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

Akira Endoh and Isao Okada
Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Z. Naturforsch. **43a**, 638–642 (1988); received April 26, 1988

For molten (Li, Na, K)Cl of the eutectic composition (53.5–8.6–37.9 mol%), in the temperature range from 773 K to 973 K the relative differences in the internal cation mobilities have been measured by the Klemm method, and the conductivity by a direct current method. From these data and the molar volumes, evaluated from those of the pure salts on the assumption of additivity, internal mobilities of the cations, b_{Li}, b_{Na} and b_K, have been calculated. Below ca. 873 K $b_{Li} < b_K < b_{Na}$, and above $b_{Li} < b_{Na} < b_K$. These orders are interpreted in terms of the potential profiles for cations located between two Cl^- ions. b_{Li} and b_K in the present ternary system can be fairly well expressed by function of the number density of Cl^- ions presented previously for the binary system (Li, K)Cl.

Introduction

We have so far measured internal cation mobilities, b, in 10 molten binary alkali nitrates (see Refs. in [1] and [2, 3]) by Klemm's countercurrent electromigration method [4]. We have found for these systems that, when the Coulombic attraction can be expected to be the dominant factor for the mobility, the internal mobilities are well expressed by [5]

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

where V is the molar volume of the mixture and A, E, and V_0 are parameters characteristic of the cation of interest and independent of the cocation and the temperature. Moreover, also in the molten ternary (Li, Na, K)NO_3 of the eutectic composition this equation appears to hold well [6].

For b_{Li} and b_K in the molten binary (Li, K)Cl [7], we have presented quite a similar equation in which V_0, however, depends on temperature.

The main purpose of the present study is to explore in this respect a ternary chloride system. We have chosen the ternary (Li, Na, K)Cl of the eutectic composition (53.5–8.6–37.9 mol% [8]), whose structure has been studied by X-ray diffraction [9], neutron diffraction [10] and molecular dynamics simulation [9].

Reprint requests to Professor Isao Okada, Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan.

Experimental

The chemicals LiCl, NaCl, and KCl were of reagent grade. These salts were vacuum-dried at 430 K for one day, mixed in the eutectic ratios, melted in a crucible, stirred sufficiently and stored in a small quartz vessel.

A setup of the electromigration cell is shown in Figure 1. The separation tube (width 4 mm, length 20 cm) of Vycor was packed with alumina powder of 150–180 μm as diaphragm.

Chlorine gas, which was produced by electrolysis of a 12 mol dm^{-3} hydrochloric acid solution and passed through concentrated sulfuric acid with nitrogen as carrier gas, was bubbled into the melt around the cathode to convert the otherwise electrodeposited metal into the original salt. About 3 times the amount of chlorine gas theoretically needed for the conversion was introduced to the cathode compartment. Also the catholyte had the eutectic composition. Both electrodes were carbon rods of 3 mm in diameter. During electromigration, the temperature of the catholyte was kept constant within ± 2 K with a temperature controller. The electric current was kept constant with a constant DC supplier (Model PAD 500–0.6 made by Kikusui Electric Co. Ltd., Tokyo).

After electromigration of several hours, quantitative analysis of the cations in the separation tube was performed by flame spectrophotometry.

Other procedures were similar to those described previously [7, 11].

0932-0784 / 88 / 0700-0638 $ 01.30/0. – Please order a reprint rather than making your own copy.

