

Internal Mobilities in the Molten Binary System (K, Rb)NO₃

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Z. Naturforsch. **42a**, 1017–1020 (1987); received July 7, 1987

Ratios of internal cation mobilities in the molten binary system (K, Rb)NO₃ have been measured with the Klemm method in a wide range of concentration ($0.0537 < x_{\text{Rb}} < 1.00$; x_{Rb} denotes mole fraction of RbNO₃) and temperature ($603 \text{ K} < T < 783 \text{ K}$). From these and available data on the densities and conductivities, the internal mobilities of the two cations, b_{K} and b_{Rb} , have been calculated. At high temperature and high x_{Rb} , the Chemla effect has been observed, whereas in previous similar experiments* the Chemla effect had not been observed. Except for $x_{\text{Rb}} > 0.9$, b_{K} can be expressed by $b_{\text{K}} = [A/(V - V_0)] \exp(-E/RT)$, where V is the molar volume; A , E and V_0 are constants having almost the same values as in the molten binary system (K, Cs)NO₃.

Introduction

We have so far measured ratios of internal mobilities of two cations in various binary alkali nitrate melts (see Table 1 in [1]) with Klemm's countercurrent electromigration method [2]. In the system (K, Rb)NO₃ Ekhed and Lundén [3] measured the internal mobilities of the two cations with the same method. Their main aim was to determine the isotope effect of these cations and they did not cover a wide range of concentration and temperature. Thus, they did not clearly observe the Chemla effect [4, 5]. In all binary alkali nitrates except this system the Chemla effect has been observed and no plausible reason could be found that only this system is exceptional. In some binary alkali nitrate melts such as (Na, K)NO₃ [6] and (Rb, Cs)NO₃ [1], in which the relative differences in the radii of the cations are small, the Chemla effect occurs at high concentration of larger cation at high temperature. Therefore, also in (K, Rb)NO₃ the Chemla effect was supposed to occur under such conditions.

It has been found [6, 7] that, when the Coulombic attraction is expected to play a dominant role for the internal mobility, the internal mobility of cation 1 can be expressed by

$$b_1 = [A/(V - V_0)] \exp(-E/RT), \quad (1)$$

* A. Ekhed and A. Lundén, Z. Naturforsch. **34a**, 1207 (1979).

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where A , V_0 and E are constants characteristic of cation 1 and nearly independent of the co-cation and temperature. It was another aim to learn whether (1) also holds in the present case.

Experimental

The chemicals KNO₃ and RbNO₃ used were prepared by Soekawa Chem. Co., Tokyo; the former was of reagent grade and the purity of the latter was better than 99%. The salts were dried at 120 °C overnight, mixed in a chosen ratio and melted.

The electromigration cell and experimental procedure were quite similar to the previous ones [5]. In most of the runs the temperature could be kept within $\pm 2^\circ\text{C}$ with a temperature controller.

At $x_{\text{Rb}} = 1.00$ (x_{Rb} : mole fraction of RbNO₃), radioactive ⁴²K, whose half life is 12.36 hr, was employed; this was produced by irradiating ca. 20 mg KNO₃ with thermal neutrons at a Triga II type nuclear reactor at Atomic Energy Research Laboratory, Musashi Institute of Technology. The irradiated KNO₃ was poured into ca. 20 g of RbNO₃ melt contained in a small quartz vessel; the concentration of KNO₃, x_{K} , was about 0.0015. After electromigration, the radioactivity in each fraction (1.5–2.0 cm long) of the separation tube was measured with a well type NaI(Tl) scintillation counter, and then the radioactivity at a fixed time was calculated by extrapolation.

The content of K⁺ and Rb⁺ in each fraction was determined with flame spectrophotometry; about

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1000 ppm of Cs⁺ were added to each solution in order to depress the easy ionization of Rb.

