

Internal Cation Mobilities in the Molten Binary Systems

$\text{KNO}_3 - \text{Sr}(\text{NO}_3)_2$ and $\text{KNO}_3 - \text{Ba}(\text{NO}_3)_2$

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The relative differences in internal cation mobilities for the molten binary systems $(\text{K}, \text{Sr}_{0.5})\text{NO}_3$ and $(\text{K}, \text{Ba}_{0.5})\text{NO}_3$ have been measured with the Klemm method in the concentration range up to 34 mol% of the alkaline earth cations. From these and available data on the densities and conductivities, the internal mobilities of these cations, b_{K} , b_{Sr} and b_{Ba} , have been calculated. In these systems b_{K} and b_{Sr} or b_{Ba} decrease with decreasing concentration of the K^+ ion. b_{K} is well expressed by $b_{\text{K}} = f_{\text{K}} \cdot b_{\text{K}}^* = f_{\text{K}} \cdot [A/(V - V_0)] \exp(-E/RT)$, where b_{K}^* is the internal mobility of the K^+ ion in such melts as $(\text{K}, \text{Cs})\text{NO}_3$ in which the Coulombic attraction is the dominant factor for the internal mobility of the K^+ ion, the constants A , V_0 , and E being independent of the cation, V is the molar volume of the present mixture and f_{K} the volume fraction of KNO_3 in the mixture. At a given mole fraction of K^+ ions, the internal mobilities are in the order: $\text{Ca} < \text{Sr} < \text{Ba}$. This order could be interpreted as the decreasing order of the Coulombic attraction of these cations with the anion.

Introduction

We have systematically measured the internal mobilities of 10 binary alkali nitrates with Klemm's countercurrent electromigration method (see Refs. in [1]). In all these systems the Chemla effect occurs in a certain range of concentration and temperature. We have found [2] that, when the Coulombic attraction is a dominant factor influencing the mobilities b , as is the case for the system $(\text{K}, \text{Cs})\text{NO}_3$, they can be expressed by

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

where V is the molar volume of the mixture and A , E and V_0 are constants characteristic of the cation of interest and nearly independent of the other cation and temperature.

In a previous study [3] we applied the Klemm method on the binary system $(\text{K}, \text{Ca}_{0.5})\text{NO}_3$ and measured the internal mobilities. In this system the mobility of K^+ , b_{K} , is well expressed by

$$b_{\text{K}} = b_{\text{K}}^* \cdot f_{\text{K}}, \quad (2)$$

where b_{K}^* is the value of b_{K} according to (1) with V the molar volume, of the present mixture and the values of A , V_0 and E from the case of $(\text{K}, \text{Cs})\text{NO}_3$, and f_{K} is the volume fraction of KNO_3 in the mixture with $\text{Ca}_{0.5}\text{NO}_3$. Both b_{K} and

b_{Ca} decrease with increasing concentration of $\text{Ca}_{0.5}\text{NO}_3$.

The main aim of the present study was to see whether these trends also hold in case of the systems $(\text{K}, \text{Sr}_{0.5})\text{NO}_3$ and $(\text{K}, \text{Ba}_{0.5})\text{NO}_3$.

Experimental

The chemicals KNO_3 , $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ were of reagent grade. The salts were dried at 120°C for several hours and stored in a desiccator. After mixing in a chosen ratio they were put in a small quartz vessel and melted.

A separation tube of Vycor (int. diam: 4 mm) packed with quartz powder of 80–100 mesh was dipped into the vessel, and the melt was sucked up to the top of the diaphragm part of the separation tube. Then the separation tube was transferred into an electromigration cell, and electromigration was started. The cell was similar to those used in previous studies [4]. The temperature was kept within 2°C by use of a temperature controller.

As the relative difference in internal mobilities was supposed to be rather great in these systems, the electromigration was terminated with smaller transported charge than in the experiments on binary alkali nitrates. Otherwise, concentrated alkali earth nitrates around the anode, which even could freeze in some cases, would have increased

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the electric resistivity so much as to impede electromigration.

After electromigration the separation tube was cut into pieces of ca. 1 cm length for chemical analysis. The content of the cations in each fraction was determined by flame spectrophotometry.

Results

The relative differences in the internal mobilities of the two cations, ε_{12} , for the systems (K, Sr_{0.5})NO₃ and (K, Ba_{0.5})NO₃ are given to-

Table 1. Experimental conditions and relative difference in internal cation mobilities, ε_{12} in the system KNO₃–Sr_{0.5}NO₃.

