Internal Cation Mobilities in the Molten Binary System $(Na, NH_4)NO_3$

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Relative differences in the internal cation mobilities in the molten binary system $(Na, NH_4)NO_3$ have been measured by Klemm's countercurrent electromigration method at $NaNO_3$ mole fractions 0–0.3 and temperatures 433–453 K. Also the densities and electric conductivities of this system have been measured. From these data the internal cation mobilities, b_{Na} and b_{NH_4}, were calculated. Under all accessible conditions, b_{NH_4} is greater than b_{Na}. The results are discussed in terms of the interaction between unlike ions and free space.

Introduction

In a previous study [1], ^6Li was enriched by countercurrent electromigration; molten $LiNO_3$ and NH_4NO_3 were arranged in a separation tube at about 573 K and cathode compartment at about 453 K, respectively. ^6Li was enriched in the boundary region between the two salts, which was located near the end of the separation tube open to the large cathode compartment. For high enrichment of ^6Li the boundary should be kept as stable and sharp as possible by balancing the internal electromigration flow of the Li^+ ions and the counter flow of the salt. One of the difficulties of this method was to balance them. In order to prevent Li^+ from entering the cathode compartment due to an uncontrollable over-electromigration flow, we have introduced small zone of another salt between the two salts [2]; the mobility of its cation should be intermediate between those of the Li^+ and NH_4^+ ions. One of the potential third salts is $NaNO_3$.

It is known that $b_{Li} < b_{Na}$ at all concentrations in the system $(Li, Na)NO_3$ [3], and that $b_{Li} < b_{NH_4}$ under all accessible conditions of concentration and temperature in the system $(Li, NH_4)NO_3$ [4], where b_M is the internal mobility of cation M.

In order to confirm that $b_{Na} < b_{NH_4}$ under all accessible conditions, we have measured internal cation mobility ratios in the molten binary system $(Na, NH_4)NO_3$. To our knowledge, there are no available data on the density and the electric conductivity in this molten system. Therefore, to calculate the internal cation mobilities, the densities and the electric conductivities have also been measured.

Experimental

The chemicals $NaNO_3$ and NH_4NO_3 were vacuum-dried overnight at 400 K and 330 K, respectively, before use. The densities, electric conductivities and internal cation mobility ratios were measured at 433 to 453 K for $x_{NH_4} > 0.7$ (x_{NH_4}: mole fraction of NH_4NO_3), the ranges being limited by the phase diagram [5] and the thermal decomposition of NH_4NO_3 [6].

The density was measured with a cell made of transparent silica glass whose volume was calibrated by using water at 298 K. A narrow neck of the cell is essential for an accurate measurement of the volume; however, as it is difficult to fill molten salt into a cell with a narrow neck, the neck had an inner diameter of 4 mm. A pipette of special design was used to fill the cell, which was immersed in a melt bath. The height of the meniscus from a marked line on the neck was read with a cathetometer.

Since most molten salts have a high electric conductivity, the usual alternating current measurements imply capillary tubes for achieving sufficiently high resistances. As pointed out by King and Duke [7], however, direct-current conductivity measurement techniques enable one to dispense with capillary tubes. This is advantageous in our case since NH_4NO_3 easily

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decomposes, generating bubbles. Therefore this method was employed. The silica cell of the type proposed by Duke and Bissell [8] had an inner diameter of 5 mm, and the distance between the two Ag wire electrodes was about 5 cm. The cell constant was measured to be 15.53 cm^{-1}. The temperature of the cell was kept within ± 0.5 K by keeping it in a melt bath.