Results

The relative difference in internal cation mobilities $\varepsilon = (b_K - b_{Rb})/\bar{b}$; $\bar{b} = x_K b_K + x_{Rb} b_{Rb}$ was calculated in the usual way [8]. In the case of $x_{Rb} = 1$, the equation (2) of [9] was used to calculate ε .

From the ε value thus obtained and available data [10] on the densities and the conductivities, the internal mobilities b_K and b_{Rb} were calculated.

The main experimental conditions and the results are listed in Table 1.

In Fig. 1 the isotherms of b_K and b_{Rb} obtained in the present study are shown together with those obtained by Ekhed and Lundén [3].

Discussion

Figure 1 shows that the present isotherms agree well with those estimated from the data by Ekhed and Lundén [3].

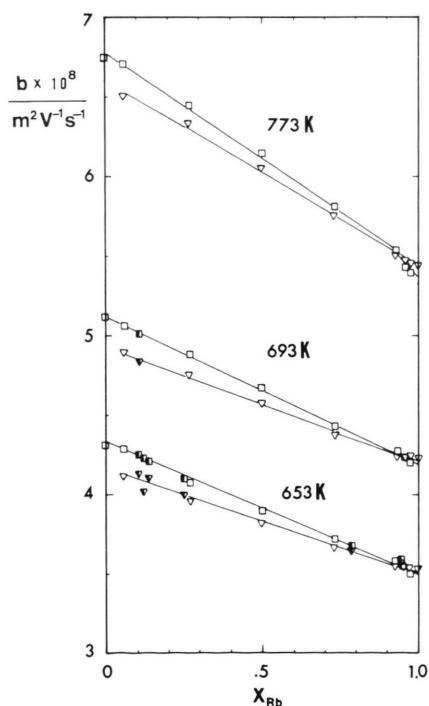


Fig. 1. The isotherms of internal cation mobilities in the system (K, Rb)NO₃. □: b_K [this work], ■: b_K [3], ▽: b_{Rb} [this work], ▼: b_{Rb} [3].

Table 1. Experimental conditions and results.

x_{Rb}	T/K	t/hr	Q/C	ε
0.054 ± 0.003	673	7.3	3668	0.0372 ± 0.0062
	723	8.0	3911	0.0301 ± 0.0053
	783	7.0	3961	0.0250 ± 0.0056
0.257 ± 0.002	603	8.3	3681	0.0291 ± 0.0088
	673	8.0	3603	0.0270 ± 0.0087
	783	7.6	3616	0.0182 ± 0.0102
0.496 ± 0.001	648	7.0	2476	0.0030 ± 0.0096
	693	7.5	2827	0.0223 ± 0.0098
	723	7.3	2550	0.0174 ± 0.0083
0.731 ± 0.002	773	7.5	2983	0.0153 ± 0.0071
	603	8.8	3140	0.0200 ± 0.0063
	643	7.0	2913	0.0156 ± 0.0044
0.935 ± 0.002	673	7.5	3302	0.0117 ± 0.0033
	723	7.8	2957	0.0124 ± 0.0033
	733	7.7	3649	0.0109 ± 0.0030
0.968 ± 0.003	783	8.1	3176	0.0104 ± 0.0043
	603	8.2	3635	0.0123 ± 0.0050
	643	8.2	3616	0.0114 ± 0.0078
0.983 ± 0.003	673	8.0	3566	0.0104 ± 0.0046
	723	8.1	3420	0.0077 ± 0.0060
	783	7.8	3350	0.0057 ± 0.0040
1.00	643	8.3	3816	-0.0010 ± 0.0032
	723	8.2	3869	-0.0030 ± 0.0016
	753	8.2	3927	-0.0049 ± 0.0070
0.983 ± 0.003	783	7.8	3467	-0.0047 ± 0.0050
	681	7.5	3215	-0.0051 ± 0.0038
	715	7.3	2874	-0.0095 ± 0.0060
1.00	735	8.0	3912	-0.0102 ± 0.0062
	774	7.9	3265	-0.0130 ± 0.0046
	653	13.8	2222	-0.0038 ± 0.0018
1.00	693	4.5	2250	-0.0051 ± 0.0031
	723	6.0	1974	-0.0042 ± 0.0052
	773	24.0	3302	-0.0030 ± 0.0038

In the present isotherms the Chemla effect occurs and the crossing point shifts toward higher concentration of the smaller cation with increasing temperature. This is a trend observed in all other systems so far studied. Our interpretation has been stated in previous papers [6, 11].