Exp. No.	x_{Sr}	T/K	t/hr	Q/C	ε_{12}
1	0.020	688	5.4	1012	0.275 ± 0.008
2		708	6.0	1088	0.272 ± 0.003
3		623	5.0	934	0.216 ± 0.002
4	0.026	650	5.5	1012	0.261 ± 0.002
5		680	4.5	1191	0.301 ± 0.003
6		723	4.0	1092	0.292 ± 0.002
7	0.052	613	4.0	1157	0.307 ± 0.002
8		643	6.0	1093	0.321 ± 0.001
9		683	5.5	1034	0.332 ± 0.002
10	0.125	723	6.0	1070	0.363 ± 0.001
11		613	6.0	963	0.341 ± 0.002
12		643	4.0	935	0.384 ± 0.001
13	0.271	665	5.5	1321	0.380 ± 0.002
14		693	5.0	1204	0.385 ± 0.002
15		623	5.0	1002	0.282 ± 0.006
16	0.335	658	5.5	1334	0.349 ± 0.008
17		723	6.0	1044	0.376 ± 0.007
18		698	4.0	605	0.334 ± 0.004
19		723	5.5	1097	0.337 ± 0.003

Table 2. Experimental conditions and relative difference in internal cation mobilities, ε_{12} , in the system KNO₃–Ba_{0.5}NO₃.

Exp. No.	x_{Ba}	T/K	t/hr	Q/C	ε_{12}
1	0.037	623	5.5	1052	0.153 ± 0.002
2		633	4.0	863	0.173 ± 0.002
3		673	4.2	1043	0.215 ± 0.006
4	0.099	703	5.0	809	0.283 ± 0.003
5		772	4.5	1139	0.322 ± 0.002
6		623	6.5	1233	0.110 ± 0.003
7	0.142	658	6.7	1065	0.145 ± 0.002
8		723	6.5	1152	0.268 ± 0.006
9		773	7.0	1526	0.302 ± 0.005
10	0.204	623	5.0	891	0.079 ± 0.005
11		658	5.5	1055	0.152 ± 0.002
12		723	6.0	1039	0.244 ± 0.005
13	0.338	753	6.0	992	0.263 ± 0.006
14		703	6.5	939	0.183 ± 0.005
15		723	6.0	918	0.190 ± 0.004
16		758	6.2	1001	0.223 ± 0.004
17		773	5.0	1061	0.220 ± 0.003
18		780	6.3	1127	0.224 ± 0.005

gether with the main experimental conditions in Tables 1 and 2, respectively. The ε_{12} values are calculated according to equation (2) in [3].

The internal mobilities of the cations are calculated from ε_{12} and the data on the conductivities, κ , [5] and densities [6] by [3]

$$b_1 = (\kappa V/F)(1 + \varepsilon_{12}x_2), \quad (3a)$$

$$b_2 = (\kappa V/F)(1 - \varepsilon_{12}x_1), \quad (3b)$$

where V is the molar volume of the mixture of interest, x is the mole fraction and the suffixes 1 and 2 refer to the monovalent and divalent cation, respectively. Here, Sr_{0.5}NO₃ and Ba_{0.5}NO₃ are regarded as molar units.

Discussion

In Figs. 1 and 2, the isotherms of b_1 and b_2 at 673 K are given for the systems (K, Sr_{0.5})NO₃ and (K, Ba_{0.5})NO₃, respectively. The dotted lines refer to the isotherms of b_K evaluated from (1) with the parameters A , V_0 and E for the system (K, Cs)NO₃ and V the molar volume of the present mixture.

b_K is greater than b_{Sr} or b_{Ba} in the investigated range, which may be attributed to the fact that the Coulombic interaction of a K⁺ ion with the anion is smaller than that of these alkali earth cations.

As has been done in the study on (K, Ca_{0.5})NO₃ [3], the internal mobilities of K⁺ ions evaluated from (2) are shown as dashed-dotted lines in these figures in comparison with the experimentally obtained ones. In the present cases

$$f_K = x_K V_K / (x_K V_K + x_M V_M), \quad (4)$$

where V_K and V_M are the molar volumes of pure KNO₃ and Sr_{0.5}NO₃ or Ba_{0.5}NO₃, respectively, the additivity of the molar volumes being verified for these alkali, alkaline earth nitrate melts [5]. The b_K 's evaluated from (2) with (4) agree with the experimentally obtained ones within 2.5% errors in the investigated range.