The relative differences in the internal cation mobilities were measured by Klemm's countercurrent electromigration method. The electromigration cell and the procedure were similar to those previously used for the study of (Li, NH_4)NO_3 melts [4]. The large cathode compartment contained (Na, NH_4)NO_3 of the eutectic composition ($x_{NH_4} = 0.80$). In the present study, an ion chromatographic analyser recently commercialised (IC500S made by Yokogawa Electric Co. Ltd., Tokyo) was used for the quantitative analysis of the Na^+ and NH_4^+ ions, whereas in the previous study [4] flame spectrophotometry and the Kjeldahl method were employed for the determination of Li^+ and NH_4^+ ions, respectively. For the analysis of NH_4^+, the ion chromatographic method is superior to the Kjeldahl method as to precision and rapidity.

Results

The fitted densities and conductivities (previously called specific conductivities) are given as linear functions of temperature in Tables 1 and 2, respectively.

The relative difference, ε, in the internal mobilities of the two cations is defined as

$$\varepsilon = (b_{Na} - b_{NH_4})/\bar{b}, \tag{1}$$

where $\bar{b} = x_{Na} b_{Na} + x_{NH_4} b_{NH_4}$ (x: mole fraction). The ε values are calculated from the amount of the cations in the separation tube and the transported charge in the usual way [9]. Measured values of ε are given along with the main experimental conditions in Table 3.

Discussion

Reliable measurements of the density of pure NH_4NO_3 could not be achieved owing to evolution of bubbles. The molar volumes of pure NH_4NO_3 melt were taken from [10], by extrapolating the values in the system $NH_4NO_3 - H_2O$ with respect to concentration and temperature.

Table 1. Parameters of the equation for the density in the system (Na, NH_4)NO_3.
$\varrho = a - (b \times 10^{-3})\,T$ (ϱ in g cm^{-3} and T in K)

x_{NH_4}	a	b	Temp. range (K)	Ref.
0.000	2.320	0.715	490–600	[11]
0.699	2.038	1.050	432–450	
0.795	1.869	0.767	428–453	
0.899	1.854	0.846	432–450	
1.000	1.661	0.508	443–503	[10]

Table 2. Parameters of the equation for the electric conductivity in the system (Na, NH_4)NO_3.
$\varkappa = a + (b \times 10^{-3})\,T$ ($\varkappa$ in S cm^{-1} and T in K)

x_{NH_4}	a	b	Temp. range (K)	Ref.
0.000	−1.5713	4.3835	590–700	[11]
0.700	−1.096	3.171	435–452	
0.801	−1.191	3.432	431–454	
0.893	−1.189	3.469	428–455	
1.000	−1.158	3.444	443–456	

Table 3. Experimental conditions and relative differences in internal mobilities, ε. Q is the transported charge and t the duration of the runs.

T (K)	x_{NH_4}	Q (C)	t (hr)	ε
433	0.753	1642	6.1	-0.149 ± 0.005
	0.764	1608	8.0	-0.185 ± 0.002
	0.897	1484	5.4	-0.228 ± 0.001
443	0.723	1627	9.8	-0.167 ± 0.003
	0.829	1559	5.8	-0.189 ± 0.003
	0.894	1555	7.7	-0.230 ± 0.001
448	0.802	1566	5.8	-0.201 ± 0.004
	0.901	1619	5.9	-0.260 ± 0.002
453	0.669	1506	7.5	-0.175 ± 0.005
	0.816	1587	5.8	-0.230 ± 0.005
	0.897	1569	7.0	-0.297 ± 0.002

The accuracy of the measured electric conductivities given in Table 2 was checked by comparing with the corresponding available data on molten $NaNO_3$ [11]. The deviations turned out to be less than 2%. Since NH_4NO_3 slightly decomposes even at the melting point, one of the decomposition products being water [12], the bubbles and the water are supposed to have affected the accuracy of the conductivities to some extent. The reproducibility of the data is within 0.3%. The conductivity of pure NH_4NO_3 obtained in the present study is ca. 18% greater than reported in

Table 4. Internal mobilities of Na^+ and NH_4^+ in the system (Na, NH_4)NO_3.