In order to see whether (1) holds, we plotted the reciprocals of b_K and b_{Rb} against the molar volume in Figs. 2 and 3, respectively.

In Fig. 2, the solid lines are drawn according to (1) with the parameters $A = 4.21 \times 10^{-11} \text{ m}^5 \text{ V}^{-1} \cdot \text{s}^{-1} \text{ mol}^{-1}$, $E = 16.74 \text{ kJ mol}^{-1}$ and $V_0 = 10.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, which were previously calculated from the system (K, Cs)NO₃ [6].

Figure 2 shows that b_K in the present system deviates negatively from (1) at high x_{Rb} . A negative deviation has also been observed for b_{Na} in the system (Na, Rb)NO₃ [12] and was explained as follows: At high concentration of RbNO₃ free space is expected to be relatively great, and therefore an

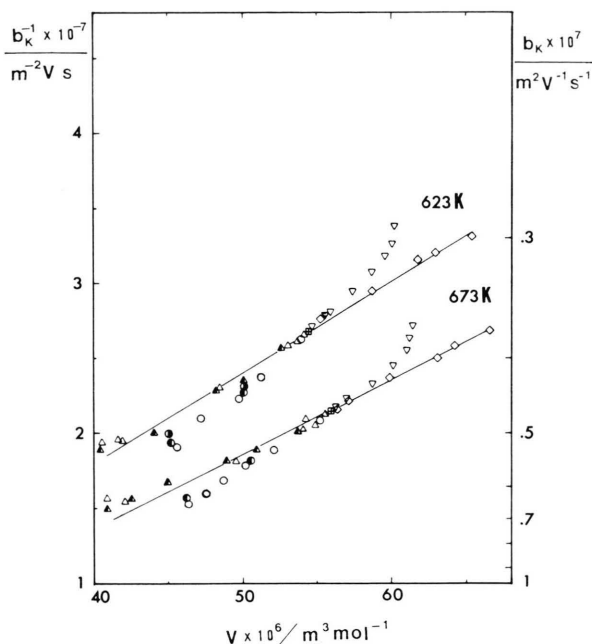


Fig. 2. The reciprocal of b_K vs. molar volume in the molten binary systems (K, M')NO₃; \triangle : M' = Li [14], \blacktriangle : Li [15], \circ : Na [6], \bullet : Na [16], \odot : Na [17], \boxplus : pure KNO₃, ∇ : Rb [this work], \diamond : Cs [6].

Na⁺ ion is attracted by the nearest neighbouring NO₃⁻ ion with less interference from other neighbouring NO₃⁻ ions. In other words, neighbouring Na⁺–NO₃⁻ ion pairs are more structured and therefore their separating motion is retarded.

Very strong interaction of a small cation with anions at low density of the anions has been substantiated also in the MD simulation of molten (Li, K)Cl by Lantelme and Turq [13], where the Li–Cl distance is 212 pm at $x_K = 0.90$ while 221 pm in pure LiCl.