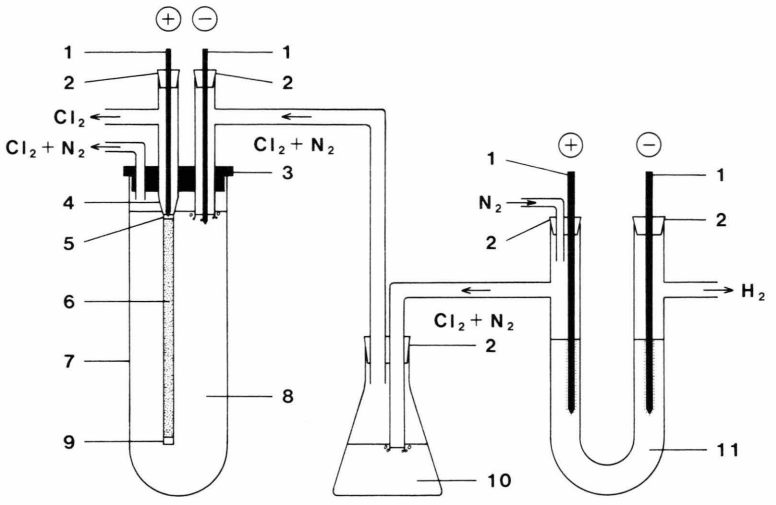

Fig. 1. Setup of the electromigration cell. 1: carbon electrode, 2: Teflon stopper, 3: graphite cover, 4: separation tube, 5: quartz wool, 6: alumina powder, 7: quartz vessel, 8: (Li, Na, K)Cl melt of nearly eutectic composition, 9: quartz filter, 10: conc. sulfuric acid, 11: ca. 12 mol dm^{-3} hydrochloric acid.

Table 1. $\varepsilon_{\alpha\beta}$ values defined in (2).

T/K	t/hr	Q/C	ε_{LiNa}	ε_{NaK}	ε_{LiK}
773	5.1	5264	-0.130 ± 0.005	0.019 ± 0.003	-0.111 ± 0.005
823	6.0	6289	-0.125 ± 0.008	0.008 ± 0.004	-0.117 ± 0.008
873	5.2	5227	-0.137 ± 0.005	0.000 ± 0.004	-0.137 ± 0.005
923	5.0	5192	-0.147 ± 0.005	-0.020 ± 0.004	-0.167 ± 0.005
973	4.5	4815	-0.128 ± 0.005	-0.033 ± 0.004	-0.161 ± 0.005

Table 2. The electric conductivity of the entectic ternary (Li, Na, K)Cl.

T/K	723	748	773	798	823	846	873	896	923	946	973
$\varkappa$/S cm^{-1}	1.549	1.696	1.861	2.005	2.150	2.261	2.397	2.579	2.776	2.980	3.068

The electric conductivity of the mixture was measured by the direct current method described by Duke and Bissell [12]. Two Ag/AgCl reference electrodes were used. The cell constant was measured at 298 K to be 14.40 cm^{-1}, using KCl standard aqueous solutions prepared according to the specifications by Jones and Bradshaw [13]. The accuracy of this cell was checked by measuring the electric conductivity of molten $NaNO_3$.

Results

Table 1 shows the main experimental conditions and the obtained values of $\varepsilon_{\alpha\beta}$ defined as

$$\varepsilon_{\alpha\beta} = (b_\alpha - b_\beta)/\bar{b}, \tag{2}$$

where the suffixes refer to two cations among Li^+, Na^+ and K^+ and

$$\bar{b} = x_{Li}\, b_{Li} + x_{Na}\, b_{Na} + x_K\, b_K = \varkappa V/F. \tag{3}$$

Here the x_i are mole fractions, $\varkappa$ is the conductivity of the mixture and F the Faraday constant. The ε values can be obtained from an equation based on the material balance and the charge balance (cf. [6]).

Data on the electric conductivity are given in Table 2. From a least squares regression, these are expressed by

$$\varkappa = -0.9507 + 1.76 \times 10^{-3}\, T + 2.763 \times 10^{-6}\, T^2 \ (\mathrm{S\,cm^{-1}}). \tag{4}$$

The average deviation is 0.94%. Also with the linear equation

$$\varkappa = -2.919 + 6.161 \times 10^{-3}\, T \ (\mathrm{S\,cm^{-1}}) \tag{5}$$

Table 3. Internal cation mobilities.

T	$\varkappa$	V	b_{Li}	b_{Na}	b_K	b^*_{Li}	b^*_K	$\Delta b_{Li}/b^*_{Li}$	$\Delta b_K/b^*_K$
K	$S\,cm^{-1}$	$cm^3\,mol^{-1}$	$10^{-8}\,m^2\,V^{-1}\,s^{-1}$						
773	1.841	34.33	6.20 ± 0.01	7.05 ± 0.02	6.93 ± 0.02	6.52	7.75	−0.049	−0.106
823	2.136	34.87	7.29 ± 0.02	8.26 ± 0.04	8.20 ± 0.03	7.50	8.47	−0.028	−0.032
873	2.444	35.45	8.41 ± 0.02	9.64 ± 0.03	9.64 ± 0.02	8.47	9.44	−0.007	0.021
923	2.766	36.03	9.54 ± 0.02	11.06 ± 0.03	11.27 ± 0.03	9.41	10.54	0.014	0.069
973	3.101	36.63	10.92 ± 0.02	12.43 ± 0.04	12.82 ± 0.03	10.31	11.74	0.059	0.092