T (K)	x_{NH_4}	$\varkappa$ (10^2 S m^{-1})	V (10^{-6} m^3 mol^{-1})	b_{Na} (10^{-8} m^2 V^{-1} s^{-1})	b_{NH_4} (10^{-8} m^2 V^{-1} s^{-1})
433	0.753	0.2863	52.21	1.38 ± 0.01	1.61 ± 0.00
	0.764	0.2871	52.36	1.34 ± 0.00	1.63 ± 0.00
	0.897	0.3117	54.12	1.39 ± 0.00	1.79 ± 0.00
443	0.723	0.3150	52.07	1.50 ± 0.00	1.78 ± 0.00
	0.829	0.3320	53.48	1.55 ± 0.00	1.90 ± 0.00
	0.894	0.3450	54.35	1.54 ± 0.00	1.99 ± 0.00
453	0.669	0.3168	51.61	1.49 ± 0.01	1.79 ± 0.00
	0.816	0.3630	53.58	1.64 ± 0.01	2.10 ± 0.00
	0.897	0.3794	54.67	1.56 ± 0.00	2.22 ± 0.00

[4] and [13]. As our previous data [4] were obtained by an AC capillary method, these may have been affected by the bubbles. The present data should be more accurate.

As seen from Table 3, ε is negative under all accessible conditions, that is, the mobility of the larger NH_4^+ ion is greater than that of the smaller Na^+ ion. Thus, as far as the mobilities are concerned, molten $NaNO_3$ can be used as the third salt located between $LiNO_3$ and NH_4NO_3 in the separation tube. $-\varepsilon$ increases at constant temperature with increasing NH_4^+ content, and it increases at constant NH_4^+ content with increasing temperature. These features are characteristic for systems showing the Chemla effect. If higher Na^+ contents were accessible, the cross over of the mobility isotherms could be observed. Our interpretation of the Chemla effect for the present system is quite similar to that previously presented for the (Li, NH_4)NO_3 system [4].

$-\varepsilon$ tends to increase with temperature because the decrease in concentration due to the increase in temperature is less unfavourable for the mobility of the larger NH_4^+ ions than for that of the smaller Na^+ ions.

The internal mobilities are calculated from

$$b_{Na} = (\varkappa V/F)(1 + x_{NH_4}\varepsilon), \tag{2a}$$

$$b_{NH_4} = (\varkappa V/F)(1 - x_{Na}\varepsilon), \tag{2b}$$

where $\varkappa$ and V are the conductivity and the molar volume of the mixture, respectively, and F is the Faraday constant.

The isotherms of b_{Na} and b_{NH_4} are shown in Figure 1. As seen from Fig. 1, the internal mobility of the larger cation, NH_4^+, distinctly decreases with increasing concentration of Na^+. This may be mainly due to the reduced free space resulting from the increasing concentration of Na^+.

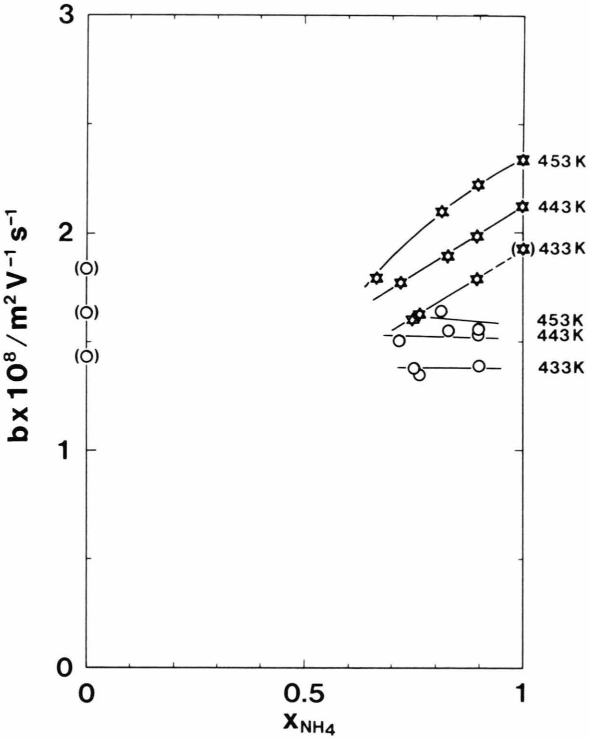

Fig. 1. Internal mobility isotherms in the molten (Na, NH_4)NO_3 system. ○: Na, ✡: NH_4. Internal mobilities of fictive supercooled pure $NaNO_3$ [11] and pure NH_4NO_3 melts are also shown in parentheses.

