Internal Cation Mobilities in the Molten Binary System $KNO_3-Ca(NO_3)_2$

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Internal mobility ratios in the molten binary system $KNO_3-Ca_{0.5}NO_3$ have been measured with the Klemm method in a range up to 50 mol% $Ca_{0.5}NO_3$. From these and available data on the densities and conductivities, the internal mobilities of K^+ and Ca^{2+} ions (b_K and b_{Ca}, respectively) have been calculated. With an increase of Ca^{2+} concentration, both b_K and b_{Ca} decrease. The decrease of b_K is presumed to be attributable to the "tranquillisation effect" caused by clustering of NO_3^- ions around Ca^{2+} ions due to the strong Coulombic interaction. The increase of b_{Ca} with increasing concentration of K^+ ions may be attributed to the agitation effect by K^+ ions.

I. Introduction

In previous studies [1] we have determined the internal mobilities of various binary alkali nitrate molten systems using Klemm's countercurrent electromigration method [2]. In many cases the internal mobility b_1 of the cation 1 could be expressed by the equation [3]

$$b_1 = [A_1/(V - V_1^0)] \exp(-E_1/RT), \qquad (1)$$

where V is the molar volume of the mixture, and A_1, E_1 and V_1^0 are constants which are nearly independent of the kind of the coions 2. In cases when (1) did not hold, this could be explained by the free space effect and/or the agitation effect [3].

In the present study we wanted to explore the validity of (1) in case of mixtures of mono- and divalent cations. For this purpose the system $KNO_3-Ca(NO_3)_2$ was chosen. Interestingly this system is readily glass-forming [4–8]. There is an argument, however, that this property is due to the presence of water in this hygroscopic material [9].

Internal mobility ratios of additive binary molten systems containing mono- and divalent cations have so far mainly been measured on chloride and bromide systems with the EMF method. There are, however, no difficulties inherent in using Klemm's method in these cases, and we suppose this method to be presently the most accurate one.

II. Experimental

$Ca(NO_3)_2 \cdot 4\,H_2O$ of reagent grade was vacuum-dried in an oven at 120 °C for several hours. Then it was mixed with dried KNO_3 in a chosen ratio. The mixture was melted and kept at ca. 300 °C in a small quartz vessel.

A separation tube packed with quartz powder of 80–100 mesh was immersed in the sample melt to be sucked up to the top of the diaphragm part of the separation tube. Then the tube was transferred into the large container of the electromigration cell which contained molten $LiNO_3-NaNO_3-KNO_3$ (30–17–53 mol%). Details of the electromigration cell and the experimental procedure were similar to those described in previous papers [1].

After electromigration for several hours, the separation tube was taken out of the large container and cut into several pieces for determining the K^+ and Ca^{2+} ions with emission spectrophotometry. For the measurement of Ca^{2+} a proper amount of KNO_3 was added to the Ca^{2+} standard solution to avoid the effect of ionization interference of the samples.

III. Results

According to Ljubimov and Lundén [10], for an additive binary mixture with the cations 1 and 2 the quantity

$$\varepsilon_{12} = -(F/Q)\,[(N_1/x_1) - (N_2/x_2)], \qquad (2)$$

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Table 1. Relative difference in internal mobilities.

Run	x_{Ca}	T/K	t/hrs	Q/C	ε_{12}
1	0.035	633	4.5	1172	0.316 ± 0.008
2	0.035	653	6.0	1224	0.351 ± 0.007
3	0.064	573	5.2	998	0.325 ± 0.018
4	0.064	623	5.0	959	0.300 ± 0.023
5	0.064	653	5.0	1034	0.318 ± 0.013
6	0.064	673	5.0	950	0.367 ± 0.016
7	0.095	623	5.8	2091	0.560 ± 0.010
8	0.182	623	4.9	1760	0.609 ± 0.009
9	0.182	623	3.8	1384	0.623 ± 0.010
10	0.333	623	2.9	570	0.884 ± 0.028
11	0.507	473	4.9	708	0.812 ± 0.038
12	0.507	523	16.9	2021	0.708 ± 0.050
13	0.507	573	2.5	430	0.818 ± 0.027
14	0.507	623	5.9	441	0.795 ± 0.033
15	0.507	673	2.1	543	0.648 ± 0.028

where x_1 and x_2 are equivalent fractions before the electrolysis, can be obtained from measurements of the number Q/F (Q: transported charge, F: Faraday's constant) of equivalents of anions which have passed the mixture and the number of equivalents N_1 and N_2 which after the electrolysis are found between the anode and a region in the separation tube where the concentrations have not yet changed. Here