$\Delta b = b - b^*$; b^* represents the value calculated from the parameters presented for the binary system [7].

the experimental data are well expressed, the average deviation being about 0.96%. Here, the quadratic equation is adopted.

From ε and $\varkappa$ values thus obtained, the internal cation mobilities are calculated (cf. [6]):

$$b_{Li} = (\varkappa V/F)(1 + x_{Na}\,\varepsilon_{LiNa} + x_K\,\varepsilon_{LiK}), \quad (6a)$$

$$b_{Na} = (\varkappa V/F)(1 - x_{Li}\,\varepsilon_{LiNa} + x_K\,\varepsilon_{NaK}), \quad (6b)$$

$$b_K = (\varkappa V/F)(1 - x_{Li}\,\varepsilon_{LiK} - x_{Na}\,\varepsilon_{NaK}). \quad (6c)$$

The molar volumes V were calculated from those of the pure melts on the assumption of additivity. This assumption is justified because the excess molar volumes on mixing two molten alkali chlorides are very low [14].

Discussion

Internal mobilities calculated from (6a–6c) are given in Table 3.

Below ca. 873 K,

$$b_{Li} < b_K < b_{Na}, \quad (7)$$

and above this temperature,

$$b_{Li} < b_{Na} < b_K. \quad (8)$$

Thus, the Chemla effect occurs in all combinations of two cations except for the Na^+ and K^+ ions below ca. 873 K.

We will explain these orders in the following by considering superpositions of two pair potentials, as we previously did [15]. Let us assume that a cation is located on a straight line between two Cl^- ions separated by the distance l. If the mixture at $V = 35.45\,cm^3\,mol^{-1}$, the molar volume at which b_{Na} and b_K are nearly equal, would have the NaCl type structure, the distance between two nearest neighbouring Cl^- ions would be 617.5 pm. For $l = 600$ pm and $l = 620$ pm the potentials experienced by the cations, if located between the two Cl^- ions, are depicted in Figure 2. These potentials are obtained by a superposition of two pair potentials given by Tosi and Fumi

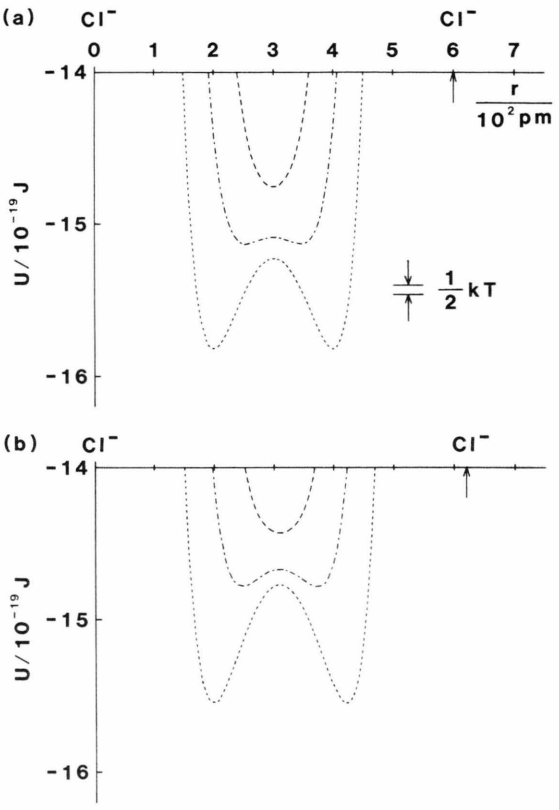

Fig. 2. Schematic description of the potential profiles felt by Li^+, Na^+ and K^+ ions located between two Cl^- ions separated by the distance $l = 600$ pm (a) and $l = 620$ pm (b). For comparison, the magnitude of (1/2) k T at 900 K is also shown.
----: Li^+, – – – –: Na^+, ————: K^+.

