Internal Mobilities in the Binary Molten System (Na, Tl)NO_3

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Internal mobility ratios of the cations in the molten binary system (Na, Tl)NO_3 have been measured with the Klemm method. From these values and available data on the densities and electric conductivities, the internal mobilities, *b*, of Na^+ and Tl^+ ions have been calculated. The Chemla effect occurs at high x_{Tl} (x_{Tl}: mole fraction of $TlNO_3$). At low x_{Tl}, b_{Tl} sharply decreases with decreasing x_{Tl}, which may be attributed to the free space effect.

Introduction

In our previous investigations, we have measured internal cation mobilities, *b*, in molten binary alkali nitrate mixtures (see Table 1 in [1]) by the Klemm method [2]. In all these systems, in a certain range of concentration and temperature the Chemla effect was observed, i. e., the mobility of the larger cation is greater than that of the smaller one. Further, we have found that, when Coulombic interaction between the cations and anions is the predominant factor influencing the cationic mobilities, the internal mobilities *b* are well expressed by [3, 4]:

$$b = [A/(V - V_0)] \exp(-E/RT) , \tag{1}$$

where V is the molar volume of the mixture and A, E, V_0 are the parameters characteristic of the cation of interest, and almost independent of the co-cation and temperature.

Mainly in order to learn whether this equation holds also for an alkali metal ion if the co-cation is a mono-valent non-alkali metal ion, the system (Na, Tl)NO_3 has been chosen in the present work.

For this system the cation mobilities had been measured at 316 °C by means of zone electromigration using radioactive isotopes by Forcheri and coworkers [5, 6].

Experimental

Sodium nitrate of reagent grade and thallous nitrate of 99% purity made by Kanto Chemical Co., Tokyo were used. The chemicals were vacuum-dried at 120 °C overnight.

The requisite amount of the two salts were melted together in a small quartz vessel. After sufficient mixing, a separation tube of Vycor (internal diameter: 4 mm) densely packed with quartz powder of 80–100 mesh was inserted into the vessel. When the molten mixture was raised up to a height of about 20 cm in the separation tube by suction, the tube was inserted in an electromigration cell containing a molten (Li, Na, K)NO_3 mixture of nearly eutectic composition, and electromigration was started. The arrangement of electromigration cell and experimental procedure were similar to those used in previous studies [7, 8]. With a temperature controller, the temperature was kept constant within ± 1 °C.

From the phase diagram of the present system [9], the temperature range for the present study was chosen.

At the concentration of $x_{Tl} = 1$ (x_{Tl} is mole fraction of $TlNO_3$), radioactive ^{24}Na (half life: 15.1 h) was used which was produced by irradiating 20 mg of $NaNO_3$ with the thermal neutrons at a Triga II type nuclear reactor at Atomic Energy Research Laboratory, Musashi Institute of Technology. The irradiated $NaNO_3$ was added to about 15 g $TlNO_3$ contained in a quartz vessel. In this melt, x_{Na} (mole fraction of $NaNO_3$) was about 0.001. This melt was filled in the separation tube in the same way as described above. After electromigration, the radioactivity in each fraction (approx. 1 cm long) of the separation tube was counted with a well type NaI(Tl) scintillation counter. The amount of Tl^+ ions was measured with emission spectrophotometry.

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Results

The relative difference, ε in the internal mobilities, b, of the two cations

$$\varepsilon = (b_{\mathrm{Na}} - b_{\mathrm{Tl}})/\bar{b} \qquad (2)$$

was calculated from the amount of cations in the separation tube and the transported charge; here,

$$\bar{b} = x_{\mathrm{Na}} b_{\mathrm{Na}} + x_{\mathrm{Tl}} b_{\mathrm{Tl}} = \Lambda / F \,, \qquad (3)$$

where Λ is the molar conductivity of a mixture and F the Faraday constant.

The $TlNO_3$ containing very small amount of $NaNO_3$ including radioactive ^{24}Na could be regarded virtually as pure $TlNO_3$, in which case ε is calculated by the equation given in a previous paper (Eq. (2) in [8]).

