{Li}/10^{-8}$ m^2 V^{-1} s^{-1} [b]	$b_K/10^{-8}$ m^2 V^{-1} s^{-1} [b]
0	573	1.056	39.18	4.29	
	623	1.338	39.80	5.52	
	673	1.634	40.44	6.85	
0.01	573	1.047	39.36	4.28 ± 0.00	2.98 ± 0.02
	623	1.326	39.99	5.50 ± 0.00	4.77 ± 0.02
	673	1.618	40.65	6.82 ± 0.00	6.32 ± 0.02
0.05	573	1.011	39.93	4.20 ± 0.00	3.91 ± 0.01
	623	1.279	40.59	5.39 ± 0.00	5.13 ± 0.01
0.10	553	0.864	40.38	3.65 ± 0.00	3.28 ± 0.01
	573	0.968	40.64	4.09 ± 0.00	3.91 ± 0.01
	623	1.223	41.33	5.25 ± 0.01	5.12 ± 0.01
	673	1.475	42.05	6.42 ± 0.02	6.50 ± 0.02
0.20	573	0.887	42.06	3.90 ± 0.00	3.73 ± 0.01
0.59	452	0.288	45.49	1.41 ± 0.00	1.32 ± 0.00
	513	0.462	46.47	2.24 ± 0.00	2.21 ± 0.00
	575	0.666	47.55	3.19 ± 0.01	3.35 ± 0.00
	622	0.834	48.43	3.98 ± 0.01	4.33 ± 0.01
	672	1.032	49.43	4.93 ± 0.01	5.54 ± 0.01
	746	1.350	50.78	6.57 ± 0.02	7.50 ± 0.02
0.90	623	0.704	52.83	3.53 ± 0.01	3.89 ± 0.01
	673	0.865	53.96	4.00 ± 0.02	4.93 ± 0.02
0.95	623	0.684	53.54	3.43 ± 0.01	3.82 ± 0.01
	673	0.843	54.68	3.97 ± 0.02	4.82 ± 0.02
0.98	623	0.673	53.96	3.33 ± 0.02	3.77 ± 0.01
	673	0.831	55.11	3.97 ± 0.02	4.76 ± 0.02
0.99	623	0.669	54.10	3.36 ± 0.02	3.75 ± 0.01
	673	0.827	55.25	4.22 ± 0.02	4.74 ± 0.01
1.0	623	0.665	54.24		3.74
	673	0.823	55.40		4.72

[a] The density data are taken from [8]. The parameters for (Li, K)NO_3 in Table 6 of [8] refer to $x_K = 0.2$, 0.4, 0.6, and 0.8, not $x_{Li} = 0.2$, 0.4, 0.6, and 0.8, respectively. The density data in Tables 66(a) and (b) of [9] are based on the uncorrected paper [8] and are therefore erroneous. We have recalculated the parameters of the density formula

$$\varrho = a + bT + cC + dC^2 + eC^3 + fTC^2 + gCT^2 \text{ (g cm}^{-3}\text{)},$$

where C is mole percent KNO_3, and found

$$a = 2.07386,\ b = -5.48158 \times 10^{-4},\ c = 2.74821 \times 10^{-3},\ d = -1.26740 \times 10^{-5},$$
$$e = -1.11207 \times 10^{-8},\ f = 2.01241 \times 10^{-8}, \text{ and } g = -3.36667 \times 10^{-9}.$$

An alternative equation with only five terms has appeared as an erratum to [9] (private communication from Prof. G. J. Janz to Prof. A. Klemm). Existing minor deviations between densities calculated by means of the two equations are negligible for the interpretation of our experiments.

