Internal Mobilities in (Na-Rb)NO_3 Melts

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Internal mobility ratios in melts of the system (Na-Rb)NO_3 have been measured with the Klemm method at various temperatures and compositions. The internal mobilities have been calculated from these and the available data on densities and conductivities. The Chemla effect has been observed. For $NaNO_3$ concentrations >10 mol %, the internal mobility of the Na^+ ions obeys the formula $b_{Na}=[A/(V-V^0)]\exp(-E/RT)$, where V is the molar volume and V^0 is slightly temperature dependent. For $NaNO_3$ concentrations <10 mol %, b_{Na} becomes smaller than expected from the formula. The internal mobility of the Rb^+ ions also obeys such a formula at higher temperatures. At lower temperatures it is, like that of the Cs^+ ions, a function of the mole fraction and independent of the kind of coions.

Introduction

In Ref. [1–3] we have suggested that the dominant factors ruling the internal mobilities of molten salts are the cation-anion pair potentials and the relative volume of the free space between the ions. More specifically, it has been found [4] that for molar volumes $V>45\cdot10^{-6}\,m^3/mol$ the internal mobilities, b, of the Li^+ ions in the systems (Li-M)NO_3 [M = K, Rb and Cs] and of the Na^+ ions in the system (Na-M)NO_3 [M = Na, K and Cs] can be represented by the formula

$$b=\frac{A}{(V-V^0)}\exp\left(-\frac{E}{RT}\right), \qquad (1)$$

where the parameters A, E and V^0 differ for Li and Na, and V^0 for Na is slightly temperature dependent.

Data on the internal mobilities in the systems (M-Rb)NO_3 with M = Li [2], Na [5, 6], K [7], Ag [8, 9] and Tl [1] are available. In Ref. [5] the internal mobilities have been measured at 593 K with a disk method by Shvedov and Ivanov, and in Ref. [6] the external ones have been measured at 598, 673, and 773 K with a paper strip method by Forcheri et al. These measurements agree generally well, though the Chemla effect [10] has only been clearly observed by the former authors. Since the Chemla effect has been observed in the systems (Na-K)NO_3 [11, 12] and (Na-Cs)NO_3 [4, 13], it should exist in the system (Na-Rb)NO_3 too.

In the present study the internal mobilities in the system (Na-Rb)NO_3 have been remeasured with the Klemm method, i. e. a countercurrent electromigration method. Since this method was invented originally for the separation of isotopes, it can yield accurate data even on very small differences in internal mobilities, as in the present case.

Experiments and Results

The electromigration runs and chemical analysis were performed similarly as reported in Ref. [2]. The experimental conditions and the results are given in Table 1. With a temperature controller the temperature was kept constant within ±1 °C in most runs. The current was constant in each run.

The internal mobilities were calculated from the present data and the available data on the specific conductivities [14, 15] and densities [16]. Resulting mobility isotherms are shown in Fig. 1, together with results from Ref. [6].

Discussion

Contrary to Ref. [6], in the present study the Chemla effect was clearly found (cf. Figure 1). As the temperature increases, our Chemla crossing point

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Table 1. Conditions and results for the system (Na-Rb)NO_3. p is the mole fraction and Q the transported charge.