The experimental conditions and the results are given in Table 1. The values are plotted against temperature in Figure 1. The internal mobilities of the cations are calculated from the obtained ε values and available data [10] on the densities and electric conductivities. The isotherms of the internal mobilities at 523, 573 and 623 K are shown in Figure 2. The isotherms calculated from the external mobilities at 589 K by Forcheri et al. [5, 6] are also shown for comparison in Figure 2.

Table 1. Experimental conditions and relative difference in internal cation mobility, ε. Q is the transported charge and t the duration.

T/K	x_{Tl}	Q/C	t/h	ε
583	0.058 ± 0.004	7981	22.3	0.324 ± 0.005
603		7944	22.0	0.273 ± 0.003
623		7909	22.0	0.209 ± 0.004
573	0.136 ± 0.003	7853	22.0	0.139 ± 0.002
598		7898	22.0	0.109 ± 0.001
623		7864	22.0	0.102 ± 0.001
548	0.244 ± 0.003	6638	18.5	0.112 ± 0.002
573		6483	18.0	0.084 ± 0.001
623		6661	18.5	0.071 ± 0.001
523	0.440 ± 0.001	7589	22.0	0.070 ± 0.001
573		7862	22.0	0.047 ± 0.001
623		7614	22.0	0.040 ± 0.001
483	0.748 ± 0.001	6728	22.0	0.071 ± 0.001
523		2807	8.0	0.033 ± 0.002
573		3555	10.0	0.028 ± 0.001
623		2924	8.0	0.005 ± 0.003
523	0.856 ± 0.004	3888	14.0	0.014 ± 0.001
573		4442	14.5	0.003 ± 0.001
603		5121	14.0	−0.002 ± 0.001
473	0.924 ± 0.004	2921	16.0	0.009 ± 0.001
523		4589	16.0	0.004 ± 0.001
573		4915	16.0	−0.012 ± 0.001
603		4667	16.0	−0.016 ± 0.001
573	1.00	1192	4.0	−0.020 ± 0.003

Discussion

Figure 1 shows that ε decreases with increasing temperature and concentration. Finally, in the high x_{Tl} region at higher temperature, ε becomes negative, that is, the Chemla effect occurs. The Chemla crossing point shifts toward lower x_{Tl} with increasing temperature. These trends are commonly observed in binary alkali nitrates and our interpretation has already been given in previous papers [3, 4, 7, 8].

Figure 2 shows that at higher temperature b_{Na} decreases with decreasing x_{Na}, as has been seen in other systems such as (Na, Rb)NO_3 [11]. However, at low temperature such as 523 K, at which the molten state can be achieved over a sufficient

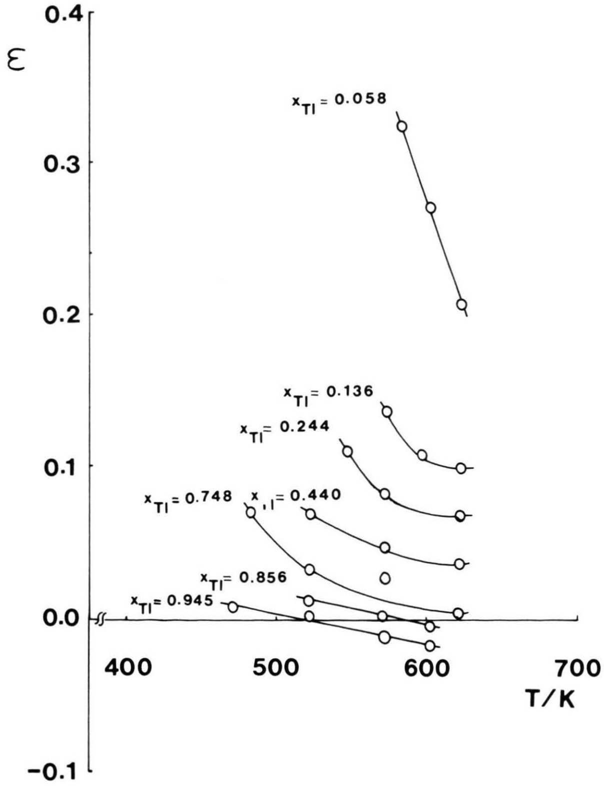

Fig. 1. Relative difference in internal cation mobilities, ε vs. temperature. The numbers in the figure represent mole fraction of $TlNO_3$, x_{Tl}. For "$x_{\mathrm{Tl}} = 0.945$" read "$x_{\mathrm{Tl}} = 0.924$".

