Internal Cation Mobilities in the Molten Systems $LiNO_3$-$TlNO_3$ and $RbNO_3$-$TlNO_3$

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The relative differences in internal cation mobilities are measured for the molten systems $LiNO_3$-$TlNO_3$ and $RbNO_3$-$TlNO_3$ over a wide range of temperature and concentration by means of countercurrent electromigration technique (Klemm's method), and the internal mobilities are calculated from the existing data on the electric conductivity for these systems. For the system $LiNO_3$-$TlNO_3$, a marked dependence of the relative internal mobility differences on temperature is found particularly in the Li^+ rich region, and a considerable concentration dependence is found over the investigated temperature range. This is qualitatively explained in terms of a model which takes into account mainly the differences of the cation-anion pair potentials and of the sizes of the two cations. On the other hand, for the system $RbNO_3$-$TlNO_3$, only a slight temperature dependence is observed and no concentration dependence, if present, is detected within the experimental accuracy.

Introduction

Since the rather surprising finding by Chemla and coworkers [1, 2] that under certain conditions K^+ is more mobile than Li^+ in the molten mixture LiBr-KBr, the study on the mobilities of binary molten systems with monovalent cations and a common anion has attracted much attention, and for systems of chlorides [3], bromides [4, 5], nitrates [6] and sulphates [7, 8], mobilities, mobility differences or transport numbers have been investigated systematically by means of zone electrophoresis, countercurrent electromigration, Hittorf's method and EMF measurement [9]. The investigation of cation mobilities in binary mixtures offers useful information on what factors affect the electromigration process since the mobilities of two different cations can be studied at the same time under various conditions.

In the present work the dependence of relative differences in the internal cation mobilities on temperature and concentration is studied for the systems $LiNO_3$-$TlNO_3$ and $RbNO_3$-$TlNO_3$, the differences of the cation radii being large in the former and very small in the latter (Li^+: 0.60 Å, Rb^+: 1.48 Å, Tl^+: 1.40 Å [10]). The countercurrent electromigration method (Klemm's method) is adopted here, with which even very small relative mobility differences of two cations can be accurately measured, although the informations on the external mobilities cannot be obtained. By using the salts only in a small-volume separation tube, the countercurrent method is readily applicable to such expensive salts as $RbNO_3$ and $TlNO_3$.

Experimental

The arrangement of the electromigration cell was similar to that previously employed for isotope effect measurements [11]. A separation tube of Vycor (int. diam.: 4 mm) packed with quartz powder of 80–100 mesh was inserted into a small vessel containing a molten mixture of $LiNO_3$-$TlNO_3$ or $RbNO_3$-$TlNO_3$. The chemicals were of special reagent grade and fully dried before use without further purification. When the salts permeated the diaphragm by capillary action, the separation tube was transferred to a large vessel containing a eutectic mixture of $NaNO_3$-KNO_3 or $LiNO_3$-KNO_3 which was to serve as a cathode compartment, and immediately electrolysis was started. After several hours' electromigration, the separation tube was taken out of the large vessel, cooled and cut into several fractions for chemical analysis. An aliquot of each fraction was subjected to the determination of the cations by flame spectrophotometry. On the other hand, the total amount of cations in each fraction was checked by eluting another aliquot through a column of H^+-type ion exchanger and titrating the eluted solution with a standard NaOH solution.

The lowest limit for the electromigration temperature was chosen in the light of the phase diagrams of the system [12, 13].

Radioactive tracer ^{204}Tl ($T_{1/2} = 4.1$ y) was purchased from New England Nuclear Corp. in U.S.A. and measured with a GM counter.