[b] b_{Li} and b_K are calculated from $b_{Li} = (\varkappa V/F)(1 + \varepsilon_c x_K)$ and $b_K = (\varkappa V/F)(1 - \varepsilon_c x_{Li})$, where $\varkappa$ is the conductivity and F the Faraday constant. The sign ± stands for the standard deviation resulting from that of ε_c and x_{Li} (x_K) only.

with the (Li, K)Cl system, see Fig. 3 of [6]. The present scatter is probably due to the fact that the difference between the slopes of the isotherms of b_{Li} and b_K is smaller in the (Li, K)NO_3 system than in the (Li, K)Cl system. The decrease of the crossing point x_K with increasing temperature is, however, clearly seen in Figure 4.

The relative magnitude of the cation mobilities depends on several factors. If the Coulombic attraction is the dominant one, it has been found that the internal mobility of a cation in a binary mixture of alkali nitrates is well expressed by the equation [13]

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

where A, E and V_0 are constants that should be characteristic of the cation in question, i.e. independent of the co-cation, and V is the molar volume of the mixture. The validity of this statement can be

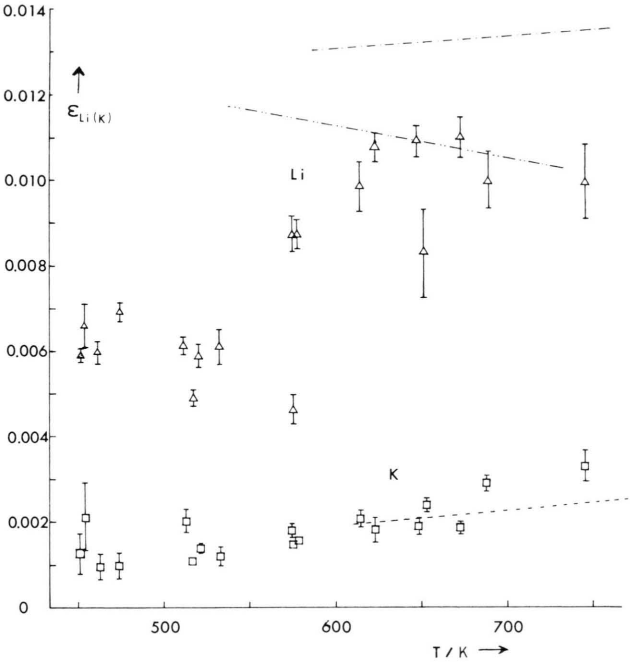

Fig. 3. The isotope effects of cation mobility ε_{Li} and ε_K vs. temperature near the eutectic composition. For comparison the isotope effects for pure LiNO$_3$ (– – –: [16], – · – ·: [17]) and KNO$_3$ (— — —: [19]) are also shown.

Table 3. Parameters of (3).

Cation	A	E	V_0
	10^{-11} m^5 V^{-1} · s^{-1} mol^{-1}	kJ mol^{-1}	10^{-6} m^3 mol^{-1}
Li (I)	2.84	17.80	24.7
(II)	2.78	16.38	19.0
K	4.21	16.74	10.5

tested for both b_{Li} and b_K from the present experiments.

The parameters of (3) are given in Table 3, where two alternatives have been chosen for b_{Li}. Calculation I is based on the data of the previous experiments with (Li, Rb)NO$_3$ and (Li, Cs)NO$_3$ [5] plus those of the (Li, K)NO$_3$ experiments that were made at nearly the eutectic composition; at this concentration the data should be most reliable due to the large number of experiments. For calculation II only the data of the (Li, K) experiments were used. In Fig. 5 the reciprocal of b is plotted against V at 573, 623, and 673 K. Two interpretations are pos-

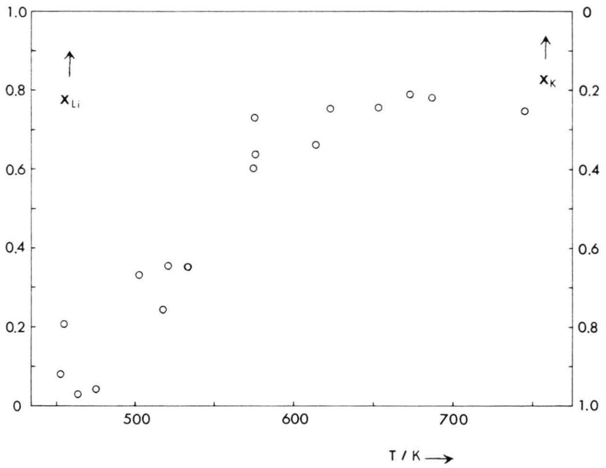

Fig. 4. Final composition near the anode vs. temperature for experiments with the initial composition $x_K = 0.59$.

