Internal Mobilities in Molten Systems $(Na\text{-}K)NO_3$ and $(K\text{-}Cs)NO_3$

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

Internal mobility ratios in melts of the binary systems $(Na\text{-}K)NO_3$ and $(K\text{-}Cs)NO_3$ have been measured with the Klemm method in a wide range of concentration and temperature. From these and the available data on densities and conductivities, the internal mobilities have been calculated. In both systems the Chemla effect has been observed at relatively high temperature. The internal mobilities of Na^+ and K^+ seem to be well expressed by $b = [A/(V - V_0)] \exp(-E/RT)$ (V: molar volume; V_0, A and E are parameters) in the respective systems $(Na\text{-}M)NO_3$ (M = K, Rb and Cs) and $(K\text{-}M)NO_3$ (M = Rb and Cs). The internal mobilities in the binary alkali nitrate melts can be qualitatively rationalised in terms of the attraction effect, the free space effect and the agitation effect.

Introduction

In previous studies we have measured the ratios of the internal mobilities of two cations in binary alkali nitrate melts with a countercurrent electromigration method, the Klemm method [1]. The binary alkali nitrate systems whose internal mobility ratios have so far been studied with this method are listed in Table 1.

Besides in these systems, we have also studied the internal mobilities in $(Li\text{-}Tl)NO_3$ [8], $(Rb\text{-}Tl)NO_3$ [8] and $(Li\text{-}NH_4)NO_3$ [9]. In all these systems except $(K\text{-}Rb)NO_3$ [3] and $(Rb\text{-}Tl)NO_3$ [8], the Chemla effect [10, 11] has been observed for the isotherms of the internal mobilities, that is, the reversal of the relative velocities of the two cations in certain ranges of concentration and temperature.

In the present study two systems $(Na\text{-}K)NO_3$ and $(K\text{-}Cs)NO_3$ were chosen, which will be referred to as (I) and (II), respectively.

In (I), the ratio of the internal mobilities had already been measured at one concentration and temperature with the Klemm method [2], while that of the external mobilities had been measured with the Hittorf method [12] and the glass-fibre-paper method [13]. There is a large discrepancy between these data. Thus, it is one aim of the present study to remeasure the ratios in a wide range of concentration and temperature with the Klemm method. It has been undertaken also in the hope that it will validate the empirical formula which had been obtained for the internal mobility of Na^+ ions, b_{NA}, in the systems $(Na\text{-}M)NO_3$ (M = Rb [6] and Cs [5]):

$$b_{Na} = \frac{A}{(V - V_0)} \exp\left(-\frac{E}{RT}\right), \tag{1}$$

where V is the molar volume of the mixtures, R the gas constant, T the temperature, and A, E and V_0 parameters, independent of M.

As regards (II), it is particularly interesting to learn whether the Chemla effect occurs in this system, as it had not been found in binary systems consisting of K^+ and another cation larger than K^+.

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_2 M_1	Na	K	Rb	Cs
Li	[5]	[7]	[4]	[4]
Na	–	[2][a], this work	[6]	[5]
K	–	–	[3]	this work
Rb	–	–	–	–

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

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Experimental

$NaNO_3$ and KNO_3 of reagent grade were used. The $CsNO_3$ was provided by Soekawa Chemicals Ltd. in Tokyo with a purity more than 99%. Possible moisture was removed with the procedure described previously [4, 5].

The electromigration cell and the experimental procedure were similar to those used in previous studies [4–6].

In (I) at a concentration of $p_K = 1$ (p_K: mol fraction of KNO_3), radioactive ^{24}Na whose half life is ca. 15.0 h was employed, which was produced by irradiating ca. 20 mg $NaNO_3$ with thermal neutrons at a Triga II type nuclear reactor at Atomic Energy Research Laboratory, Musashi Institute of Technology. The irradiated $NaNO_3$ was poured into a ca. 30 g KNO_3 melt contained in a small quartz vessel; the concentration of the Na^+ ions in this melt was virtually negligible. The way by which the separation tube was filled with the KNO_3 melt containing ^{24}Na was similar to that used in other runs in the present study, previously described in [14]. After electromigration, the radioactivity in each fraction (about 1 cm long) of the separation tube was counted with a well type NaI(Tl) scintillation counter for more than 30 h; then, the radioactivity at a fixed time was calculated by extrapolation of the decay curve.

Table 2. Results for the system $(Na\text{-}K)NO_3$. Q is the transported charge.