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Results

The salts in the large cathode compartment diffused into the separation tube during electromigration. If the duration of electromigration t, was adjusted, however, so that

$$t < l^2/\{\pi(\sqrt{D_{s\,eff}}+\sqrt{D_{c\,eff}})^2\}$$ [14, 15],

there existed an extended part around the middle of the separation tube where the initial chemical composition remained unchanged. Here, l is the length of the diaphragm part, and $D_{s\,eff}$ and $D_{c\,eff}$ the effective diffusion coefficients of the investigated salts and of the salts in the cathode compartment into the diaphragm part, respectively. In this case the relative difference in internal mobilities of two cations 1 and 2 can be calculated by [7, 15]:

$$\varepsilon_{12} \equiv (b_1-b_2)/b = (F/Q)\left(\sum_i n_{2i}/p_2 - \sum_i n_{1i}/p_1\right), \quad (1)$$

where Q is the transported charge in Coulomb, F the Faraday constant, n_{1i} and n_{2i} the equivalent quantities of cation 1 and 2 in the i-the fraction, respectively, and p_1 and p_2 the initial equivalent fractions of the corresponding cations. The summation is made from the fraction nearest to the anode to the fraction where the initial composition remains unchanged. When cation 2, that is Tl^+ in the present case, is of tracer scale, Eq. (1) is modified as:

$$\varepsilon_{12} = F/Q\left((n_2^0/c_2^0)\sum_i c_{2i} - \sum_i n_{1i}\right) \quad (2)$$

where c_{2i} is the radioactivity in cpm of cation 2 in the i-th fraction, and (c_2^0/n_2^0) the specific activity of cation 2 in cpm/eq of the initial sample.

Experimental conditions and the results are tabulated in Tables 1 and 2.

The relative internal mobility differences are plotted against temperature in Figs. 1 and 2.

From the present data and the existing data on the electric conductivities for the systems $LiNO_3$-$TlNO_3$ [16, 17] and $RbNO_3$-$TlNO_3$ [16–18], the internal mobilities of these cations are calculated according to Eqs. (3) and (4).

$$b_1 = (\Lambda/F)[1+\varepsilon_{12}(1-p_1)], \quad (3)$$

$$b_2 = (\Lambda/F)[1-\varepsilon_{12}(1-p_2)] \quad (4)$$

where Λ is the equivalent conductivity of the mixture.

The isotherms of internal mobilities for the systems $LiNO_3$-$TlNO_3$ and $RbNO_3$-$TlNO_3$ are shown in Figs. 3 and 4, respectively.

Table 1. Conditions and the results of electromigration in the system $LiNO_3$-$TlNO_3$.

Exp. No.	Temp. (°C)	Mole fraction of $TlNO_3$ (%)	Electromign. duration (hr)	Transported charge (C)	$(b_{Li}-b_{Tl})/b$
1	288	0	6.5	2211	0.821±0.009
2	370	0	5.0	1545	0.413±0.003
3	375	0	6.4	2054	0.351±0.011
4	397	0	5.9	1999	0.300±0.009
5	415	0	5.9	2054	0.330±0.002
6	440	0	6.8	2144	0.390±0.002
7	443	0	6.1	1929	0.473±0.006
8	467	0	5.3	1849	0.650±0.003
9	284	3.87±0.01	4.5	1560	0.226±0.020
10	285	3.87±0.01	5.2	1702	0.236±0.017
11	312	3.87±0.01	5.0	1622	0.214±0.019
12	367	3.87±0.01	4.6	1403	0.153±0.018
13	396	3.87±0.01	4.3	1347	0.192±0.023
14	416	3.87±0.01	4.5	1527	0.178±0.020
15	224	25.6±0.1	6.9	2229	0.398±0.003
16	256	25.6±0.1	7.2	2376	0.118±0.002
17	308	25.6±0.1	7.1	2417	0.051±0.002
18	350	25.6±0.1	8.7	3041	0.026±0.001
19	400	25.6±0.1	7.2	2658	0.036±0.002
20	245	50.9±0.1	7.0	2410	0.011±0.001
21	270	50.9±0.1	7.1	2430	−0.011±0.001
22	310	50.9±0.1	6.8	2299	−0.032±0.002
23	328	50.9±0.1	7.0	2293	−0.026±0.002
24	225	68.0±0.2	6.0	1679	−0.001±0.001
25	274	68.0±0.2	5.2	1654	−0.003±0.001
26	327	73.8±0.1	6.8	2370	−0.044±0.001
27	377	73.8±0.1	7.0	2239	−0.064±0.001
28	380	83.6±0.1	6.8	2290	−0.084±0.001
29	388	83.6±0.1	6.6	2254	−0.095±0.002
30	230	88.8±0.4	5.8	1921	−0.076±0.006
31	275	88.8±0.4	6.5	2236	−0.071±0.005
32	305	88.8±0.4	6.5	2169	−0.064±0.006
33	334	88.8±0.4	5.2	1733	−0.087±0.008
34	340	88.8±0.4	6.5	2130	−0.082±0.006
35	372	88.8±0.4	5.8	1947	−0.080±0.007