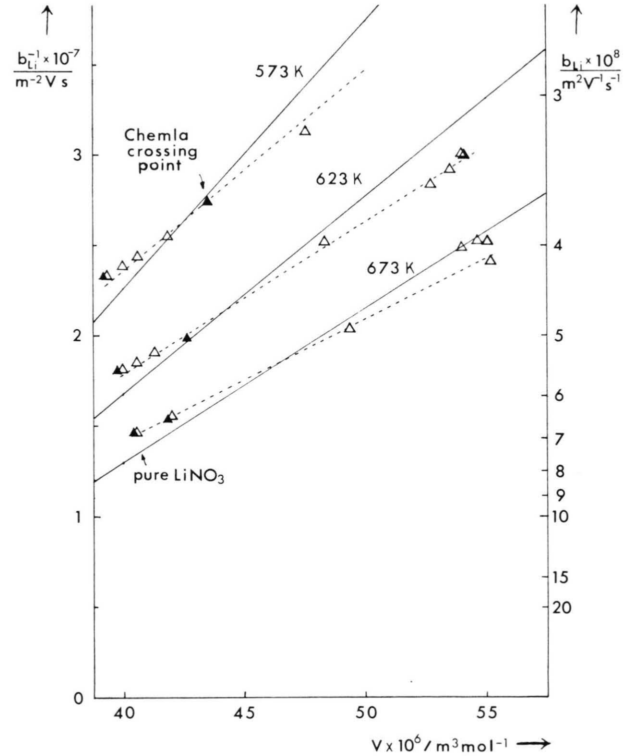

Fig. 5. Reciprocals of the internal mobilities of Li$^+$ vs. molar volume. The solid and broken lines are drawn according to the parameters of (I) and (II) of Table 3, respectively.

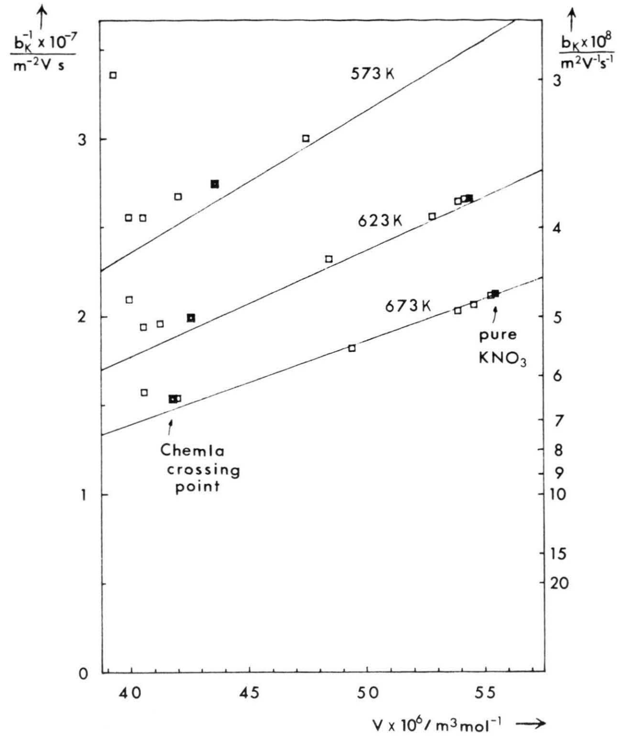

Fig. 6. Reciprocals of the internal mobilities of K$^+$ vs. molar volume. The solid lines are drawn according to the parameters of Table 3.

sible. The first is that the parameters of (3) are actually independent of the co-cations, alternative I, and that for small V the deviations of the experimental data from the solid line of Fig. 5 are due to the free space effect, while for large V, that is high concentration of KNO$_3$, the deviation is due to the large experimental errors of ε_c in the high x_K region.