Run	T/K	p_K	Q/C	ε_{12}
1	633	1.0	3971	0.009 ± 0.001
2	655		5172	0.005 ± 0.001
3	675		2497	− 0.001 ± 0.002
4	710		2328	− 0.004 ± 0.001
5	673	0.941 ± 0.001	2505	0.002 ± 0.001
6	704		2623	− 0.001 ± 0.001
7	710		3229	− 0.002 ± 0.001
8	628	0.929 ± 0.001	2866	0.009 ± 0.001
9	645		2703	0.007 ± 0.001
10	661		2748	0.006 ± 0.002
11	688		2808	0.002 ± 0.001
12	697		2800	0.002 ± 0.001
13	602	0.815 ± 0.001	2107	0.013 ± 0.001
14	634		2159	0.010 ± 0.001
15	693		2048	0.004 ± 0.001
16	549	0.629 ± 0.004	2041	0.021 ± 0.001
17	568		2030	0.019 ± 0.001
18	597		1875	0.016 ± 0.001
19	683		2875	0.006 ± 0.002
20	566	0.441 ± 0.007	2997	0.018 ± 0.001
21	582		1965	0.017 ± 0.001
22	622		2501	0.014 ± 0.002
23	683		2511	0.007 ± 0.002
24	566	0.280 ± 0.008	2616	0.017 ± 0.001
25	598		1913	0.015 ± 0.003
26	649		2797	0.012 ± 0.002
27	693		2860	0.007 ± 0.001
28	644	0.158 ± 0.005	2954	0.010 ± 0.001
29	686		2986	0.007 ± 0.002
30	584	0.077 ± 0.001	2931	0.016 ± 0.001
31	655		2555	0.007 ± 0.001
32	680		2750	0.006 ± 0.001
33	612	0.059 ± 0.001	2802	0.012 ± 0.001
34	621		2612	0.010 ± 0.001
35	647		2733	0.008 ± 0.001
36	673		2803	0.006 ± 0.001

Results

The relative differences in internal mobilities of two cations 1 and 2, ε_{12}, can be calculated from the equation given previously [8]. In the case of virtually pure KNO_3 containing ^{24}Na as a tracer, ε_{12} is calculated by [8]:

$$\varepsilon_{12} = \frac{F}{Q} \Sigma \left(\frac{S_i}{S_0} - 1 \right) n_i , \qquad (2)$$

Table 3. Results for the system $(K\text{-}Cs)NO_3$. Q is the transported charge.

Run	T/K	p_{Cs}	Q/C	ε_{12}
101	642	0.977 ± 0.001	2965	− 0.003 ± 0.002
102	694		2046	− 0.005 ± 0.003
103	719		2658	− 0.007 ± 0.002
104	676	0.926 ± 0.001	2879	− 0.001 ± 0.001
105	689		1998	− 0.002 ± 0.003
106	703		2252	− 0.003 ± 0.001
107	635	0.793 ± 0.002	2452	0.007 ± 0.001
108	661		3332	0.005 ± 0.001
109	696		2469	0.000 ± 0.001
110	601	0.611 ± 0.001	2026	0.013 ± 0.001
111	627		2091	0.010 ± 0.002
112	653		2654	0.010 ± 0.001
113	702		2839	0.008 ± 0.001
114	585	0.527 ± 0.001	2000	0.018 ± 0.002
115	626		2635	0.015 ± 0.001
116	680		2302	0.010 ± 0.001
117	633	0.300 ± 0.001	2727	0.018 ± 0.002
118	687		2346	0.014 ± 0.001
119	705		2230	0.013 ± 0.001
120	592	0.103 ± 0.002	2258	0.024 ± 0.001
121	660		2560	0.020 ± 0.001
122	696		3038	0.018 ± 0.001
123	624	0.062 ± 0.003	3225	0.024 ± 0.001
124	640		2634	0.023 ± 0.001
125	700		2553	0.020 ± 0.001