However, such a negative deviation has not been observed for b_{Na} in (Na, Cs)NO₃ [7] nor for b_K in (K, Cs)NO₃ [6]. Thus, this might be a phenomenon peculiar to foreign alkali cations at high concentration of RbNO₃. Also b_{Li} should be measured under

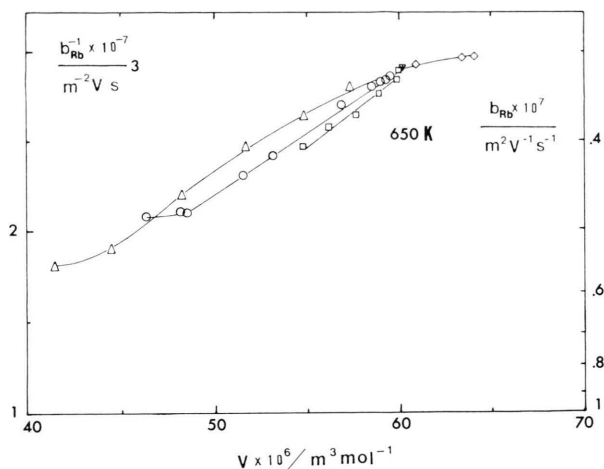


Fig. 3. The reciprocal of b_{Rb} vs. molar volume in the molten binary systems (M, Rb)NO₃; \triangle : M = Li [5], \circ : Na [12], \square : K (this work), \boxplus : pure RbNO₃, \diamond : Cs [1].

such condition. The reason for the negative deviation of b_{Na} and b_K at high concentration of RbNO₃ remains to be investigated.

Figure 3 shows that, even though b_{Rb} in the molten systems (M, Rb)NO₃ (M = Li, Na, K and Cs) is well expressed in the form of (1), the parameters A , V_0 and E are somewhat different from system to system. Figure 3 seems to indicate also that in the systems where M = Li, Na and K, the agitation effect [6] by the M⁺ ions on the internal mobilities of Rb⁺ ions might occur. At a given molar volume, i.e. number density of NO₃⁻ ions, the agitation effect becomes greater in the order Li⁺ < Na⁺ < K⁺. This is presumably because, at a fixed molar volume, the mole fraction of these agitator ions is in this order. At low molar volume b_{Rb} deviates negatively from (1), which is attributable to the free space effect [6].

This work was financially supported by the Grant-in-Aid for Special Project Research No. 61134043 from the Ministry of Education, Japan. One of us (C. Y.) gratefully acknowledges the Ishizaka Scholarship.

- [1] R. Takagi, K. Kawamura, and I. Okada, Z. Naturforsch. **39a**, 759 (1984).
- [2] A. Klemm, H. Hintenberger, and P. Hoernes, Z. Naturforsch. **2a**, 245 (1947).
- [3] A. Ekhed and A. Lundén, Z. Naturforsch. **34a**, 1207 (1979).

- [4] J. Périé and M. Chemla, C. R. Acad. Sci. Paris **250**, 3986 (1960).
- [5] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **34a**, 498 (1979).
- [6] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **38a**, 135 (1983).

- [7] C. Yang, R. Takagi, and I. Okada, *Z. Naturforsch.* **35a**, 1186 (1980).
- [8] V. Ljubimov and A. Lundén, *Z. Naturforsch.* **21a**, 1592 (1966).
- [9] K. Kawamura, I. Okada, and O. Odawara, *Z. Naturforsch.* **30a**, 69 (1975).
- [10] G. J. Janz, V. Krebs, H. F. Siegenthaler, and R. P. T. Tomkins, *Phys. Chem. Ref. Data* **1**, 581 (1972).
- [11] I. Okada, R. Takagi, and K. Kawamura, *Z. Naturforsch.* **35a**, 493 (1980).
- [12] I. Okada, R. Takagi, and K. Kawamura, *Z. Naturforsch.* **36a**, 381 (1981).
- [13] F. Lantelme and P. Turq, *J. Chem. Phys.* **77**, 3177 (1982).
- [14] A. Lundén, J. Habasaki, and I. Okada, *Z. Naturforsch.* **42a**, 683 (1987).
- [15] F. Lantelme and M. Chemla, *Electrochim. Acta* **10**, 663 (1965).
- [16] F. Lantelme and M. Chemla, *Bull. Soc. Chim. Fr.* **1963**, 2200.
- [17] E. P. Honig and J. A. A. Ketelaar, *Trans. Faraday Soc.* **62**, 190 (1966).