Run	T/K	p_{Rb}	Q/C	$(b_{Na} - b_{Rb})/\bar{b}$
1	582	0.051 ± 0.001	2170	0.221 ± 0.007
2	594		1988	0.230 ± 0.011
3	610		2460	0.186 ± 0.044
4	654		2096	0.182 ± 0.003
5	606	0.177 ± 0.001	2778	0.128 ± 0.004
6	674		2557	0.104 ± 0.005
7	594	0.200 ± 0.001	2621	0.125 ± 0.002
8	600		2346	0.123 ± 0.006
9	636		2568	0.113 ± 0.003
10	677		2571	0.085 ± 0.003
11	579	0.404 ± 0.002	1887	0.091 ± 0.017
12	599		2668	0.090 ± 0.005
13	615		2258	0.078 ± 0.012
14	641		2214	0.066 ± 0.004
15	688		2690	0.055 ± 0.013
16	561	0.515 ± 0.003	2219	0.085 ± 0.005
17	600		2314	0.073 ± 0.006
18	634		2384	0.063 ± 0.004
19	690		2389	0.039 ± 0.006
20	590	0.775 ± 0.002	2377	0.062 ± 0.006
21	626		2519	0.051 ± 0.005
22	661		3091	0.029 ± 0.011
23	688		2682	0.031 ± 0.008
24	572	0.881 ± 0.003	2075	0.063 ± 0.016
25	590		2146	0.054 ± 0.005
26	643		2487	0.030 ± 0.006
27	693		2200	0.014 ± 0.009
28	602	0.922 ± 0.001	2947	0.035 ± 0.004
29	610		2932	0.028 ± 0.005
30	651		2931	0.005 ± 0.003
31	677		2770	− 0.001 ± 0.008
32	614	0.929 ± 0.002	2821	− 0.012 ± 0.006
33	643		2946	− 0.016 ± 0.007
34	604	0.939 ± 0.003	2862	− 0.024 ± 0.009
35	691		2805	− 0.039 ± 0.011
36	587	0.958 ± 0.003	2429	− 0.030 ± 0.014
37	616		2404	− 0.071 ± 0.011
38	647		2926	− 0.055 ± 0.010
39	694		2323	− 0.099 ± 0.014

shifts toward higher concentrations of the smaller cation, as is normal. The crossing point at $p_{Rb} = 0.65$ for 593 K given in Ref. [5] is at variance with our results. At high concentrations of Rb ($p_{Rb} > 0.9$), b_{Na} decreases sharply. In the system (Na-Cs)NO_3, such a sharp decrease of b_{Na} is not observed [4] though the free volume behaves similarly in both systems. Evidently the sharp de-

▶

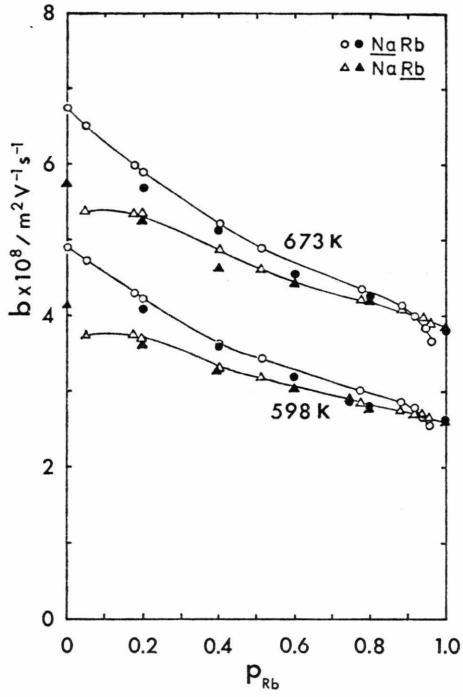

Fig. 1. Internal cation mobilities vs. mole fraction of $RbNO_3$ in the system (Na-Rb)NO_3. ○, △ this work; ●, ▲: [6]. In this and the following figures the pairs of coions are listed, the underlined symbol referring to the coion whose mobility is plotted.

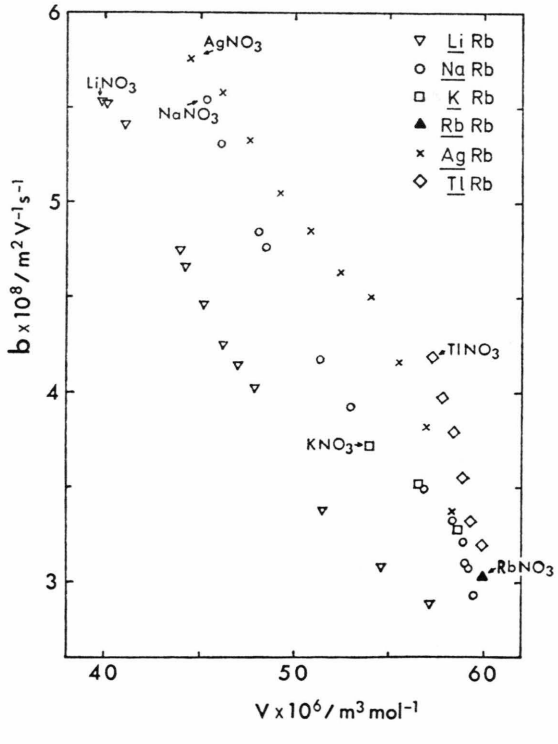

Fig. 2. Internal mobilities at 623 K of ions M^+ vs. molar volume in systems (M-Rb)NO_3 ▽: [2]; ○: this work; □: [7]; ▲: [14, 16]; ×: [8]; ◇: [1]. The arrows indicate the internal mobilities of the pure salts.

crease of b_{Na} in (Na-Rb)NO_3 cannot be accounted for in terms of an increase in free space alone.