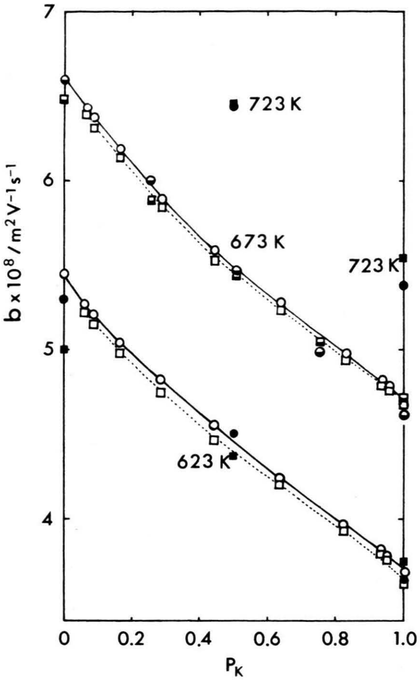

Fig. 1. Internal cation mobilities vs. mole fraction of KNO_3 in the system $(Na\text{-}K)NO_3$. ○: b_{Na}; ◒: $b_{Na}{}^a$ [12]; ●: $b_{Na}{}^a$ [13]; □: b_K; ⊟: $b_K{}^a$ [12]; ■: $b_K{}^a$ [13]. – (^{a} evaluated from external mobility.)

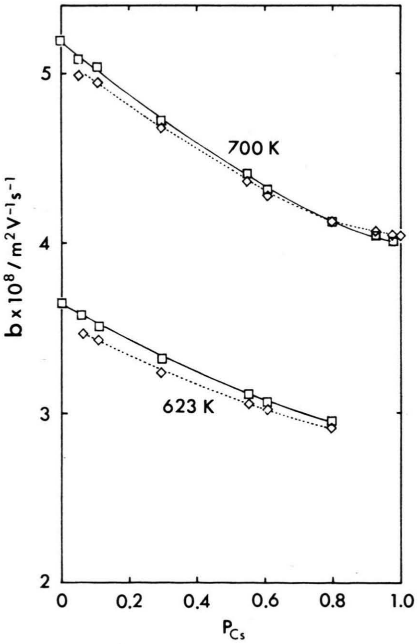

Fig. 2. Internal cation mobilities vs. mol fraction of $CsNO_3$ in the system $(K\text{-}Cs)NO_3$. □: b_K; ◇: b_{Cs}.

where n is the quantity of KNO_3, $S = c/n$ the specific radioactivity, (c: radioactivity, e.g., counts per minute), F the Faraday constant, and Q the transported charge; the suffixes i and 0 refer to the samples in the i-th fraction and before electromigration, respectively. The summation was taken from the fraction nearest to the anode up to the sample in which the specific activity was practically the same as before electromigration.

The values of ε_{12} are given together with the main experimental conditions in Table 2 for (I) and in Table 3 for (II).

The internal mobilities of the cations were calculated from the present data and the available data on the densities and conductivities [15]. The resulting mobility isotherms are shown in Fig. 1 for (I) together with the results derived from the Hittorf method [12] and the glass-fibre-paper method [13] and in Fig. 2 for (II).

Discussion

In (I), b_{Na} and b_K obtained in the present study are in satisfactory agreement with those estimated from the external mobilities obtained with the Hittorf method [12] and the glass-fibre-paper method [13]. The Chemla effect is observed also in the present study, as seen from Table 2. The cross points of the isotherms, however, appear at somewhat higher concentration of KNO_3 in the present study than in the latter two studies; for example, at 673 K the cross point is found at $p_K \simeq 1$ in the present work, whereas it is observed at $p_K \simeq 0.6$ in the Hittorf method [12].

Since the Klemm method enables one to measure accurately very small differences in the internal mobilities of two ions (e.g. isotopic differences) [1], we believe this method is preferable in the present case.

Our data are in contrast to those obtained by Lundén with the Klemm method [2], in which the value of ε_{12} is very large ($\varepsilon_{12} = 0.59$ at $p_{Na} = 0.918$ at 376 °C). The reason of this discrepancy is not clear.

In order to learn whether b_{Na} in (I) obeys Eq. (1) as found for the systems $(Na\text{-}Rb)NO_3$ [6] and $(Na\text{-}Cs)NO_3$ [5], the reciprocal of b_{Na} in these three systems are plotted at 573 K, 623 K and 673 K against the molar volume in Figure 3. The values of b_{Na} in the system $(LI\text{-}Na)NO_3$ [5] are also shown in Fig. 3 for comparison. The solid lines in Fig. 3 are