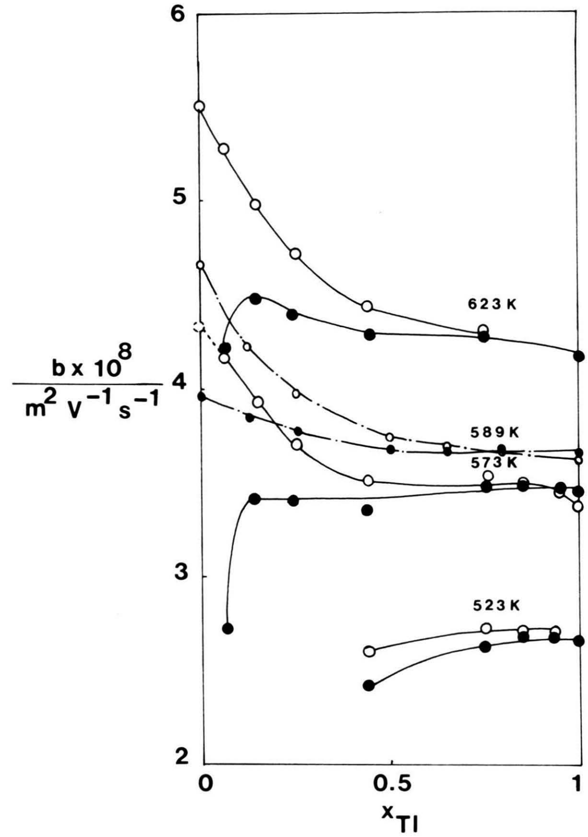

Fig. 2. Isotherms of internal mobilities in the system (Na, Tl)NO_3. ○: Na (this work); ○: Na at 589 K [5, 6], ●: Tl (this work); ●: Tl at 589 K [5, 6]. The value for pure $NaNO_3$ fictive melt at 573 K is extrapolated from the melts at higher temperature.

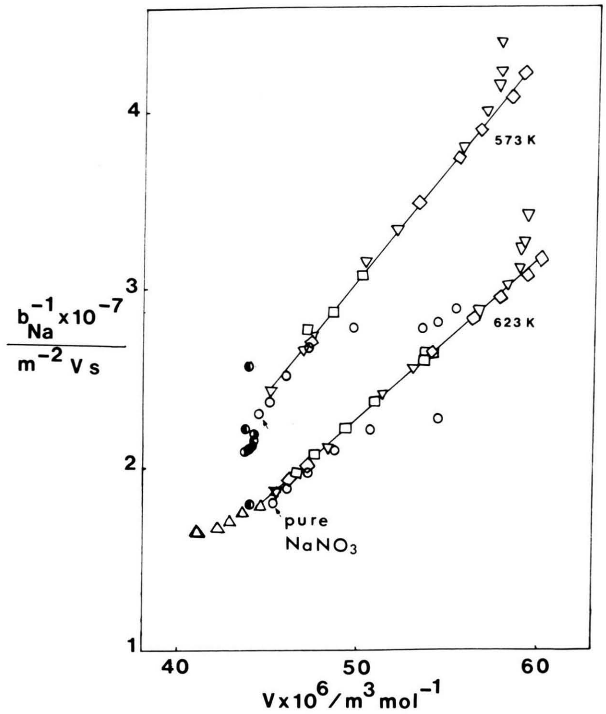

Fig. 3. The reciprocal of the internal mobilities of Na^+ vs. molar volume of the mixtures (Na, M)NO_3. △: M=Li [3]; □: K [4]; ▽: Rb [11]; ◇: Cs [3]; ◐: Ag at 563 K [12], ◑: Ag [13]; ○: Tl (this work). The solid lines are drawn according to (1) having the following parameters: $A = 4.94 \times 10^{-10}$ $m^5 V^{-1} s^{-1} mol^{-1}$, $E = 19.71$ kJ mol^{-1} and $V_0 = 24.2 \times 10^{-6}$ $m^3 mol^{-1}$ [14].

concentration region owing to the low melting point of $TlNO_3$, b_{Na} decreases with increasing x_{Na}; this may be attributed to the smaller free space at a greater x_{Na}.