In Fig. 2 the isotherms of the internal mobilities at 623 K in the systems (M-Rb)NO_3 (M = Li, Na, K, Rb, Ag and Tl) are plotted against the molar volume. The figure shows that the internal mobilities of the foreign ions become nearly equal at high concentrations of $RbNO_3$, as do the external mobilities of trace amounts of Na^+ and Cs^+ in $RbNO_3$: $u_{Na} = 1.48$, $u_{Cs} = 1.43$ at 609 K and $u_{Na} = 2.20$, $u_{Cs} = 2.24$ at 708 K, where u is the external mobility in $10^{-8}\,m^2\,V^{-1}\,mol^{-1}$ [17]. In the systems (Li-Cs)NO_3 [2] and (Na-Cs)NO_3 [4] such a trend is not found for b_{Li} and b_{Na}. Thus, this seems to be a phenomenon peculiar to foreign cations in nearly pure $RbNO_3$.

In Fig. 3 the reciprocal of b_{Na} is plotted against the molar volume. As expected from the previous paper [4], the values of $(1/b_{Na})$ for the system

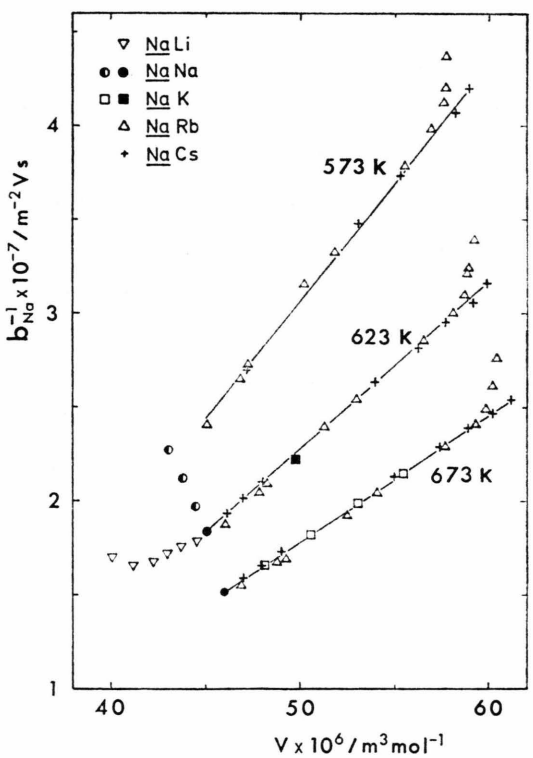

Fig. 3. Reciprocal of internal mobilities of Na^+ ions vs. molar volume in systems (Na-M)NO_3. ▽: [4]; ●[a]: [20]; ◐[b]: [18, 19]; □[c]: [11]; ■[c]: [12]; △: this work; +: [4].
[a] pure $NaNO_3$,
[b] at high pressure at 623 K,
[c] evaluated from external mobility.

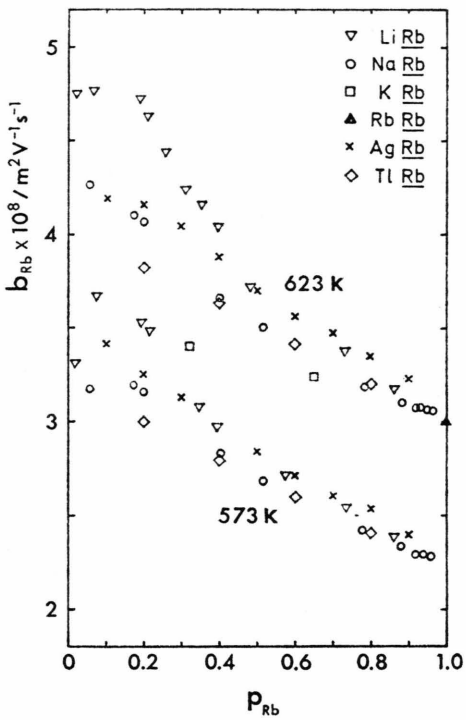

Fig. 4. Internal mobilities of Rb^+ ions vs. mole fraction of $RbNO_3$ in systems (M-Rb)NO_3. References as in Figure 2.