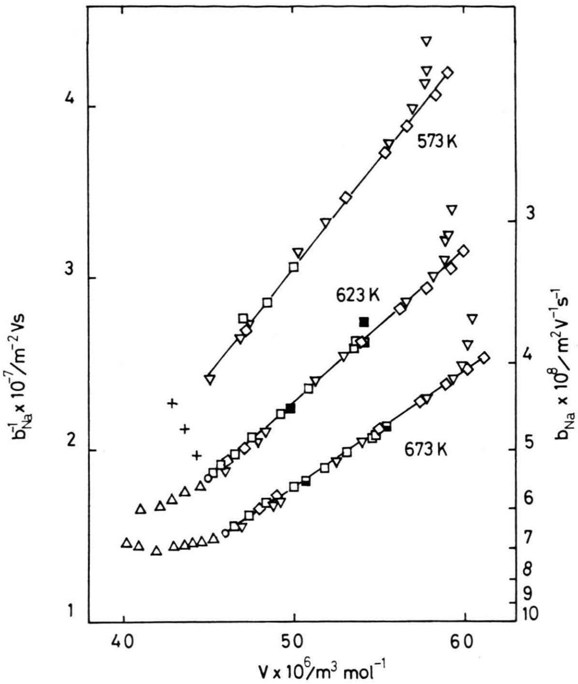

Fig. 3. The reciprocal of the internal mobilities of Na^{+} vs. molar volume in binary systems (Na-M)NO$_3$. △: M = Li [5]; ○: Na^{a}; +: Na^{a} under high pressure at 623 K [16, 17]; □: K; ⬓: K^{b} [12]; ■: K^{b} [13]; ▽: Rb [6]; ◇: Cs [5]. – (^{a} pure NaNO$_3$. ^{b} evaluated from external mobility.)

drawn according to Eq. (1) with the parameter values listed in Table 4, which were calculated previously [6]. Thus, it is ascertained that b_{Na} in the systems (Na-M)NO$_3$ (M = K, Rb and Cs) is well expressed by Eq. (1) with the same parameters for all M, except for Rb in the low concentration region of NaNO$_3$ ($p_{Na} < 0.1$) [6].

In order to learn whether similar formulas hold also for b_K and b_{Cs}, the reciprocals of b_K and b_{Cs} are plotted against V in Figs. 4 and 5, respectively. In the systems (K-Rb)NO$_3$ [3] and (K-Cs)NO$_3$, b_K seems to be expressed by Eq. (1) with the parameters given in Table 4, although there is only a limited number of data in the case of Rb. In the systems (Li-K)NO$_3$ and (Na-K)NO$_3$, b_K seems to

Table 4. Parameter values for the empirical equation $b_{M_1} = \{A/(V - V_0)\} \exp(-E/RT)$ in the alkali nitrate systems $(M_1 - M_2)$NO$_3$ ($M_1 \leqq M_2$ in size).

M_1	$A \times 10^{11}$ / m^5 V^{-1} s^{-1} mol^{-1}	E / kJ mol^{-1}	$V_0 \times 10^6$ / m^3 mol^{-1}	Ref.
Li	2.84	17.80	24.7	[5]
Na	4.94	19.71	25.8 (573 K) 25.0 (623 K) 24.2 (673 K)	[6]
K	4.21	16.74	10.5	This work

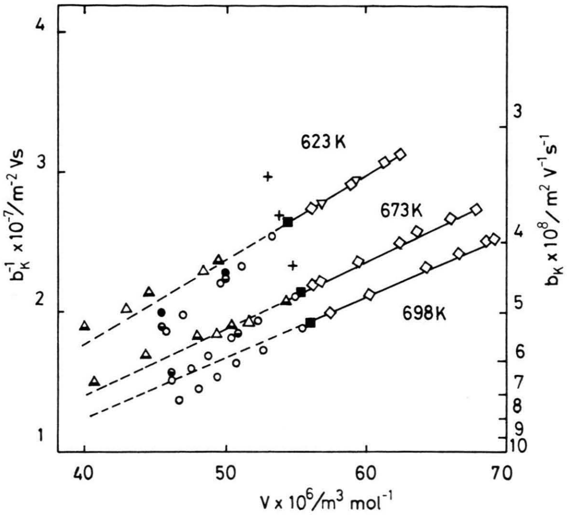

Fig. 4. The reciprocal of the internal mobilities of K^{+} vs. molar volume in binary systems (K-M)NO$_3$. △: M = Li [7]; △: Li^{a} [18]; ○: Na; ◒: Na^{a} [12]; ●: Na^{a} [13]; ■: K^{b}; +: K^{b} under high pressure at 673 K [16, 17]; ▽: Rb [3]; ◇: Cs. – (^{a} evaluated from external mobility. ^{b} pure KNO$_3$.)

