Internal Mobilities in the Molten Ternary System (Li,K,Cs)NO_3 of the Eutectic Composition

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The ε values in the internal cation mobilities of (Li,K,Cs)NO_3 of the eutectic composition (35.2–39.8–25.0 mol%) in the temperature range from 453 to 673 K were measured by Klemm's countercurrent electromigration method, where ε is defined as $(b_i-b_j)/b_a$; b_a is the average internal cation mobility and the subscripts i and j refer to any two out of these three cations. The conductivity was measured by a direct current method. From these data and the molar volume calculated from those of the pure salts on the assumption of additivity, the internal cation mobilities, b_{Li}, b_K and b_{Cs}, have been calculated. The b_{Li} is well expressed by the empirical equation presented for binary alkali nitrates; the negative deviation for b_K and b_{Cs} may be accounted for on the assumption of the tranquilization effect of Li^+. The orders of those internal cation mobilities are $b_{Cs}<b_K<b_{Li}$ at 453–473 K, $b_{Cs}<b_{Li}<b_K$ at 473 –583 K, and $b_{Li}<b_{Cs}<b_K$ at 583–673 K. These orders can be interpreted in terms of the dynamic dissociation model previously presented.

Key words: Internal Mobility; Molten (Li,K,Cs)NO_3; Dynamic Dissociation Model.

Introduction

We have so far measured the internal cation mobilities, b, in molten binary monovalent cation systems such as nitrates by Klemm's countercurrent electromigration method. In previous papers we have tested the following rule mainly for nitrates: for melts (M_1,M_2) X, M_1 being a given monovalent cation, M_2 any other monovalent cation and X a given anion, the mobility of M_1 depends only on the molar volume of the mixture if M_1 is a relatively small cation such as Li^+, Na^+, K^+ or Ag^+. In other words, at a given temperature and pressure, in salt-mixtures with one kind of anions the mobility of one kind of cations depends only on the density of the anions and not on the densities of the cations. This is plausible since the internal mobility of a cation depends mainly on its nearest neighbours. Quantitatively, the mobilities of monovalent cations such as Li^+, Na^+, K^+, and Ag^+ can be well expressed by the empirical equation [1, 2]

$$b = \{A/(V_m - V_0)\} \exp(-E/RT), \quad (1)$$

where V_m is the molar volume of the mixture and A, V_0 and E are constants which are nearly independent of the second cation. However, a perturbation concerning (1) should also be taken into account in some cases. If b deviates from (1), the upper and lower deviations could be interpreted in terms of the agitation effect and the free space or tranquilization effect, respectively [2], caused by the coions (see later).

We have measured the internal mobilities of the ternary system (Li,Na,K)NO_3 of the eutectic composition (30.0–17.0–53.0 mol%) [3] and found that (1) holds also for this ternary system, and the order of the internal mobilities of the cations is $b_{Li}<b_K<b_{Na}$ in the investigated temperature range from 473 to 673 K.

In order to test the extended rule over a wider temperature range we have now chosen the mixture (Li,K,Cs)NO_3 at its eutectic composition (45.2 mol% Li, 39.8 mol% K, 25.0 mol% Cs [4]).

Experimental

The $LiNO_3$ and KNO_3 of the reagent grade made by Kanto Chemical Co., Ltd. and $CsNO_3$ of the same grade made by Wako Chemical Co., Ltd. were used without further purification. These salts were vacuum-dried at

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180 °C for 48 hr, mixed at the eutectic ratio by weighing and stored in a desiccator.

An electromigration cell was similar to that described in [5] and the experimental procedure was the same as described therein. After electromigration the contents of Li^+ and K^+ in the separation tube were determined by flame spectrophotometry, and Cs^+ by atomic absorption spectrophotometry.

The electric conductivity of the ternary mixture was measured by the direct current method described by Duke and Bissell [6]. Two $Ag/AgNO_3$ reference electrodes were used. The cell constant was measured at 298 K to be 23.26 cm^{-1} using a KCl standard aqueous solution.

Results

The differences of b's for the three cations pairs are defined as

$$\varepsilon_{LiK} = (b_{Li} - b_K)/b_a \,, \tag{2a}$$

$$\varepsilon_{LiCs} = (b_{Li} - b_{Cs})/b_a \,, \tag{2b}$$

$$\varepsilon_{KCs} = (b_K - b_{Cs})/b_a \,, \tag{2c}$$

and the average cation mobility b_a is

$$b_a = x_{Li}\, b_{Li} + x_K\, b_K + x_{Cs}\, b_{Cs} = \kappa\, V_m/F \,, \tag{3}$$

where x is the mole fraction. The measured values of ε_{LiK}, ε_{LiCs} and ε_{KCs} are given in Table 1.