The free space effect is more clearly seen for b_{Tl} from the following facts. At 573 K and 523 K b_{Tl} slightly decreases with increasing x_{Na}, while at 623 K b_{Tl} slightly increases. In the high x_{Na} region b_{Tl} drastically decreases. The maximum of the isotherm of b_{Tl} seems to shift toward higher concentration of the small cation like in other systems [8].

The isotherms at 589 K calculated from the external cation mobilities by Forcheri et al. [5, 6] are consistent with ours except for the mobilities of Tl^+ in the high x_{Na} region. Their results do not show the free space effect. This discrepancy might be due to experimental errors in the zone electromigration.

At very high x_{Tl}, b_{Na} decreases rather sharply with increasing x_{Tl}. A similar phenomenon has been observed for b_{Na} in (Na, Rb)NO_3 [11]. At low number density of the NO_3^- ions, the small Na^+ ions will be strongly clustered with neighbouring NO_3^- ions, which reduces their mobility.

We have shown that in most cases b_{Na} in molten alkali nitrates can be well expressed by (1) with a set of parameters given in the caption to Figure 3. In order to see whether this holds for the present mixture, the b_{Na}^{-1}s in the present system are compared with those in alkali nitrate mixtures in Figure 3. The b_{Na}^{-1}s in (Na, Ag)NO_3 are also given for comparison. The data from two groups [12, 13] are considerably different from each other; the data of one group [12] deviate negatively from the empirical equation in a certain range of concentration ($x_{Na} > 0.55$) and positively deviate in the other

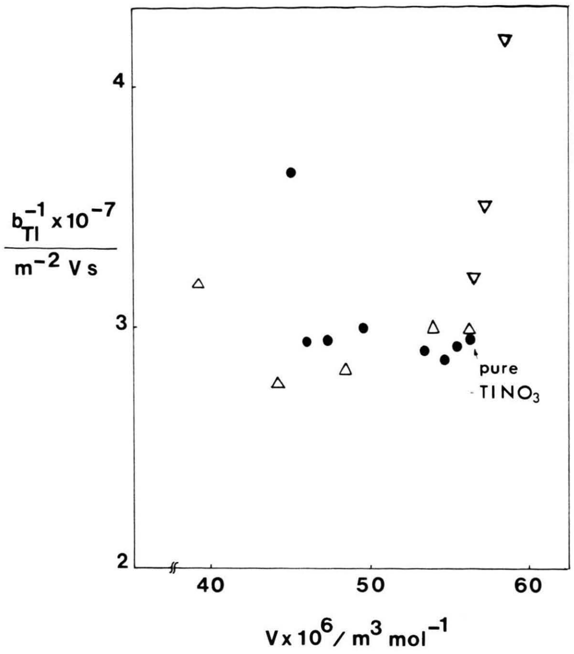

Fig. 4. The reciprocal of the internal mobilities of Tl^+ vs. molar volume of the mixtures (Tl, M′)NO_3 at 573 K. △: M′=Li [8]; ●: Na (this work); ▽: Rb [8]. The small difference in the plots for pure $TlNO_3$ is due to the different origins of the data (△: [9], ●: [10]).

range, whereas those from the other group [11] deviate positively in the whole concentration range. (As the reciprocal of b is given in Fig. 3, a positive deviation appears as the negative one there, and vice versa.) Figure 3 shows that the b_{Na} s in (Na, Tl)NO_3 deviate from the empirical equation. These deviations suggest that in these mixtures inter-ionic forces other than the Coulombic one would also play an appreciable role for the ionic mobility. The positive deviation in the present system might be related to the high molar conductivity of molten $TlNO_3$ as compared with the alkali nitrates. This may be related also with the low melting point of $TlNO_3$. However, it remains to be further studied why it has a high molar conductivity and a low melting point.

In order to see whether a formula like (1) holds for b_{Tl}, the reciprocals in the systems so far studied are plotted against the molar volume in Figure 4. This figure shows that the b_{Tl}s cannot be expressed by (1) with parameters independent of the cocations.

Data for the systems (Tl, Alk)NO_3(Alk = K and Cs) are needed to further discuss b_{Tl} in mixtures with alkali nitrates.

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