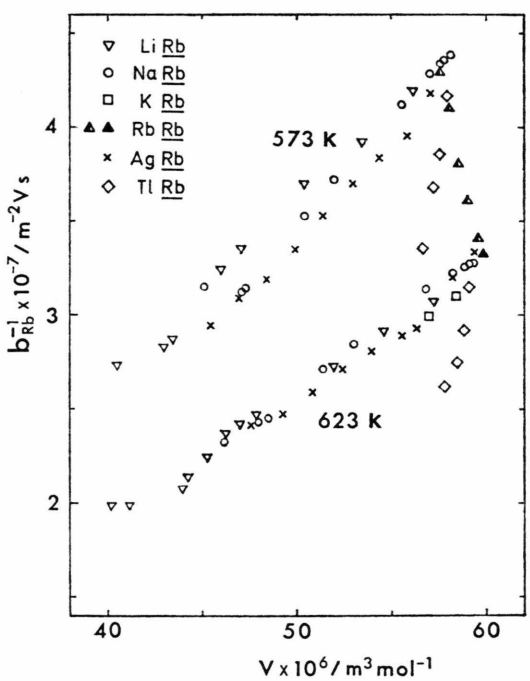

Fig. 5. Reciprocal of internal mobilities of Rb^+ ions vs. molar volume in systems (M-Rb)NO_3. ◭: pure $RbNO_3$ at high pressure [18, 19]. Other references as in Figure 2.

(Na-Rb)NO_3 lie, except at high concentrations of $RbNO_3$, on the same straight lines as for the other systems. From the straight lines drawn in Fig. 3 the parameters of (1) are recalculated to be: $A = 4.94 \times 10^{-1}\ m^5\ V^{-1}\ s^{-1}\ mol^{-1}$, $E = 1971\ kJ\ mol^{-1}$ and $V^0 = 25.8$, 25.0 and $24.2 \times 10^{-6}\ m^3\ mol^{-1}$ at 573, 623 and 673 K, respectively. Thus it is confirmed that V^0 depends slightly on temperature for b_{Na}.

In Fig. 4, b_{Rb} is plotted against p_{Rb} at 573 K and 623 K. At 573 K and $p_{Rb} > 0.3$, b_{Rb} is seen to be independent of the sort of coion (Li^+, Na^+, Ag^+ or Tl^+) as was found to be true for b_{Cs} in the systems (Li-Cs)NO_3 and (Na-Cs)NO_3 [4].

In Fig. 5, $(1/b_{Rb})$ is plotted vs. V for the systems so far investigated. It is seen that also b_{Rb} increases at ambient pressure with decreasing molar volume and decreases in pure $RbNO_3$ with increasing pressure. The latter values are calculated from the specific conductivities [18] and the densities [19] at elevated pressures. Thus, the increase of b_{Rb} in the mixtures with decreasing molar volume cannot be attributed to a decrease of free space alone. Figure 5 shows that, except in the system (Tl-Rb)NO_3, b_{Rb} can at 623 K be roughly expressed by an equation similar to (1). At this temperature, b_{Rb} is approximately represented by $b_{Rb} = 1.41 \times 10^{-12}/(V - 14.1 \times 10^{-6})$ $[m^5\ V^{-1}\ s^{-1}\ mol^{-1}]$, where V is in $m^3\ mol^{-1}$. The deviation from this behaviour of b_{Rb} for the system (Tl-Rb)NO_3 seems to be correlated with the extraordinarily high external transport number of the NO_3^- ions ($t_- = 0.69$ at 495 K) in molten $TlNO_3$ [20].

Thus, at the higher temperature b_{Rb} is, like b_{Li} and b_{Na}, a function of the molar volume of the binary nitrate mixture (cf. Fig. 5), while at the lower temperature b_{Rb} is, like b_{Cs}, a function of the mole fraction (cf. Figure 4). The mobility of the larger cation in such binary systems seems to be governed by more complex factors than that of the smaller coion.

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