	$A/10^{-10}$ $m^5 V^{-1} s^{-1} mol^{-1}$	E/kJ mol^{-1}	$V_0/cm^3 mol^{-1}$	Ref.
b_{Li}	0.4858	26.62	$35.54-0.0169(T/K)$	[7]
b_K	6.080	38.86	$99.16-0.1079(T/K)$	[7]
[a] b_{Li}	2.781	37.75	$57.13-0.0458(T/K)$	This work
[a] b_{Na}	2.884	34.55	$58.21-0.0555(T/K)$	This work
[a] b_K	7.567	38.62	$87.01-0.1029(T/K)$	This work

Table 4. Parameters for b in (l) in the molten systems (Li, K)Cl and (Li, Na, K)Cl.

[a] The parameters in the present work are calculated only from the present data by a least squares fit, the errors being within 0.8%.

for NaCl-type crystals [16]; here, the combination rule of $\varrho_m = \varrho_{Li}x_{Li} + \varrho_{Na}x_{Na} + \varrho_K x_K (= 33.8\,pm)$ is employed for the softness parameter ϱ_m for the repulsive terms in the mixture. The magnitude of the one-dimensional kinetic energy $(1/2)kT$ at $T = 900\,K$ is also shown in Figure 2.

The internal mobilities have been shown to increase with the separating motion of neighbouring unlike ion pairs [15, 17–19]. Figure 2 visualizes how the height of the barrier, which hinders the separating motion changes, with the distance l of the Cl^- ions, i.e. with the molar volume, i.e. in our case with the temperature. On considering especially the behaviour of the barrier for the Na^+ ions, the temperature dependent orders (7) and (8) of the mobilities become plausible. Self-exchange velocities in the present system, calculated by molecular dynamics simulation, reproduce these orders [20].

The polarization model [21–23] presented to interpret the Chemla effect could not explain the different sequences in (7) and (8).

Structural investigations by X-ray and neutron diffraction of the present system [9, 10] indicate that the mean distance between neighbouring Cl^- ions changes in accordance with the molar volume, whereas the distances between neighbouring unlike ions do not appreciably change with temperature or composition. This fact supports our above-stated interpretation of the Chemla effect.

In a previous study on mobilities in the molten binary system (Li, K)Cl [7] we have presented parameters A, E and V_0 in (1) as summarized in Table 4; b^*_{Li} and b^*_K calculated from these parameters are compared with the present values in Table 3.

As seen from Table 3, b_{Li} in the present system appears to be fairly well expressed by the empirical equation with the parameters obtained for the binary system, although systematically a negative deviation is observed at the lower temperatures and a positive deviation at the higher temperatures. A similar trend has been observed for the ternary system

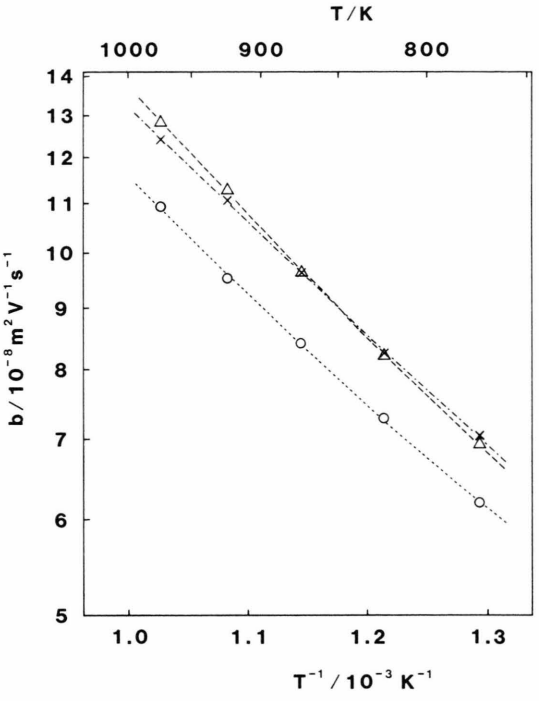

Fig. 3. Logarithm of internal mobilities of molten (Li, Na, K)Cl at the eutectic composition vs. 1/T.
○----: Li^+, ×——: Na^+, △——: K^+.