The data on the electric conductivity κ are given in Table 2. From a least squares regression, these are expressed as a function of T by

$$\kappa = -0.78836 + 0.0016307\, T + 1.0102 \cdot 10^{-6}\, T^2 \quad (\mathrm{S\ cm^{-1}}) \tag{4}$$

Here, T is the temperature in Kelvin.

The standard deviation is 0.25%.

From these ε and κ values, the internal cation mobilities are calculated from [3]

$$b_{Li} = (\kappa\, V_m/F)\,(1 + x_K\, \varepsilon_{LiK} + x_{Cs}\, \varepsilon_{LiCs}) \tag{5a}$$

$$b_K = (\kappa\, V_m/F)\,(1 - x_{Li}\, \varepsilon_{LiK} + x_{Cs}\, \varepsilon_{KCs}) \tag{5b}$$

$$b_{Cs} = (\kappa\, V_m/F)\,(1 - x_{Li}\, \varepsilon_{LiCs} - x_K\, \varepsilon_{KCs}) \tag{5c}$$

where V_m is the molar volume of the ternary system, which was calculated from those of the pure melts on the assumption of additivity. The excess molar volume may be negligibly small [7, 8].

Table 1. ε values for internal mobilities of the 3 cations.

T/K	Q/C	ε_{LiK}	ε_{KCs}	ε_{LiCs}
453	3411	0.013±0.002	0.037±0.002	0.051±0.005
473	3420	0.014±0.000	0.052±0.000	0.067±0.002
493	3197	–0.061±0.001	0.096±0.004	0.079±0.003
523	3059	–0.037±0.001	0.099±0.002	0.061±0.002
543	3107	–0.053±0.001	0.090±0.003	0.036±0.002
573	3002	–0.075±0.001	0.087±0.002	0.012±0.001
603	2721	–0.095±0.004	0.067±0.005	–0.028±0.003
623	2580	–0.087±0.005	0.058±0.004	–0.028±0.007
673	2300	–0.104±0.003	0.055±0.004	–0.048±0.003

Q: transported charge.

Table 2. Conductivity data.

T/K	κ/S cm^{-1}	T/K	κ/S cm^{-1}	T/K	κ/S cm^{-1}
453	0.160	528	0.353	603	0.564
458	0.172	533	0.360	608	0.578
463	0.184	538	0.381	613	0.593
468	0.196	543	0.394	618	0.607
473	0.209	548	0.409	623	0.623
478	0.220	553	0.422	628	0.637
483	0.233	558	0.436	633	0.651
488	0.246	563	0.450	638	0.664
493	0.259	568	0.464	643	0.678
498	0.271	573	0.479	648	0.693
503	0.285	578	0.493	653	0.707
508	0.298	583	0.507	658	0.720
513	0.312	588	0.521	663	0.733
518	0.325	593	0.536	668	0.748
523	0.339	598	0.550	673	0.762

Discussion

For two mixtures $(M_1,M_2)X$ and $(M_1,M_3)X$, the mole fractions of M_2X and M_3X can generally be chosen such that the molar volumes of the two mixtures and thus, according to (1), the mobilities of M_1 are equal. The cases $M_1X = LiNO_3$, KNO_3 and $CsNO_3$ are shown in Figs. 1, 2, and 3, respectively.

In a ternary mixture $(M_1,M_2,M_3)X$, the mobilities of M_1, M_2, and M_3 equal the mobilities of M_1, M_2, and M_3, respectively, in the binary mixtures $(M_1,M_2)X$ and $(M_1,M_3)X$, and $(M_2,M_3)X$, if the mole fractions are chosen such that the four mixtures have the same molar volume.