The temperature was controlled within ±3 °C in most of experiments. The sign ± in the column $\Delta b/b$ represents the standard deviation resulting from the errors of chemical analysis and radioactivity counting. The mole fraction 0 of $TlNO_3$ means that radioactive tracer (^{204}Tl) is used.

Discussion

It is known that trivalent Tl ions are unstable in molten nitrates and, if present, are converted into the monovalent state. The fact that radioactive Tl does not show any irregular behaviour in the system $RbNO_3$-$TlNO_3$ ($RbNO_3$: 100%), as seen from Figs. 2 and 4, excludes the possibility that, because of its extremely low concentration, radioactive Tl behaves irregularly. The quite negligible radioactivity in the washed diaphragm powder after

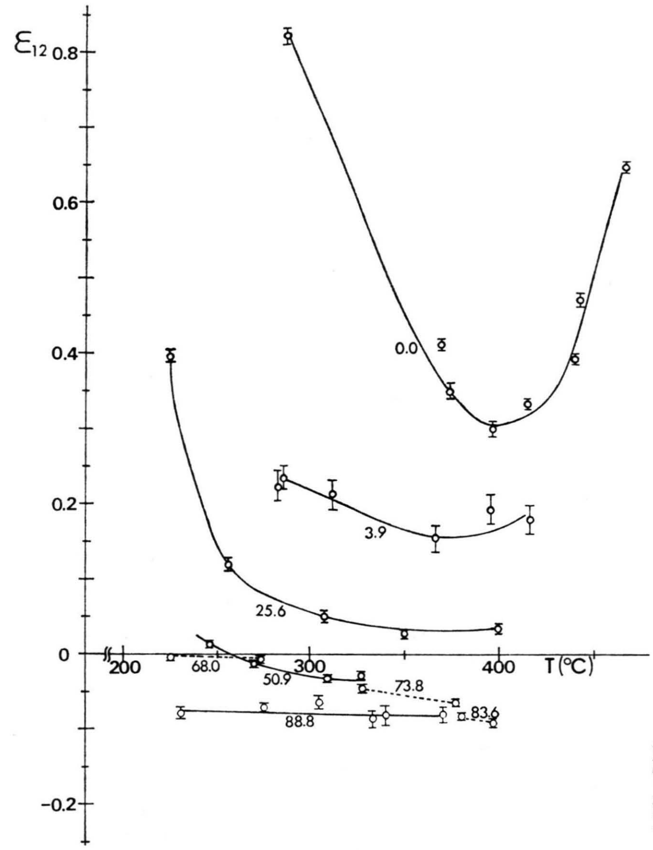

Fig. 1. Relative difference in internal cation mobilities $(b_{Li}-b_{Tl})/b$ against temperature in the system $LiNO_3$-$TlNO_3$. The numbers in the figure represent the mole fraction of $TlNO_3$ in %.

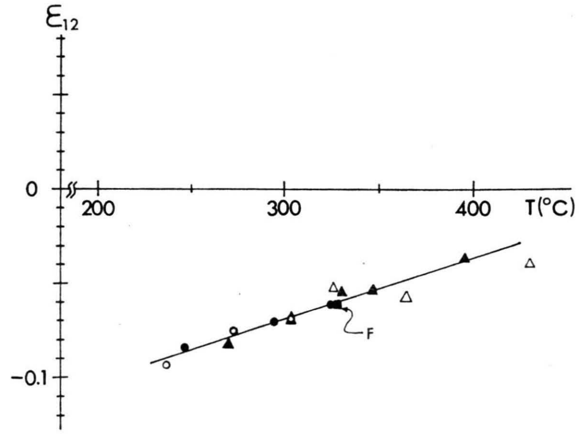

Fig. 2. Relative difference in internal cation mobilities $(b_{Rb}-b_{Tl})/b$ against temperature in the system $RbNO_3$-$TlNO_3$ ($TlNO_3$ mole fraction: △ 0%, ▲ 27.6%, ○ 50.1% and ● 74.4%). The data by Forcheri et al.[23] are also plotted for comparison (F in the figure).

