Internal Cation Mobilities in the Ternary Molten System (Li, Na, K)NO_3 of the Eutectic Composition

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With the Klemm method, ratios of internal mobilities in a ternary molten mixture (Li, Na, K)NO_3 of the eutectic composition (30–17–53 mol%) have been measured in the temperature range 473 K–673 K. The electric conductivity has been measured with a D. C. method. From these data the internal mobilities, b_{Li}, b_{Na} and b_K, have been obtained on the assumption of additivity for the molar volume. In most cases, b is well represented by the following equation which is known to be valid in binary alkali nitrates. Negative deviations from this equation particularly for b_K at lower temperature may be attributed to the free space effect. $b = \{A/(V - V^0)\} \cdot \exp(-E/RT)$, where V is the molar volume of the mixture and A, E and V^0 are parameters dependent on the cation of interest and independent of temperature and the sort of cocations.

Introduction

We have found that in binary alkali nitrate melts the internal mobilities b_i $(i = 1, 2)$ are well represented by (1), when the Coulombic attraction effect is expected to be the dominant factor for b_i [1–3].

$$b_i = \{A_i/(V - V_i^0)\} \exp(-E_i/RT), \quad (1)$$

where V is the molar volume of the mixture and A_i, E_i and V_i^0 are constants depending only on the cation i and almost not on temperature. When a cation is large (like Rb^+ and Cs^+), the agitation effect by the cocations and the free space effect are not, in general, negligible [3]. In such cases (1) must be modified to some extent, and therefore (1) holds well particularly for small cations such as Li^+ and Na^+.

In order to ascertain that (1) holds independently of the kind of cocations, internal mobilities in a ternary molten (Li, Na, K)NO_3 mixture of eutectic composition have been measured and compared with those of the corresponding binary mixtures. 3 different eutectic compositions have been reported: (Li, Na, K)NO_3 = 37.3–17.8–44.9 mol% [4, 5], 37.5–18–44.5 mol% [4, 6] and 30–17–53 mol% [4, 7]. A mixture of the last composition was chosen in this study.

The ratios of internal mobilities have been measured with Klemm's countercurrent electromigration method [8]. As conductivity data were not available for this composition (the data at 37.53–16.28–46.19 mol% are available [9]), we have measured the conductivity. The molar volume of the mixture has been calculated on the assumption that additivity holds for the molar volume. From these data the internal mobilities have been derived.

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Experimental

The chemicals $LiNO_3$, $NaNO_3$ and KNO_3 were of reagent grade. After drying 120 °C in vacuo overnight, they were mixed in the prescribed ratio. The experimental procedure was quite similar to that for the binary alkali nitrates [10, 11]. In most of the runs the temperature was kept within ± 2 °C with a temperature controller.

The electrical conductivity of the mixture was determined with a direct current method as described by King and Duke [12]. Two $Ag/AgNO_3$ reference electrodes described by Inman [13] were used. The cell constant was determined to be 14.67 cm^{-1} using KCl standard solutions [14].

Results

The relative differences of the b's for the 3 cation pairs are defined as

$$\varepsilon_{12} = (b_1 - b_2)/\bar{b}, \quad (2a)$$

$$\varepsilon_{23} = (b_2 - b_3)/\bar{b}, \quad (2b)$$

$$\varepsilon_{31} = (b_3 - b_1)/\bar{b}, \quad (2c)$$

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where the subscripts 1, 2 and 3 denote Li, Na and K, respectively, and

$$\bar{b} = x_1 b_1 + x_2 b_2 + x_3 b_3 = \varkappa V/F\,, \tag{3}$$

where x_i are the mole fractions of the salts ($x_1 + x_2 + x_3 = 1$), $\varkappa$ is the conductivity and F Faraday's constant.

The $\varepsilon_{\alpha\beta}$ can be determined from chemical analysis and the transported charge quite similarly to the case of binary mixtures [15, 16]:

$$\varepsilon_{\alpha\beta} = -\frac{F}{Q}\left(\frac{N_\alpha}{x_\alpha^0} - \frac{N_\beta}{x_\beta^0}\right), \tag{4}$$

where N_α and N_β are the total amounts of species α and β ($\alpha, \beta = 1, 2, 3$) in the pieces of the separation tube, respectively, after passage of the charge Q, in which the mole fractions are different from the original ones x_α^0 and x_β^0, respectively.

The ε_{12}, ε_{23} and ε_{31} values thus obtained are tabulated in Table 1.