$$\varepsilon_{12} = (b_1 - b_2)/(x_1 b_1 + x_2 b_2)\,, \tag{3}$$

where b_1 and b_2 are the internal mobilities. From (3), the mobility ratio $\beta_2 = b_2/b_1$ follows to be

$$\beta_2 = (1 - x_1 \varepsilon_{12})/(1 + x_2 \varepsilon_{12})\,. \tag{4}$$

If also the equivalent volume V_e and the conductance $\varkappa$ are known, from (2) and the relation

$$\varkappa V_e = F(x_1 b_1 + x_2 b_2)\,, \tag{5}$$

one obtains

$$b_1 = \varkappa V_e (1 + x_2 \varepsilon_{12})/F\,, \tag{6a}$$

$$b_2 = \varkappa V_e (1 - x_1 \varepsilon_{12})/F\,. \tag{6b}$$

The mole fractions y_1 and y_2 of potassium nitrate and calcium nitrate, respectively, are related with x_1 and x_2 by

$$y_1 = 2x_1/(1 + x_1)\,, \tag{7a}$$

$$y_2 = x_2/(2 - x_2)\,. \tag{7b}$$

If one prefers to use SI units, one has to replace in (2)–(7) the equivalent fractions, the numbers of equivalents and the equivalent volume by corresponding molar quantities, where KNO_3 and $Ca_{0.5}NO_3$ are considered as the molecules involved.

The obtained values of ε_{12} are summarized in Table 1 with the main experimental conditions. As seen from Table 1, the temperature dependence of ε_{12} at a constant concentration is small, while the concentration dependence is relatively large.

In Table 2, b_1 and b_2 are given together with the molar volume [11] and the electric conductivity [12] used for the calculations in (6a) and (6b).

IV. Discussion

In Fig. 1, the isotherms of b_K and b_{Ca} at 623 K are shown. b_K according to (1) in alkali nitrate melts such as (K, Cs)NO_3 [3] is shown by the dotted line. With increasing x_{Ca} the molar volume V decreases and therefore according to (1) b_K increases, whereas actually it decreases. We found that the experimental b_K can be expressed by the relation

$$b_K = b_K^* [x_K V_K/(x_K V_K + x_{Ca} V_{Ca})] \tag{8}$$

(broken line in Fig. 1), where b_K^* corresponds to the dotted line in Fig. 1 obtained by (1).

The internal mobilities may be interpreted in terms of separating motions of unlike ion pairs, as has successfully been done for binary alkali nitrates [3]. Since the NO_3^- ions cannot readily move away from the divalent Ca^{2+} ions, clustering of NO_3^- around Ca^{2+} will occur. This will retard the exchange rate of the NO_3^- ions coordinating to K^+ ions. Thus divalent coions have a "tranquillisation effect" on monovalent coions, just as heavy coions have a tranquillisation effect on light coions [13].

The factor $f_K = x_K V_K/(x_K V_K + x_{Ca} V_{Ca})$ appearing in (8) can be interpreted as the volume fraction of regions of "KNO_3-like" circumstances in which motion of K^+ according to (1) is expected. In the "$Ca_{0.5}NO_3$-like" regions, separating motion of K^+ and NO_3^- ions will be suppressed. Thus, b_K is well expressed by $b_K^* \cdot f_K$. f_K may be regarded as the factor for the tranquillisation effect.

The trend of decreasing b_K with increasing concentration of divalent cocations is generally observed in many other systems (K, M)X (M = Ca, Sr and Ba; X = Cl and Br [14–19]). Also the decrease of b_{Ca} with decreasing concentration of the monovalent coion is seen in other systems (Li, Ca)X (X = NO_3

Table 2. Internal cation mobilities.