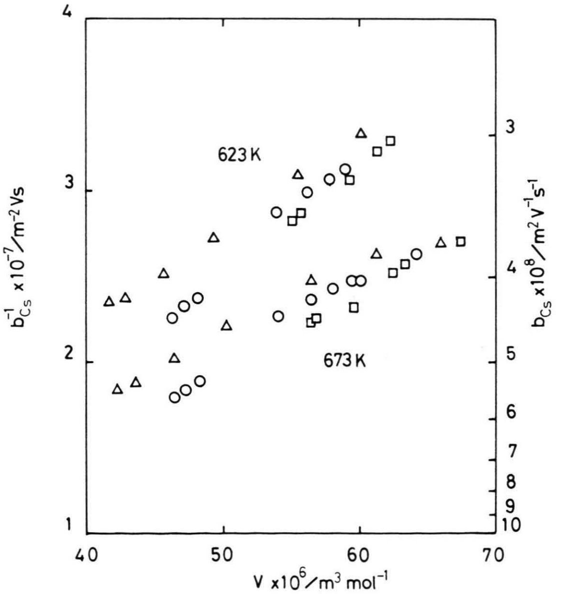

Fig. 5. The reciprocal of the internal mobilities of Cs^{+} vs. molar volume in binary systems (Cs-M)NO$_3$. △: M = Li [4]; ○: Na [6]; □: K.

deviate slightly from Eq. (1), while b_{Cs} could not be expressed by Eq. (1), as can be seen from Figure 5.

Previously we have assumed that the internal mobility is strongly related to the separating motion of neighbouring unlike ions [8], and have shown further that apparently anomalous phenomena concerning electric transport of ionic melts (such as the Chemla effect and the conductivity maximum against temperature) can be well explained qualitatively on the basis of this assumption. Taking the alkali nitrates as examples, we will show that the following three factors mainly rule the separating motion of unlike ions: (i) the attraction effect, (ii) the free space effect and (iii) the agitation effect.

The pair potential wells between M^+ and NO_3^- are very deep compared with the kinetic energy and therefore an ion pair M-NO_3 cannot be separated unless other ions are present near it. When another NO_3^- (*S* in Fig. 6) is present, the M^+ can be moved away from the referenced NO_3^- (*R* in Figure 6). The separating motion of M^+ is assumed to be strongly related to the probability of finding another NO_3^- toward which the M^+ is to move. This probability may be related also to the coordination number of M^+. As the ionic "size" of M^+ becomes larger, the variation in this probability combined with the variation in the distance between the two NO_3^- (*R* and *S*) will become less sensitive, as schematically shown in Figure 6. The average distance between two neighbouring NO_3^- should be a function of the number density of NO_3^- and hence of the molar volume of the nitrate melts. Therefore, as the size of M^+ becomes larger, the separating motion of the M^+ and hence b_M will be less sensitive to the variation in molar volume. This might be the main reason for the Chemla effect.

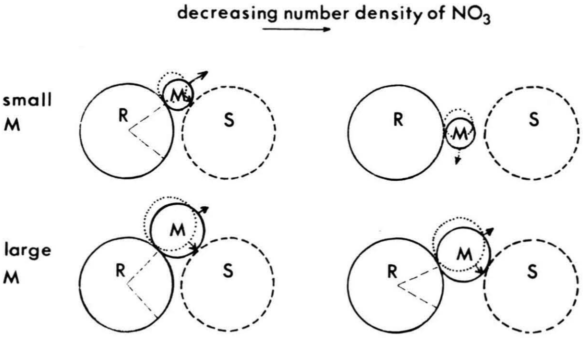

Fig. 6. Schematic representation of the motion of a small and a large ion (M) from the referenced NO_3^- (R) toward another NO_3^- (S) at high and low number densities of the NO_3^-. For simplicity, NO_3^- is roughly approximated to be of spherical shape.

In brief, a cation is attracted by a neighbouring anion and then moves away from its referenced anion. We will name it the *attraction effect* that causes the separating motion on the basis of the above mentioned mechanism. If the cation moves from one anion to another with the mechanism based only on the attraction effect, the velocity of the separating motion may be determined by the pair potential between unlike ions, the size and mass of the cation and the number density of the anion, and should not be explicitly related to the kind of coexisting cations. Equation (1) satisfies these requirements for the separating motion. Therefore, (1) could be considered to express mainly the attraction effect.