Conductivity data are given in Table 2. With a least squares fit, the conductivity is expressed in the range 523 K ≦ T ≦ 673 K by

$$\varkappa = -0.2473 + 2.143 \times 10^{-3}\,(T-273) + 2.701 \times 10^{-6}\,(T-273)^2\,, \quad (\mathrm{S\,cm^{-1}})\,. \tag{5}$$

It follows from (2) and (3) that

$$b_1 = (\varkappa V/F)\,(1 - x_3\,\varepsilon_{31} + x_2\,\varepsilon_{12})\,, \tag{6a}$$

$$b_2 = (\varkappa V/F)\,(1 - x_1\,\varepsilon_{12} + x_3\,\varepsilon_{23})\,, \tag{6b}$$

$$b_3 = (\varkappa V/F)\,(1 - x_2\,\varepsilon_{23} + x_1\,\varepsilon_{31})\,. \tag{6c}$$

These values are tabulated in Table 3; the molar volumes are calculated from the density data of the pure salts [17] assuming additivity, since e.g. the molar volume of the binary melt (Li, Na)NO_3 has been reported to deviate positively from additivity by only $0.26\,x\,(1-x)\ \mathrm{cm^3\,mol^{-1}}$ (x: mole fraction) [18].

Table 1. Relative differences in internal mobilities (1 = Li, 2 = Na, 3 = K).

T/K	Q/C	ε_{12}	ε_{23}	ε_{31}
473	4450	−0.067 ± 0.002	0.011 ± 0.001	0.056 ± 0.002
523	4050	−0.094 ± 0.002	0.087 ± 0.003	0.006 ± 0.003
543	4170	−0.027 ± 0.001	0.013 ± 0.001	0.014 ± 0.002
573	2510	−0.070 ± 0.002	0.023 ± 0.002	0.047 ± 0.002
593	3010	−0.088 ± 0.002	0.035 ± 0.003	0.052 ± 0.003
633	5610	−0.117 ± 0.002	0.019 ± 0.001	0.098 ± 0.002
673	2620	−0.118 ± 0.003	0.020 ± 0.002	0.098 ± 0.003

Table 2. Conductivity data. Errors of $\varkappa$ are estimated to be within ± 0.005 S cm^{-1}.

T/K	$\varkappa$/S cm^{-1}
523	0.451
553	0.568
573	0.657
598	0.762
623	0.815
643	0.901
673	1.048

Discussion

Table 1 shows that $b_{Li} < b_K < b_{Na}$ at all the experimental temperatures in the present mixture; the Chemla effect [11, 19], which occurs for pairs of Li-Na and Li-K ions, is thus not limited to additive binary salts.

In many cases the internal mobilities b_{Li}, b_{Na} and b_K in binary alkali nitrates are well represented by (1) [3]. We considered V_{Na}^0 to be slightly dependent on temperature (V_{Na}^0 = 25.8, 25.0 and 24.2 cm^3 mol^{-1}

Table 3. Internal mobilities.

T	$\varkappa$	V	b_{Li} [a]	b_{Na} [a]	b_K [a]	b_{Li}^*	b_{Na}^* (b_{Na}^{**})	b_K^*	Δ_{Li}/b_{Li}^* [b]	Δ_{Na}/b_{Na}^* [b]	Δ_K/b_K^* [b]
K	S cm^{-1}	cm^3 mol^{-1}	10^{-8} m^2 V^{-1} s^{-1}			10^{-8} m^2 V^{-1} s^{-1}					
473	0.289	46.00	1.32	1.41	1.40	1.44	1.51 (1.77)	1.68	−0.084	−0.062	−0.167
523	0.457	46.82	2.18	2.38	2.19	2.14	2.35 (2.63)	2.47	0.016	0.015	−0.113
543	0.528	47.16	2.55	2.62	2.59	2.45	2.73 (3.01)	2.81	0.040	−0.042	−0.082
573	0.639	47.67	3.04	3.26	3.19	2.95	3.36 (3.61)	3.37	0.031	−0.030	−0.055
593	0.715	48.02	3.41	3.72	3.59	3.29	3.81 (4.02)	3.76	0.034	−0.024	−0.045
633	0.874	48.73	4.10	4.61	4.53	4.02	4.76 (4.89)	4.58	0.025	−0.030	−0.010
673	1.042	49.97	4.96	5.59	5.48	4.76	5.77 (5.77)	5.42	0.041	−0.032	0.010

[a] The errors resulting from those of ε and x (± 0.01) are less than 0.3%. [b] $\Delta/b^* = (b - b^*)/b^*$.