Run no.	x_{Ca}	y_2	T (K)	V (10^{-6} m^3 mol^{-1}) [11]	$\varkappa$ (10^2 S m^{-1}) [12]	b_K [b] (10^{-8} m^2 V^{-1} s^{-1})	b_{Ca} [b] (10^{-8} m^2 V^{-1} s^{-1})
1	0.035	0.018	633	54.21	0.690	3.92 ± 0.03	2.72 ± 0.02
2	0.035	0.018	653	54.66	0.739	4.24 ± 0.03	2.79 ± 0.02
3	0.064	0.033	573	52.37	0.472	2.61 ± 0.01	1.83 ± 0.03
4	0.064	0.033	623	53.50	0.632	3.57 ± 0.035	2.44 ± 0.035
5	0.064	0.033	653	54.20	0.722	4.14 ± 0.025	2.76 ± 0.03
6	0.064	0.033	673	54.60	0.781	4.52 ± 0.02	2.97 ± 0.015
7	0.095	0.050	623	53.01	0.614	3.53 ± 0.03	1.83 ± 0.025
8	0.182 [a]	0.100	623	51.68	0.5646	3.36 ± 0.02	1.52 ± 0.02
9	0.182 [a]	0.100	623	51.68	0.5646	3.37 ± 0.02	1.49 ± 0.02
10	0.334 [a]	0.200	623	49.37	0.4754	3.15 ± 0.03	0.998 ± 0.050
11	0.502 [a]	0.335	473	44.38	0.0594	0.385 ± 0.006	0.164 ± 0.006
12	0.502 [a]	0.335	523	45.18	0.156	0.993 ± 0.019	0.476 ± 0.019
13	0.502 [a]	0.335	573	45.98	0.2569	1.73 ± 0.02	0.730 ± 0.019
14	0.502 [a]	0.335	623	46.80	0.3808	2.59 ± 0.03	1.12 ± 0.03
15	0.502 [a]	0.335	673	47.63	0.4984	3.27 ± 0.04	1.68 ± 0.04
	0	0	623	54.46	0.6515	3.68	
	0	0	623	54.49 [c]	0.659 [c]	3.72	

[a] The conductivity data at these compositions are taken from [12]. b_K and b_{Ca} are calculated by assuming ε_{12} to be equal to the values at almost the same compositions in Table 1. The conductivities at other concentrations are obtained by interpolation of the data in [12].

[b] For the calculation of the standard deviation, errors originating from x_{Ca} (± 0.01) and ε_{12} are taken into account.

[c] Values taken from recently recommended data [28].

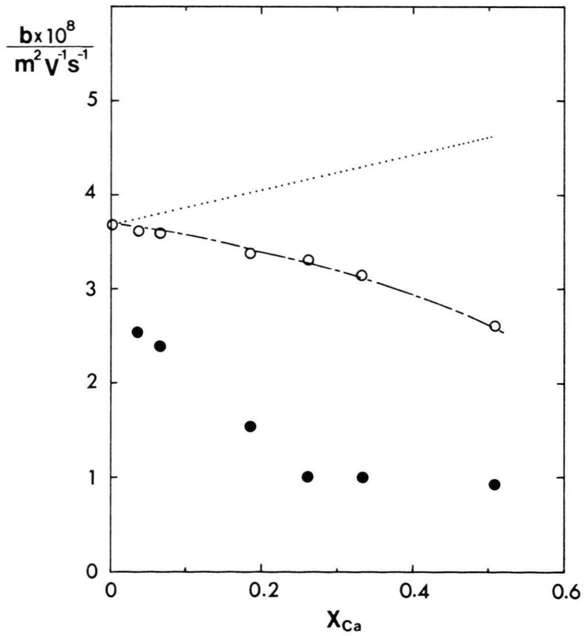

Fig. 1. Internal mobilities at 623 K. ○: b_K, ●: b_{Ca}, ·····: b_K^* drawn according to (1), where the parameters are taken from those in the system (K, Cs)NO_3 ($A = 4.21 \times 10^{-11}$ m^5 · V^{-1} s^{-1} mol^{-1}, $E = 16.74$ kJ mol^{-1} and $V^0 = 10.5 \times 10^{-6}$ m^3 mol^{-1} [3]).

[20], Cl [16, 17] and Br [21]). This may be attributed to a decrease of the agitation effect [13, 22] exerted by the monovalent cocations.

Klemm [23] has presented expected profiles of internal mobility isotherms in additive binary mixtures containing mono- and divalent cations. The present case agrees well with one of the typical cases given by him. He has defined *d* as a coefficient describing the magnitude of the intercationic "drag effect"; the intercationic drag effect refers to the phenomena that the fast cations are hampered in their migration by the slow cations and that the migration of the slow cations is accelerated by the fast cations. Thus, the former phenomenon corresponds to our tranquillisation effect and the latter to our agitation effect. It is interesting to note that the profiles of the isotherms in the present system well resemble those given by him for the case $d = 0.75$ (see Fig. 4a in [23]), although it should be taken into account that mobilities are plotted against y_2 instead of x_2 in his figure. This means that the agitation and the tranquillisation effect are rather great in the present system.