The interpretation according to alternative II is that the parameters of (3) are appreciably influenced by the co-cations, dashed line of Figure 5. Actually the b_{Li} reported previously for the high x_{Na} region of (Li, Na)NO$_3$ (see Fig. 4 in [5]) are considerably greater than those that would be obtained by using the parameters (I) of Table 3. Therefore, it would not be surprising if b_{Li} of (Li, K)NO$_3$ actually deviates from the alternative (I, solid line of Fig. 5) based mainly on the data from the two other systems (Li, Rb)NO$_3$ and (Li, Cs)NO$_3$; it also seems reasonable that the deviation of b_{Li} from alternative I is smaller in (Li, K)NO$_3$ than in (Li, Na)NO$_3$. It follows from Fig. 5 that the b_{Li} of (Li, K)NO$_3$ can be expressed about as well by the assumption that the parameters of (3) depend on the co-cations or not.

The parameters for b_K in Table 3 are calculated from the previous study of (K, Cs)NO$_3$, a system where the cation mobilities are expected to be predominantly determined by the Coulombic interaction, and Fig. 6 shows that they fit very well also to the b_K of our study of (Li, K)NO$_3$. However, it has previously been found that the b_Ks of (Na, K)NO$_3$ are appreciably larger; see Fig. 4 of [12]. Thus, it appears that for the present system the agitation of b_K by the Li$^+$ ions happens to be compensated by the free space effect, and that the coincidence of the b_K of the (Li, K)NO$_3$ and (K, Cs)NO$_3$ experiments is fortuitous.

As seen from Fig. 5, the volume V at the Chemla crossing point becomes appreciably smaller when the temperature is increased, while this volume is nearly independent of temperature for (Li, K)Cl mixtures [6]. This means that, for a given density of NO$_3^-$, an increase in temperature is more favourable for the mobility of K$^+$ than for that of Li$^+$. This is presumably because the probability of the leaving process [14, 15] of a cation toward another NO$_3^-$ ion is more strongly reduced for Li$^+$ than for K$^+$ by the rotational motion of the NO$_3^-$ ions. An Li$^+$ ion is more strongly attracted by an NO$_3^-$ ion than a K$^+$ ion is, and, owing to its small size, an Li$^+$ ion is dragged more readily by the rotational motion.

Figure 3 shows that ε_{Li} and ε_K tend to increase with temperature. The temperature dependence is more pronounced in the nitrate than in the chloride eutectic [6]. This stronger temperature dependence is likely to be due to the rotational motion of the NO$_3^-$ ions. When a cation moves from an NO$_3^-$ ion toward another one, the probability that it will come back toward the first one is reduced as the rotational motion of the NO$_3^-$ increases. This means that the probability of the coming-back process [14, 15] will decrease, which will give rise to a larger isotope effect.

In Fig. 3 ε_{Li} for the mixture is compared with two sets of data for pure LiNO$_3$ [16, 17]. There seems to be satisfactory agreement with the older one in the range 630 K to 750 K. According to a recent reinvestigation of pure LiNO$_3$ in the range 559−726 K, ε_{Li} increases in the range from 559 K to 660 K while it is almost constant above 660 K [18]. For this latter study the values of ε_{Li} and the temperature dependence are very similar to those of the present study of the eutectic mixture. Our ε_K for the mixture agrees within experimental error with what was found for pure KNO_3 [19].

A calculation of the self-exchange velocities in alkali nitrate melts would make the interpretation of the isotope effects ε_{Li} and ε_K clearer.

We are indebted to Mr. M. Lövenby for performing the mass spectrometric analysis and to the Swedish National Science Research Council and the Scientific Fund of the Ministry of Education (Nos. 60470160 and 61134043), Japan, for financial support.

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