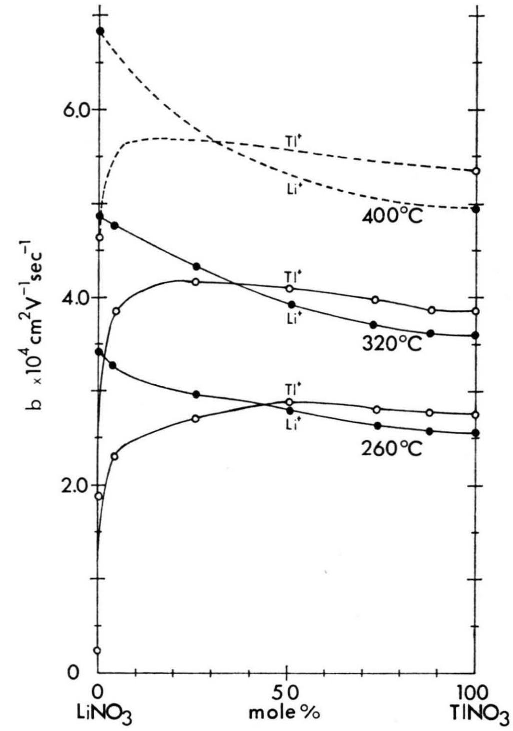

Fig. 3. Isotherms of internal mobilities in the system $LiNO_3$-$TlNO_3$. The data on the equivalent conductivities of $LiNO_3$ are taken from Ref.[31] and of $TlNO_3$ from Reference[32]. Most of the values at 400 °C are estimated from the extrapolated conductivity data.

Table 2. Conditions and the results of electromigration in the system $RbNO_3$-$TlNO_3$.

Exp. No.	Temp. (°C)	Mole fraction of $TlNO_3$ (%)	Electromign. duration (hr)	Transported charge (C)	$(b_{Li}-b_{Tl})/b$
101	325	0	7.1	2353	−0.054±0.001
102	363	0	7.7	2553	−0.058±0.001
103	430	0	6.0	1981	−0.040±0.001
104	269	27.6±0.4	7.0	2209	−0.082±0.001
105	303	27.6±0.4	7.0	2247	−0.070±0.001
106	330	27.6±0.4	7.0	2275	−0.055±0.001
107	347	27.6±0.4	7.0	2376	−0.055±0.001
108	395	27.6±0.4	7.1	2112	−0.037±0.001
109	236	50.1±0.1	8.0	1012	−0.092±0.002
110	272	50.1±0.1	9.5	2960	−0.075±0.001
111	303	50.1±0.1	10.3	3683	−0.070±0.001
112	247	74.4±0.2	6.0	1618	−0.085±0.002
113	294	74.4±0.2	7.0	2430	−0.070±0.001
114	324	74.4±0.2	7.2	1784	−0.062±0.002

See the footnote to Table 1.

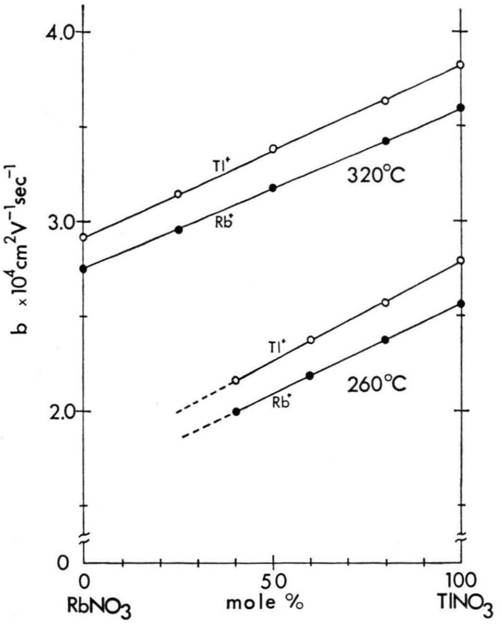

Fig. 4. Isotherms of internal mobilities in the system $RbNO_3$-$TlNO_3$. The data on the equivalent conductivity of pure $RbNO_3$ are taken from Reference [31].