The increase of b_{Sr} and b_{Ba} with increasing x_K may be attributed to the agitation effect by the K⁺ ions, as was already discussed in case of the system (K, Ca_{0.5})NO₃ [3]. The smaller increase of b_{Ba} at high x_K may be due to the large size of the Ba²⁺ ion in comparison with the free space.

The internal mobilities of the alkaline earth ions at 673 K in the systems (K, M_{0.5})NO₃ (M = Ca, Sr and Ba) are plotted against x_K in Figure 3. b_M is in

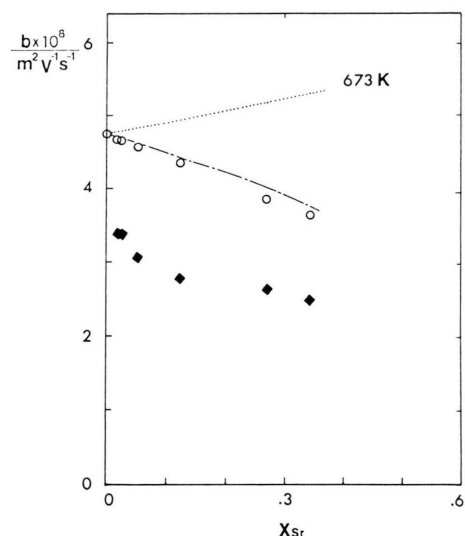


Fig. 1. The isotherms of b_K and b_{Sr} vs. x_{Sr} in the system $(K, Sr_{0.5})NO_3$ at 673 K. \circ : b_K , \blacklozenge : b_{Sr} . As for the dotted line and the dashed-dotted-line, see the text.

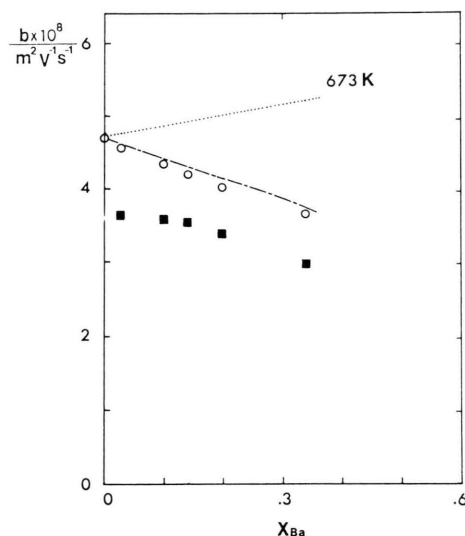


Fig. 2. The isotherms of b_K and b_{Ba} vs. x_{Ba} in the system $(K, Ba_{0.5})NO_3$ at 673 K. \circ : b_K , \blacksquare : b_{Ba} . See the legend of Figure 1.

the order of $Ca < Sr < Ba$. It should be noted that at a given x_K the mobilities of the divalent cations are the greater, the greater the ionic radii. This is probably because the Coulombic interaction of these cations with the NO_3^- ions decreases in this order; the smaller the Coulombic interaction, the more vigorous is the separating motion of unlike ion pairs, and therefore the greater in the internal mobility.

In summary, the trend seen in the previously studied system $(K, Ca_{0.5})NO_3$ holds also for the present systems. Other systems consisting of other alkali ions and alkaline earth ions should also be studied to see whether Eq. (2) holds generally.

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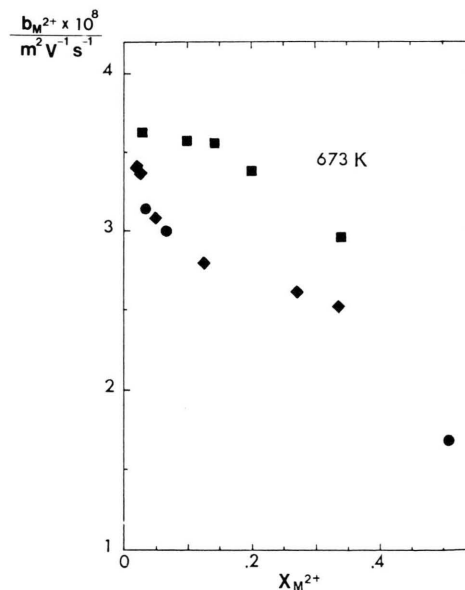


Fig. 3. The comparison of b_{Ca} , b_{Sr} , and b_{Ba} at 673 K. \bullet : b_{Ca} [3], \blacklozenge : b_{Sr} , \blacksquare : b_{Ba} .

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