Table 4. Parameter values of (1).

	A	E	V^0
	$10^{-10}\,m^5\,V^{-1}\,s^{-1}\,mol^{-1}$	$kJ\,mol^{-1}$	$10^{-6}\,m^3\,mol^{-1}$
Li	2.84	17.80	24.7
Na	4.94	19.71	24.2[a]
K	4.21	16.74	10.5

[a] b_{Na}^{**} in Table 3 is calculated according to $V^0(10^{-6}m^3mol^{-1}) = 34.97 - 0.016\,(T/K)$ [3].

at 573 K, 623 K and 673 K [3]), whereas V_{Li}^0 and V_K^0 are virtually independent of temperature. It may be more natural to regard V_{Na}^0 also as temperature independent ($24.2\,cm^3\,mol^{-1}$). The resulting positive deviation of b_{Na} in the binary nitrates from (1) at lower temperature, increasingly at higher concentrations of $NaNO_3$, could be attributed to the agitation effect by Na^+ ions. This modification would be reasonable, because the agitation effect is expected to be relatively large at low temperatures and high concentrations of the small and light cations.

In Table 3, b values from the present experiments are compared with those estimated from (1) denoted by b^*, the parameter values of which being given in Table 4. b_{Na} calculated on the old assumption of a temperature dependent V_{Na}^0 is also given as b^{**} for comparison.

We have regarded b^* as internal mobility when the Coulombic attraction effect is the dominant factor [3]; in other words, if both the agitation effect and the free space effect are negligible, the internal mobility could be well expressed by b^*.

Table 3 shows that b_{Li}, b_{Na} and b_K at 473 K deviate negatively from the respective b^*; this may be attributed to the free space effect. Otherwise, b_{Li} and b_{Na} are in agreement with b_{Li}^* and b_{Na}^*, respectively, within a relative error of 4.2%. As for b_K, it deviate negatively from the respective b^*; this may be attributed to the free space effect. Otherwise, b_{Li} temperature. This may be attributed to the free space effect for the relatively large cation. The agitation effect by Li^+ and perhaps by Na^+ on b_K may be expected, which would be, however, overcompensated by the overwhelming free space effect.

In conclusion, (1) holds well also for the ternary alkali nitrate independently of the sort of coions in most cases; in cases when an appreciable deviation is observed, it may be reasonably attributed to the free space effect.

[1] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **35a,** 1186 (1980).
[2] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **36a,** 381 (1981).
[3] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **38a,** 135 (1983).
[4] H. R. Cravith, J. Phys. Chem. **2,** 209 (1898).
[5] G. J. Janz, C. B. Allen, J. R. Downey, Jr., and R. P. T. Tomkins, Eutectic Data, ERDA-TID-27163-P2, Washington, D.C. 1976, p. 388.
[6] A. G. Bergmann and K. Nogoev, Zh. Neorg. Khim. **9,** 1423 (1964).
[7] International Critical Table **4,** 83 (1964).
[8] A. Klemm, H. Hintenberger, and P. Hoernes, Z. Naturforsch. **2a,** 245 (1947).
[9] L. A. King, C. L. Bissell, and F. R. Duke, J. Electrochem. Soc. **111,** 720 (1964).
[10] I. Okada, Z. Naturforsch. **33a,** 498 (1978).
[11] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **34a,** 498 (1979).
[12] L. A. King and F. R. Duke, J. Electrochem. Soc. **111,** 712 (1964).
[13] D. Inman, J. Sci. Instrum. **39,** 391 (1962).
[14] G. Jones and B. C. Bradshaw, J. Amer. Chem. Soc. **55,** 1780 (1983).
[15] V. Ljubimov and A. Lundén, Z. Naturforsch. **21a,** 1592 (1966).
[16] A. Lundén, Z. Naturforsch. **25a,** 1362 (1970).
[17] G. J. Janz, U. Krebs, H. F. Siegenthaler, and R. P. T. Tomkins, J. Phys. Chem. Ref. Data **10,** 581 (1972).
[18] B. F. Powers, J. L. Katz, and O. J. Kleppa, J. Phys. Chem. **66,** 103 (1962).
[19] J. Périé and M. Chemla, C. R. Acad. Sci. Paris **250,** 3986 (1960).