electromigration also denies the possibility that Tl of tracer concentrations might be absorbed in the quartz diaphragm. A change of the distribution of salts in a separation tube during solidification was not observed for samples without electromigration in some preliminary experiments for the system $LiNO_3$-$TlNO_3$ (twice for 0% $TlNO_3$ and twice for 89% $TlNO_3$).

It is indicated by molecular dynamics simulations of some alkali halides following the method of Woodcock[19] that the electric conductivity is correlated with a separating motion of the nearest neighbouring cations and anions[20]. Since the pair potential between the cations and anions is not known for molten nitrates, it is assumed in this discussion to be similar to that in the corresponding solid halides, and the following deductions are drawn in view of the findings obtained with molecular dynamics studies of molten LiCl[19, 21] and TlCl[20].

The character of the Li^+ motion might be somewhat different at low and high temperatures, while that of the Tl^+ motion might not depend appreciably on temperature. At low temperatures, the pair distribution between Li^+ and NO_3^+ would have a sharp maximum around the position where the pair potential has its deep minimum, as speculated from the findings of molecular dynamics simulation of molten LiCl (see Figure 5). This would show that a Li^+ ion moves along the surfaces of a NO_3^- ion rather than in the Li-NO_3 direction. While moving along the surface of one NO_3^- ion, a Li^+ ion will

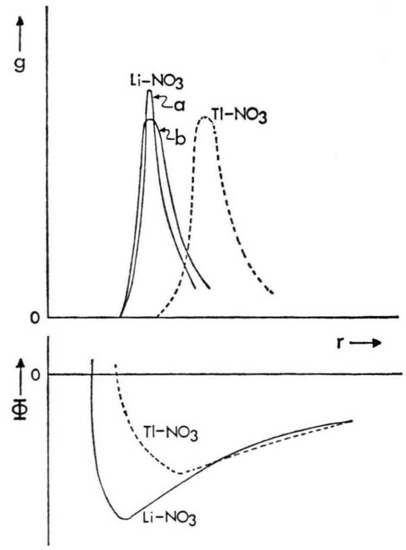

Fig. 5. Schematic representation of the pair distribution function g and of the pair potential Φ between Li^+ and NO_3^- and between Tl^+ and NO_3^-. The curves are sketched in view of the findings with molecular dynamics studies of molten LiCl[19, 21] and TlCl[20], the pair potential for the latter being taken from Reference [33]. For $LiNO_3$, a: low temp., b: high temp. For $TlNO_3$, g is much the same at low and high temperatures.

have a chance to move to the surface of a neighbouring NO_3^- ion, since the nearest neighbouring NO_3^- ions are nearly in contact with each other. The peak of the pair distribution function flattens with rising temperature. This would suggest that at high temperatures a Li^+ ion would move vigorously not only along the surface of the nearest NO_3^- ion but also in the Li-NO_3 direction. As for the Tl^+ ions, on the other hand, the valley of the pair potential curve would be shallow around the position where the pair distribution function has its maximum. A Tl^+ ion can readily withdraw from its nearest NO_3^- ion, if only there is enough electrically negative free space in the surroundings, while it may not easily circle along the surface of a NO_3^- ion because of its large size. Thus, at low temperatures, Li^+ is more mobile than Tl^+ in Li^+ rich mixtures where there is little free space large enough for Tl^+ motion. At high temperatures, it is anticipated that Li^+ will be much more mobile than Tl^+, because it is able to move along the surface of the NO_3^- ions and in the Li-NO_3 direction as well. This happens above say 400 °C at tracer concentrations of Tl^+, but it cannot be realized experimentally at high $TlNO_3$ concentrations because of thermal decomposition.