(Li, Na, K)NO_3 [6]. The negative deviation has been attributed to the free space effect [18, 19] and the positive deviation to the agitation effect [18] by the Na^+ ions. At higher temperature, i.e. at lower number density, the Na^+ ions may be more effective as agitator ions than the Li^+ ions because, at low density, the Li^+ ions will associate with the nearest counter anions with less interference from other anions, and may even play a role as tranquilliser ions [24].

Similarly, b_K in the present system deviates negatively at lower temperatures and positively at higher temperatures. The more distinct deviations for b_K than for b_{Li} may be attributed to the same reasons as for b_{Li}

stated above. It may be reasonable that the largest cation is affected by the free space at lower temperatures. The free space effect corresponds to the sharp potential walls on both sides for the K^+ ion in Figure 2.

The logarithms of b obtained in the present study are plotted against the reciprocal of temperature in Figure 3. From this figure, the free space effect [18, 19] is not distinct even for b_K. Only from the present data, the parameters corresponding to (1) are calculated with a least squares fit and given in Table 4; the lines obtained from the calculated parameters are also drawn in Figure 3. In the calculation of these parameters, effects such as the free space effect, the tranquillisation effect and the agitation effect have not been particularly excluded, whereas in the calculation for the binary system [7] at least the free space effect has been attempted to exclude. It is almost impossible to extract the term due to the Coulombic attraction effect from the b values on the basis of the limited present data.

The parameters for b^* in Table 4 are still tentative. Investigations on more systems are needed to refine the parameters representing the purely Coulombic attraction part of the internal mobilities.

The expenses of this work were defrayed by the Grant-in-Aids for Special Project Research (No. 62124039) and for Scientific Research (No. 62540353).

[1] R. Takagi, K. Kawamura, and I. Okada, Z. Naturforsch. **39a,** 759 (1984).
[2] A. Lundén, J. Habasaki, and I. Okada, Z. Naturforsch. **42a,** 683 (1987).
[3] C. Yang and I. Okada, Z. Naturforsch. **42a,** 1017 (1987).
[4] A. Klemm, H. Hintenberger and P. Hoernes, Z. Naturforsch. **2a,** 245 (1947).
[5] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **35a,** 1186 (1980).
[6] J. Habasaki and I. Okada, Z. Naturforsch. **40a,** 906 (1985).
[7] A. Lundén and I. Okada, Z. Naturforsch. **41a,** 1034 (1986).
[8] E. K. Akopov and A. G. Bergman, Zhur. Neorg. Khim. **11,** 1751 (1966).
[9] A. Endoh, T. Yamaguchi, I. Okada, and H. Ohtaki, Nippon Kagaku Kaishi **1986,** 1492 (in Japanese).
[10] A. Endoh, T. Yamaguchi, Y. Tamura, O. Odawara, I. Okada, H. Ohtaki, and M. Misawa, to be published.
[11] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **34a,** 498 (1979).
[12] F. R. Duke and L. Bissell, J. Electrochem. Soc. **111,** 717 (1964).
[13] G. Jones and B. C. Bradshaw, J. Amer. Chem. Soc. **55,** 1780 (1933).
[14] P. Fellner, I. Votava, and M. Chrenková-Paučírová, Chem. Zvesti **34,** 330 (1980).
[15] I. Okada, Z. Naturforsch. **42a,** 21 (1987).
[16] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25,** 45 (1964).
[17] K. Kawamura, I. Okada, and O. Odawara, Z. Naturforsch. **30a,** 69 (1975).
[18] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **35a,** 493 (1980).
[19] C. Yang, R. Takagi, and I. Okada, Z. Naturforsch. **38a,** 135 (1983).
[20] A. Endoh and I. Okada, unpublished.
[21] C. T. Moynihan and R. W. Laity, J. Phys. Chem. **68,** 3312 (1964).
[22] C. T. Moynihan, Ionic Interactions I, Ed. by I. Petrucci, Academic Press, New York, 1971, p. 369.
[23] S. I. Smedley, The Interpretation of Ionic Conductivity in Liquids, Plenum, New York, 1980.
[24] J. Habasaki, C. Yang, and I. Okada, Z. Naturforsch. **42a,** 695 (1987).