The observed mobilities in the eutectic $(Li,K,Cs)NO_3$ mixture at various temperatures are given in Table 3. These mobilities, together with the mobilities in $(Li,K)NO_3$ [9] and $(Li,Cs)NO_3$ [4] at mole fractions yielding at 623 K (350 °C) the same molar volume as the eutectic mixture are shown in Fig. 4. These

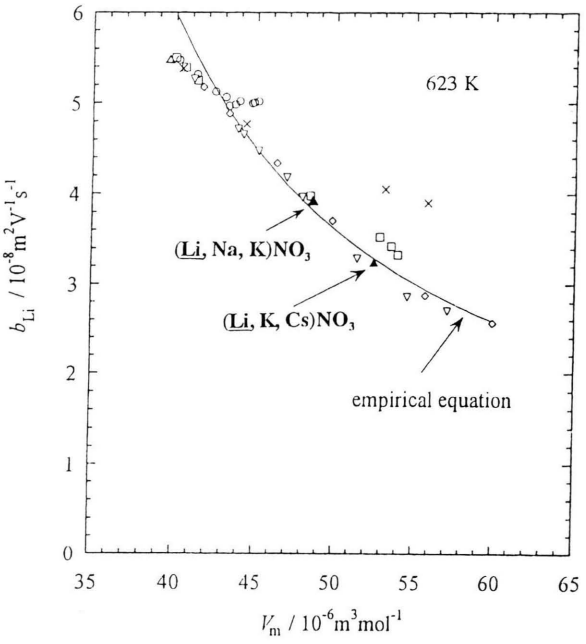

Fig. 1. Internal mobilities of Li^+ vs. molar volume in various nitrate mixtures (Li,M)NO_3 at 623 K: △: M = Li^+ (pure $LiNO_3$), ○: Na^+, □: K^+ [9], ▽: Rb^+, ◇:Cs^+ [4], ×: Tl^+. The curve is drawn according to (1) with the parameters $A = 2.84\times10^{-11}$ m^5 V^{-1} s^{-1} mol^{-1}, $V_0 = 24.7\times10^{-6}$ m^3 mol^{-1} and $E = 17.80$ kJ mol^{-1} [1]. The b_{Li} in the present ternary system and (Li,Na,K)NO_3 of the eutectic composition [3] are also shown.

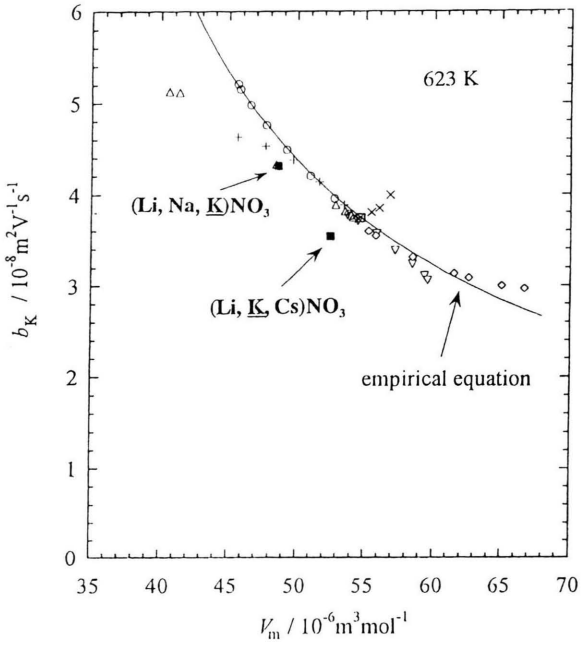

Fig. 2. Internal mobilities of K^+ vs. molar volume in various nitrate mixtures (K,M)NO_3 at 623 K: +: M = Ag^+. See also the legend of Figure 1. The curve is drawn according to (1) with the parameters $A = 3.95\times10^{-11}$ m^5 V^{-1} s^{-1} mol^{-1}, $V_0 = 22.1\times10^{-6}$ m^3 mol^{-1} and E = 18.00 kJ mol^{-1} [2]. The b_K in the present system and the (Li,Na,K)NO_3 [3] is also shown.

Table 3. Internal mobilities (in 10^{-8} m^2 V^{-1} s^{-1}).