As for the isotherms, the Li^+ mobility decreases with increasing concentration of $TlNO_3$, as seen in Figure 3. This may be so partly because the motion of a Li^+ ion around a NO_3^- ion is hindered by the presence of Tl^+ ions, particularly at low temperatures, and partly because the presence of Tl^+ ions will increase the mean distance between nearest neighbouring NO_3^- ions, which is unfavourable for the transfer of the Li^+ ions from one NO_3^- ion to another. On the other hand, in the region very rich in $LiNO_3$, the Tl^+ mobility increases rapidly as the concentration of Tl^+ increase. This may be so because, as the concentration of $TlNO_3$ increases, the volume of the free space increases to a kind of critical volume large enough for a Tl^+ motion. As the concentration increases further, the isotherms slightly decrease, presumably because the volume of the negative free space, which is favourable for Tl^+ motion, decreases due to the presence of more Tl^+ ions. The maximum of the Tl^+ mobility shifts toward higher concentrations of $TlNO_3$ with decreasing temperature. This is accounted for by the assumption that at lower temperatures, the free space being smaller, more $TlNO_3$ is required for enlarging the free space enough for a Tl^+ motion.

Incidentally, the phenomenon that for small concentrations of the larger cation its mobility increases sharply with its concentration has not been found in the systems $NaNO_3$-$TlNO_3$ [22, 23], $NaNO_3$-$RbNO_3$ [24], and $NaNO_3$-$CsNO_3$ [25], probably because, the two cations being more equal in size than in the present system $LiNO_3$-$TlNO_3$, free space for the motion of the larger cation is more readily available.

The anticipation [26] that the diffusion coefficient of Li^+ would always be greater than that of Tl^+ in the mixture is not contradictory to the model presented above. The motion of a Li-NO_3 pair would not contribute to the electrical mobility but to the diffusion coefficient.

Concerning the system $RbNO_3$-$TlNO_3$, a concentration dependence of the relative mobility difference is not detected within the experimental accuracy, as seen in Figure 2. Consequently, the mobilities of both Rb^+ and Tl^+ increase linearly with the concentration of Tl^+ as shown in Figure 4.

A slight but obvious temperature dependence of the relative mobility difference is, however, observed as seen in Figure 2.

For this system, Forcheri and coworkers have previously measured the internal mobilities at 325 °C with mole fractions of $TlNO_3$ of ca 0.25, 0.5 and 0.75 by means of zone electrophoresis [23]. The relative differences in the internal mobilities estimated from the figure they have drawn agree well with the present data (see Figure 2). They have not paid attention, however, to the temperature dependence of this quantity, and thus their presumption that the (internal) "mobilities differ by not more than 6% for this system" would be too hasty.

In this system, the ionic radii of the two cations are much the same, while the masses are very different. The similar magnitude of the mobilities of the two cations would suggest that the mass would play a minor role compared with the size of the ions. An alternative possibility is that the big difference of the masses would be compensated exactly by the difference of the pair potentials. The former suggestion would be supported by the following facts. Similar mobilities of two cations have also been found for the system $NaNO_3$-$AgNO_3$ [27] in which the radii of the two cations are much the same. In the present experiments, as the free space is enlarged with rising temperature, the relative mobility differences become smaller. Unfortunately it is impossible on account of the thermal decomposition to see whether the mobilities of Tl^+ and Rb^+ become reversed at still higher temperatures.

In conclusion, in such binary systems as the ones studied here, the volume of the free space in relation to that of the ions would be one of the main factors that affect the mobilities of the ions. When one of the cations is Li^+, the pair potential between Li^+ and the anion with the deep minimum as well as the very small size of Li^+ would have a great influence on the mobility of Li^+.

In the interpretation presented above for the system $LiNO_3$-$TlNO_3$, the pair potential is assumed to be independent of the concentration of the constituent cations, that is to say, the present model does not take into account the assumption in the polarization model [3] that the pair potential between a large cation and an anion be very much affected by a small cation present near the anion. Thus, even if the polarization is ignored or the association model[28-30] is not adopted, the isotherms of the mobilities of two cations in the present binary mixtures could be qualitatively accounted for. Further experiments as well as molecular dynamics studies on such systems as LiCl-CsCl are required to verify the present model.

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