The *free space effect* should be also taken into account only when the volume of the free space is small relative to the size of M^+. Namely, this effect plays an important role for larger cations such as Rb^+ and Cs^+ particularly at lower temperature. The free space is defined here as the total volume minus the volume occupied by ion "cores". It is clear that, if the volume of the free space is small enough, M^+ cannot be moved away from its referenced anion to another. The free space effect can be explicitly evidenced also by the decrease of b in pure salts with increasing pressure, as can be seen from Figures 3, 4. It should be mentioned that the free space effect and the attraction effect act on the separating motion in opposite directions with respect to the volume variation of free space.

The *agitation effect* can be considered to arise from the motion of a small and light ion. It can easily change the position and the shape of the free space, which will promote the separating motion of other pairs of unlike ions, as schematically shown in Figure 7. Even if a large cation M^+ is going to move away from R along the "surface" of S, it has a high probability of coming back to R, if the speed of the separating motion of the two anions (R and S) is comparatively slow and if the free space necessary of this large ion is hard to be created along the surface of S. When small and light ions coexist, however, these will give rise to the agitation effect; namely, (i) the separating motion of R and S will be increased and (ii) the free space around S toward which the M^+ can move is to be more readily

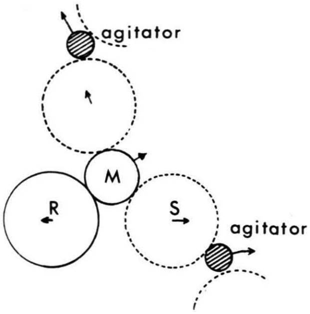

Fig. 7. Schematic representation of the agitation effect by small and light ions (agitators) on the separating motion of M^+ from the referenced NO_3^- (R).

created. These will, in turn, promote the separating motion of M^+ from R.

On the other hand, if M^+ is small in size and hence light in the present case, the M^+ will have a relatively low probability of going back to R, because the thermal motion of the M^+ is great and the free space is large enough for the M^+ to move away from R. Thus, the agitation effect for coexisting ions is expected to be less effective for internal mobilities of the smaller cations.

The existence of the agitation effect has been recognised, e.g., by molecular dynamics simulations of molten LiCl. The separating motion of given pairs of Li-Cl becomes greater when the fictive mass of other coexisting Li^+ ions becomes lighter [19].

The fact that in binary ionic melts the mobilities of the two ions are generally in the same order of magnitude even if the ionic sizes of the two ions are considerably different could be due to the agitation effect, and this is in contrast with the observation in solids where cooperative effects such as the agitation effect cannot be expected.

The attraction effect works in all cases, while the free space effect and the agitation effect effectively function only if some conditions are fulfilled.

As stated above, in the system $(Li\text{-}K)NO_3$, b_K is somewhat smaller than expressed by the empirical formula valid in the systems $(K\text{-}Rb)NO_3$ and $(K\text{-}Cs)NO_3$, whereas the opposite is true for $(Na\text{-}K)NO_3$. This is presumably because the free space effect overcompensates the agitation effect in the system $(Li\text{-}K)NO_3$ and vice versa in the system $(Na\text{-}K)NO_3$.

In the binary alkali nitrate systems $(M\text{-}Cs)NO_3$, the M^+ is smaller than Cs^+ in size and therefore, both the free space effect and the agitation effect are expected to function for b_{Cs}. Therefore, it is reasonable that b_{Cs} cannot be expressed by a unified simple function of V. b_{Cs} increases with M at a given molar volume in the order, Li, Na, K. This is presumably true because the number of M^+ which act as "agitators" is greater in this order in spite of the reversed order for the agitation effect. e.g., $p_{Li} = 0.24$, $p_{Na} = 0.30$ and $p_K = 0.52$ at $V = 60 \times 10^{-6}\ m^3\ mol^{-1}$ at 600 K. It is inferred from the above stated findings in $(Li\text{-}K)NO_3$ that also in the system $(Li\text{-}Cs)NO_3$ the free space effect would overcompensate the agitation effect.

To summarise, the electric transport in most binary alkali nitrate melts can be well interpreted in terms of the attraction effect, the free space effect and the agitation effect. In the alkali nitrate melts $(M_1 - M_2)NO_3$ ($M_1 < M_2$ in size), the internal mobilities of M_1^+ can be, in general, expressed by Eq. (1) with parameter values depending only on M_1^+ and irrespective of the kind and concentration of M_2; this equation can be attributed mainly to the attraction effect. On the other hand, for the mobilities of M_2^+, Eq. (1) should be modified. When the free space effect predominates, b_{M_2} becomes smaller than expressed by (1). Meanwhile, when the agitation effect is greater than the free space effect, b_{M_2} becomes larger than expected by this equation.

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