T/K	κ/S cm^{-1}	V_m/ cm^3 mol^{-1}	b_{Li} (b^*_{Li})	b_K (b^*_K)	b_{Cs} (b^*_{Cs})	$\Delta b_{Li}/b^*_{Li}$	$\Delta b_K/b^*_K$	$\Delta b_{Cs}/b^*_{Cs}$
453	0.160	49.06	0.828±0.001 (1.032)	0.816±0.001 (1.230)	0.785±0.001 (1.090)	–0.19	–0.33	–0.27
473	0.208	49.46	1.089±0.001 (1.240)	1.074±0.000 (1.484)	1.018±0.001 (1.323)	–0.12	–0.27	–0.23
493	0.259	49.86	1.355±0.001 (1.467)	1.378±0.001 (1.761)	1.248±0.002 (1.580)	–0.07	–0.21	–0.21
523	0.338	50.46	1.774±0.001 (1.838)	1.841±0.001 (2.217)	1.665±0.002 (2.008)	–0.03	–0.16	–0.17
543	0.394	50.87	2.056±0.001 (2.104)	2.168±0.002 (2.547)	1.980±0.003 (2.319)	–0.02	–0.14	–0.14
573	0.478	51.47	2.486±0.001 (2.528)	2.679±0.002 (3.074)	2.455±0.003 (2.825)	–0.01	–0.12	–0.13
603	0.564	52.07	2.913±0.006 (2.978)	3.204±0.006 (3.635)	3.000±0.008 (3.370)	–0.02	–0.11	–0.10
623	0.623	52.47	3.247±0.009 (3.290)	3.544±0.007 (4.026)	3.345±0.011 (3.753)	–0.01	–0.11	–0.10
673	0.762	53.47	4.003±0.007 (4.100)	4.442±0.007 (5.046)	4.207±0.009 (4.769)	–0.02	–0.11	–0.11

$\Delta b = (b - b^*)$: b^* represents the value calculated from (1) with the parameters given in the legends of Figs. 1, 2, and 3.

mobilities and their mole fractions are given also in Table 4, where the mobilities at 623 K in the ternary eutectic mixture (Li,Na,K)NO_3 previously studied [3] are also given, though the molar volume is not equal.

A) Comparison of b in the Ternary System and the Corresponding Binary System

A – a) b_{Li}

The b_{Li} in the present ternary system appears to be appreciably smaller than that in the binary system (Li,K)NO_3 [9], as seen from Figure 4. It may be assumed

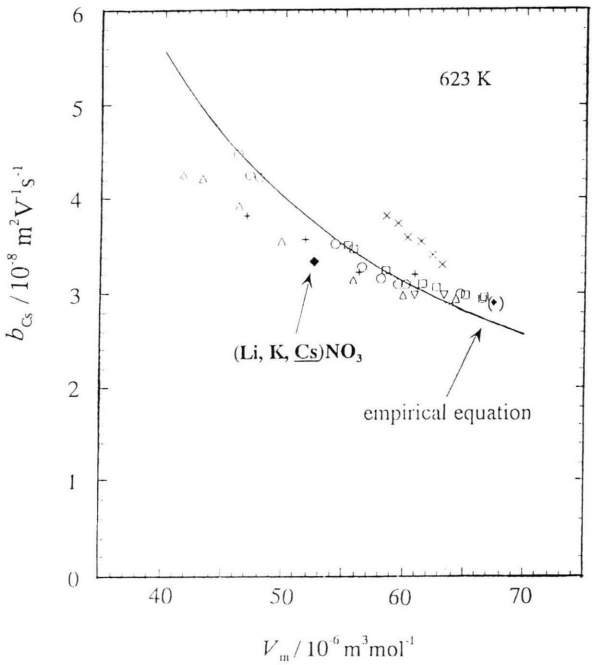

Fig. 3. Internal mobilities of Cs^+ vs. molar volume in various nitrate mixtures (Cs,M)NO_3 at 623 K: See also the legend of Figure 1. The curve is drawn for $A = 4.54\times10^{-11}$ m^5 V^{-1} s^{-1} mol^{-1}, $V_0 = 10.05+0.0068$ (T/K) and $E = 17.90$ kJ mol^{-1}. The b_{Cs} in the present system is also shown. Since the melting point of $CsNO_3$ is higher than 623 K, b_{Cs} in pure $CsNO_3$ (◆) is extrapolated with respect to temperature.