As for b_{Na}, the isotherms seem to slightly decrease with increasing x_{NH_4}. This trend can be explained in terms of a decrease in the number density of the common anion [3].

It has previously been found [3, 14] that b_{Na} in the system (Na, M)NO_3 (M = K [14], Rb [15] and Cs [3]) is well expressed by

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

where $A = 6.60 \times 10^{-11}\,m^5\,V^{-1}\,s^{-1}\,mol^{-1}$, $E = 21.31\,kJ\,mol^{-1}$, and $V_0 = (43.21 - 0.028\,(T/K)) \times 10^{-6}\,m^3\,mol^{-1}$; V is the molar volume, T the temperature and R the gas constant. The previously given values of A, E and V_0 have been somewhat revised here, more data than in the previous calculation having been used. We have checked whether there exists a combination of A, E and V_0 values which satisfies both the data for the binary alkali nitrates at higher temperature and the present data at lower temperature. Equation (3) with any combination of parameters fitting the data in binary alkali nitrates yields lower values of b_{Na} around 443 K than the experimentally obtained values in the present system. A similar trend has been found for b_{Li} in the system (Li, NH_4)NO_3 [4].

When an internal mobility of an alkali ion in nitrate mixtures is greater than expressed by (3), the excess may be regarded as attributable to the agitation effect by coexisting cations. As seen from Fig. 2, the b_{Na}'s also in the system (Na, Tl)NO_3 [17] are greater than expressed by (3), like those in the present system. It remains to be further studied, however, why NH_4^+ as well as Tl^+ apparently plays a role of agitator for the internal mobilities of coexisting cations.

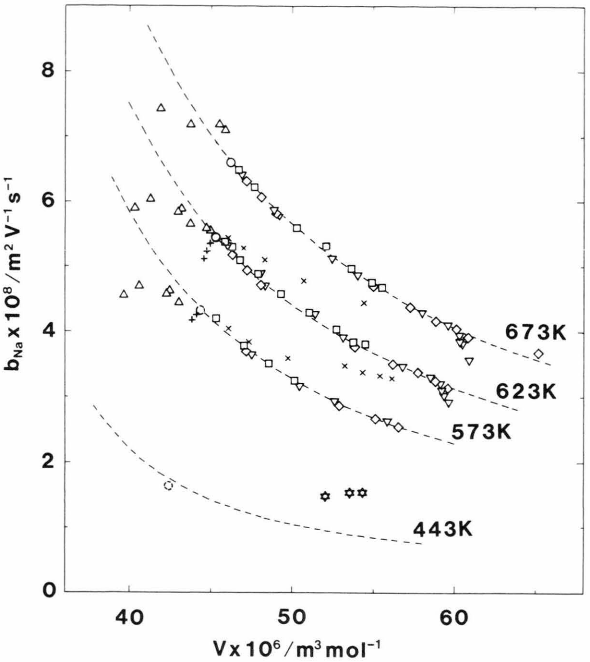

Fig. 2. Internal mobilities of Na^+ vs. molar volume of the mixtures (Na, M)NO_3. △: M = Li [3], □: K [14], ▽: Rb [15], ◇: Cs [3], +: Ag [16], ×: Tl [17], ✡: NH_4 (this work), ○: pure $NaNO_3$ [11] and ◌: fictive supercooled pure $NaNO_3$ melt obtained by extrapolation with respect to temperature [11]. The broken lines are drawn according to (3).

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