Cleaver et al. [24] explained the marked decrease in the conductivity of a KNO_3 melt on addition of

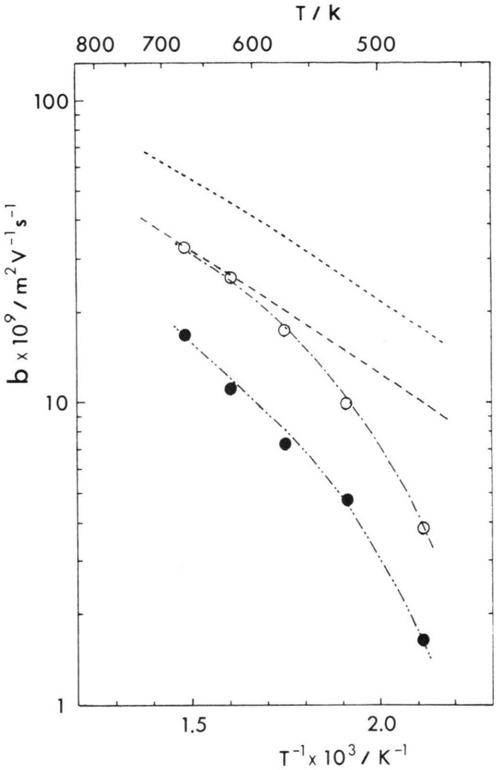

Fig. 2. Temperature dependence of internal mobilities at $x_{Ca} = 0.502$. ○: b_K, ●: b_{Ca}; ⋯⋯: b_K^* (see the caption to Fig. 1); ––––: b_K drawn according to (9).
–·–○–·○–·– $A' = 4.05 \times 10^{-6}$ $m^2 V^{-1} s^{-1} T^{1/2}$, $B = 539$ K and $T_0 = 332$ K in (9).
––●––●––● $A' = 2.69 \times 10^{-6}$ $m^2 V^{-1} s^{-1} T^{1/2}$, $B = 652$ K and $T_0 = 324$ K in (9).

divalent cations such as Ca^{2+} and Ba^{2+} ions in terms of electrostrictive shrinkage of free volume. This is in contrast with our explanation. According to our explanation, if only the Coulombic attraction effect were present, the shrinkage of free volume itself would be favourable for conductivity, as shown by (1).

In Fig. 2 the temperature dependence of b_K and b_{Ca} at $x_{Ca} = 0.502$ is shown. For comparison, b_K^* expected from (1) is shown by a dotted line. The large deviation of the observed b_K from b_K^* even at higher temperature is mainly due to the tranquillisation effect, as stated above. At moderate temperatures the Arrhenius coefficients for b of the two cations are similar, which is the case in other systems such as $LiNO_3-Ca(NO_3)_2$ [20], $NaNO_3-Ca(NO_3)_2$ [25] and $M'Cl-CdCl_2$ ($M' =$ Na, K, and Cs [26]). This also indicates that cooperative motion due to the agitation and tranquillisation effects occurs in these mixtures.

At low temperature the Arrhenius coefficients become higher both for b_K and b_{Ca} and the deviation of b_K from b_K^* becomes particularly greater. This may be attributed to the free space effect [3]; the free space is so small that ions cannot exchange neighbouring counter ions smoothly. The temperature dependence of the Arrhenius coefficients in the self-diffusion coefficients and electric conductivity of the present system has intensively been discussed on the basis of the free volume theory [4–7]. The free space in our definition is similar to the void volume in the free volume theory, but somewhat different. We have defined the free space simply as the total volume minus the volume occupied by "particle cores". On the other hand, the free volume is defined as that which can be redistributed without energy change, and the "critical void volume" should be different for different species.

When the temperature dependence of b_K and b_{Ca} is fitted with a least-squares fit to the Vogel-Tammann-Fulcher type equation

$$b = A' T^{-1/2} \exp[-B/(T - T_0)], \tag{9}$$

values of the constants A' and B result as given in the legend to Fig. 2, and T_0, which is the temperature of the critical void volume, is practically the same for K^+ ions ($T_0 = 332$ K) and for Ca^{2+} ions ($T_0 = 324$ K). Although the ionic size of a K^+ ion is greater than that of a Ca^{2+} ion, the motion in the melt is cooperative, and therefore it is not strange that T_0 is nearly the same for b_K and b_{Ca}. These values may be compared with that ($T_0 = 306$ K at $x_{Ca} = 0.502$) for the diffusion coefficient of a species derived from the conductivity on the assumption that all the constituent species have the same value for T_0 [4].

For further microscopic description of the ionic motion, molecular dynamics simulation should be helpful. Although it has been performed for the present system at $x_{Ca} = 0.5$ at 500 K [27], transport phenomena have not been obtained.

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