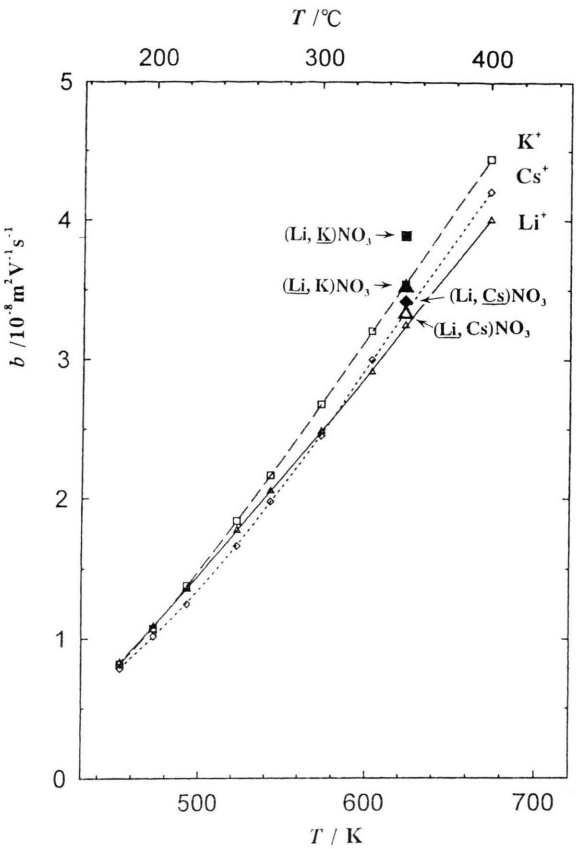

Fig. 4. Temperature dependence of b_{Li} (——), b_K (– – –) and b_{Cs} (- - - -) in the present ternary system and the corresponding value of the underlined cation in the binary systems at 623 K. See also Table 4.

from Fig. 1 that this deviation is attributable to the extraordinarily high value of the binary system. Perhaps ε in (Li,K)NO_3 should be remeasured at the low concentration of Li. Meanwhile, b_{Li} in the ternary system is much the same as that in (Li,Cs)NO_3 [4], as seen from Figure 4.

Incidentally, b_{Li} in the ternary system (Li,Na,K)NO_3 (30.0–17.0–53.0 mol%) [3] lies on the curve of the empirical equation, as shown in Figure 1.

A – b) b_K

Figure 4 reveals that b_K in the peresent ternary system is considerably smaller than that in the binary system (Li,K)NO_3 [9] as well as that calculated from the empirical equation shown in Figure 2. This is due probably to the tranquilization effect of Li^+ on b_K in the ternary

Table 4. Internal mobilities of the present ternary system and of the related ternary and binary nitrates at 623 K (350 °C).

	Li	Na	K	Cs	$V_m/10^{-6}$ m^3 mol^{-1}	Ref.
Ternary system						
(Li,K,Cs)NO_3	3.25 (35.2%)		3.54 (39.8%)	3.35 (25.0%)	52.5	Present work
(Li,Na,K)NO_3	3.93 (30%)	4.40 (17%)	4.29 (53%)		48.6	[3]
Binary system						
(Li,K)NO_3	3.52 (13.9%)		3.89 (86.1%)		52.5	[9]
(Li,Cs)NO_3	3.33 (56.1%)			3.42 (43.9%)	52.5	[4]
(K,Cs)NO_3			3.78 (100%)	(0%)	54.5	

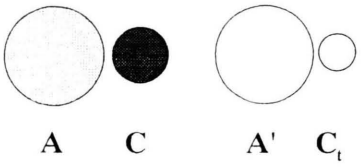

Fig. 5. Schematic representation for the dissociation motion of a cation of interest (C) from its reference anion (A). A′ is a tempter anion assisting this motion. C_t is a tranquilizer cation such as Li^+ retarding the motion of A′ directly and, in turn, the dissociating motion of C indirectly.

system; the tranquilization effect will be addressed in more detail later. As the molar ratio of the tranquilizer ion to that of interest becomes larger, the tranquilization effect will become larger. In the present system the molar ratio of the tranquilizer ion, Li^+, to K^+ is 0.88 (= 35.2 mol%/39.8 mol%), whereas in the binary system it is 0.16. This may be the main reason why b_K in the present system is considerably smaller than according to the empirical equation, while b_K in the binary system nearly lies on the empirical curve.

The b_K in the (Li,Na,K)NO_3 [3] is considerably smaller than expressed by the empirical equation (1), as seen from Figure 2. This could also be attributed to the tranquilization effect of Li^+; the molar ratio of Li to K is 0.57 there.

A – c) b_{Cs}

The b_{Cs} in the present ternary system is practically equal to that in the binary system (Li,Cs)NO_3 [4]. However, the b_{Cs}'s in both systems seem to be affected by the tranquilization of Li^+, as seen from Figure 3. The molar ratio of Li/Cs is much the same in both systems, that is 1.4 in the ternary system and 1.3 in the binary system.

Since the molar volume of (K,Cs)NO_3 is greater than that of the eutectic mixture, as given in Table 4, neither b_K nor b_{Cs} in (K,Cs)NO_3 can be included in the comparison.

B) The Tranquilization Effect

The tranquilization effect of Li^+ could be understood as follows. According to our dynamic dissociation model [10], the internal cation mobility is related to a separating motion, that is dissociation, of a cation (C) from its reference anion (A), as schematically shown in Figure 5. In the 1st movement of the dissociation a tempter anion (A′) comes closer to C. In the 2nd movement the potential barrier becomes low enough for C to move away from A toward A′. In the 3rd movement C moves away from A together with A′, and thus the dissociation of C from A is completed. If a tranquilizer ion C_t, which more strongly interacts with A′ than C does with A′, is present, the motion of A′ in the 1st and 3rd movement, and of C in the 2nd movement will be retarded. For simplicity, these ions A, C, A′ and C_t are collinearly arranged in Fig. 5, and A is assumed to stand still, as only the relative motions of these ions are concerned here.

Since the interaction of Cs^+ with the counter anion is much weaker than those of Li^+ and Ag^+, the tranquilization effect of Li^+ and Ag^+ is explicit in Figure 3. The tranquilization effect of Ag^+ has previously been discussed [11].

Incidentally, the "self-agitation effect" of Cs^+ on b_{Cs} at its high concentration can be detected from Fig. 3; the self-agitation effect has been described in detail elsewhere [12].

From the present results as well as from the previous ones shown in Figs. 2 and 3, it is ascertained that Li^+ plays the role of a tranquilizer ion for the internal mobilities of coions such as K^+ and Cs^+.

C) Order of the 3 Internal Mobilities in the Present Ternary System

Table 3 and Fig. 4 show that the order of the cation mobilities in the present system depends on the temperature and in the investigated range:

$$b_{Cs} < b_K < b_{Li} \qquad 453\text{–ca. } 473 \text{ K}, \tag{6a}$$

$$b_{Cs} < b_{Li} < b_K \qquad \text{ca. } 473\text{–ca. } 583 \text{ K}, \tag{6b}$$

$$b_{Li} < b_{Cs} < b_K \qquad \text{ca. } 583\text{–}673 \text{ K}. \tag{6c}$$

The temperature coefficients are of the order:

$$Li^+ \ll K^+ < Cs^+ \tag{7}$$

This could be accounted for in terms of the potential profile felt by a cation (C in Fig. 5) located between two anions (A and A′), as exemplified in Fig. 5 in [13]. If the kinetic energy were not taken into account, the increase in temperature, that is an increased distance between A and A′, would be unfavorable for the dissociation on the reversed order of (7).

This supposition as well as Fig. 4 suggests that, if the decomposition point were high enough, the order of b_K and b_{Cs} might be reversed at a higher temperature. However, as the tranquilization effect of Li^+ works more effectively on b_{Cs} than on b_K particularly at higher temperature, it is not clear whether b_K and b_{Cs} would be reversed

at a hypothetical high temperature. The tranquilization effect is generally expected to become more effective with increasing temperature, partly because the association of C_t to A′ becomes stronger, and mainly because the distance between A and A′ and hence between C and A′ becomes longer.

Conclusion

In the additive ternary system (Li,K,Cs)NO_3 of the eutectic composition (35.2–39.8–25.0 mol%), the electric conductivity was measured by a direct current method and the ε value by the Klemm method in the range of 453 to 673 K. From these the internal cation mobilities of the 3 cations were calculated.

The b_{Li} seems to be well expressed by (1) with the parameters which have previously been obtained from binary alkali nitrates, whereas b_K and b_{Cs} in the present system are appreciably smaller than those calculated from the empirical equation, which could be attributed to the tranquilization effect of Li^+.

The order of the cation mobilities is temperature-dependent, that is,

$b_{Cs}<b_K<b_{Li}$ 453 (lowest invest. temp.)–ca. 473 K ,

$b_{Cs}<b_{Li}<b_K$ ca. 473–ca. 583 K ,

$b_{Li}<b_{Cs}<b_K$ ca. 583–673 K (highest invest. temp.).

The order is expected from the trends found in the binary alkali nitrates and therefore can be interpreted in terms of the dynamic dissociation model.

Thus, the internal mobilities in the present system can be interpreted quite similarly to those in the binary nitrates.

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