Structural Study on Molten (^{7}Li, K)Cl and (^{7}Li, Na, K)Cl of the Eutectic Composition by Pulsed Neutron Diffraction

Akira Endoh, Toshio Yamaguchi *, Yusuke Tamura **, Osamu Odawara, Isao Okada, and Hitoshi Ohtaki ***

Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Masakatsu Misawa

National Laboratory for High Energy Physics, Oho, Tsukuba 305, Japan

Z. Naturforsch. **43a**, 961–964 (1988); received August 28, 1988

Pulsed neutron diffraction measurements have been performed on molten (^{7}Li, K)Cl and (^{7}Li, Na, K)Cl mixtures of the eutectic composition to determine the nearest neighbour distance between Li^+ and Cl^- ions. Owing to the negative scattering length of the ^{7}Li nucleus, this contribution becomes negative in the radial distribution function and can be separated from the other contributions. The nearest neighbour distance between Li^+ ion and Cl^- ion is found to be 240 pm in both the binary and ternary mixtures.

Introduction

In previous investigations, we have performed X-ray diffraction measurements on molten (Li, K)Cl [1] and (Li, Na, K)Cl [2] mixtures of the eutectic composition ((Li, K)Cl: 58.8–41.2 mol %; (Li, Na, K)Cl: 53.5–8.6–37.9 mol %), and the data were analysed with the aid of molecular dynamics (MD) simulations. By modifying the Tosi-Fumi pair potentials [3], the structure functions $s \cdot i(s)$ ($s = 4\pi \sin\theta/\lambda$, 2θ: scattering angle, λ: wavelength of the incident X-rays, $i(s)$: reduced intensity) and the X-ray weighted radial distribution functions $G^X(r)$ derived from the MD simulations could well reproduce those obtained from the X-ray diffraction method. Owing to the small atomic scattering factor of Li atom, however, it was difficult to detect the Li^+-Cl^- interaction as a distinct peak of $G^X(r)$.

The time-of-flight (TOF) neutron diffraction method became available recently for liquid structure investigations [4]. Since this method can cover a high range of the scattering vector Q, short range interaction such as Li^+-Cl^- can be determined accurately. Moreover, the negative scattering length of the ^{7}Li nucleus is favourable for detecting the Li^+-Cl^- interaction explicitly, because this interaction should appear as a negative value in the neutron-weighted radial distribution function $G^n(r)$.

In the present study, we have performed neutron diffraction on molten (^{7}Li, K)Cl and (^{7}Li, Na, K)Cl mixtures of the eutectic composition with the main aim of determining the nearest neighbour Li^+-Cl^- distance. Since the absorption cross section of ^{7}Li for thermal neutrons (2200 m s^{-1}) is very low compared with that of ^{6}Li (^{6}Li: 940×10^{-24} cm^2, ^{7}Li: 0.045×10^{-24} cm^2 [5]), the obtainable data can be expected to be more precise than those of samples containing ^{6}Li in natural abundance. Figure 1 shows the weight of various contributions to the total X-ray and neutron patterns for molten (^{7}Li, Na, K)Cl of the eutectic composition. For the X-ray pattern, the atomic scattering factor at s = 0 is employed.

We have measured internal cation mobilities in these systems [6, 7]. The structural information is useful for interpreting the mechanism of electric conductivity.

Experimental

Lithium chloride (^{7}LiCl) was prepared from $^7LiOH \cdot H_2O$ (Tomiyama Chemical Co. Ltd., Tokyo;

Present address:

* Department of Chemistry, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01, Japan
** Max-Planck-Institut für Chemie (Otto Hahn Institut), D-6500 Mainz, FRG
*** Coordination Chemistry Laboratory, Institute for Molecular Science, Myodaiji-cho, Okazaki 444, Japan

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

0932-0784 / 88 / 1100-0961 $ 01.30/0. – Please order a reprint rather than making your own copy.

^{7}Li 99.95%) by adding ca. 12 mol dm^{-3} hydrochloric acid solution. Sodium and potassium chlorides were of reagent grade. These salts were vacuum-dried at 430 K for one day and mixed in the eutectic composition by weighing. The mixture was melted and stirred sufficiently in a crucible before pouring into an alumina tube of 9 mm in inner diameter, whose one side was loosely plugged with a quartz bar. After cooling in a desiccator the solidified sample was taken out from the tube, transferred into a quartz cell for the neutron diffraction; the cell, which was 10 mm in inner diameter, 70 mm in height and 0.4 mm in wall thickness, was sealed in vacuo.

Neutron scattering measurements were performed with the High Intensity Total Scattering Spectrometer (HIT) at the National Laboratory for High Energy Physics (KEK), Tsukuba by using a pulsed spallation neutron source. The sample cell was heated with two infrared lamps facing each other. The temperature was kept at 668 K for (^{7}Li, K)Cl and at 625 K for (^{7}Li, Na, K)Cl within 1 K during the measurements. Besides the samples, scattered intensities were measured for background, an empty cell and a vanadium rod of 10 mm in diameter.

The detectors were set at the scattering angles of 8°, 14°, 21°, 27°, 42°, 91° and 150°. The beams collected at the ^{3}He detectors set at 27° and 42° were adopted for the data analyses. The detectors were connected with 2048-channel analysers. The covered Q ranges were 0.0050–0.2175 pm^{-1} for the detector at 27° and 0.0075–0.3330 pm^{-1} at 42°. Each sample was measured for ca. 9 hs; the maximum counts at a channel connected to the detector set at 150° were about 500 000. Details of the instrument and its performance have been described elsewhere [8].

The observed intensities were corrected for background, absorption and multiple and incoherent scattering, and normalised to the absolute unit by using the scattering intensity from the vanadium rod. The structure factor $S(Q)$ is defined by

$$S(Q) = [I(Q) - \sum b_i^2 + (\sum b_i)^2]/(\sum b_i)^2, \qquad (1)$$

where $I(Q)$ represents the normalised intensity and b_i is the coherent scattering length of the i-th nuclear species, which was taken from the literature [5].

$G^n(r)$ is calculated by the Fourier transformation

$$G^n(r) = 1 + (1/2\pi^2 \varrho_0 r) \int_0^{Q_{max}} Q(S(Q) - 1) \sin(r Q)\, dQ, \qquad (2)$$

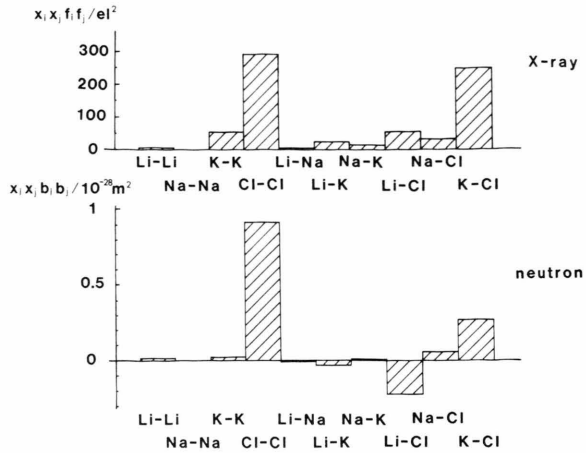

Fig. 1. Weighting of contributions of the relevant atom pairs to the total X-ray and neutron patterns for molten (^{7}Li, Na, K)Cl of the eutectic composition. The scales of the ordinates are drawn so that the sums of the absolute heights on the drawing are equal in both cases. x_i is the atomic fraction of atom i, f_i the atomic scattering factor of i at $s = 0$, and b_i the bound scattering length.

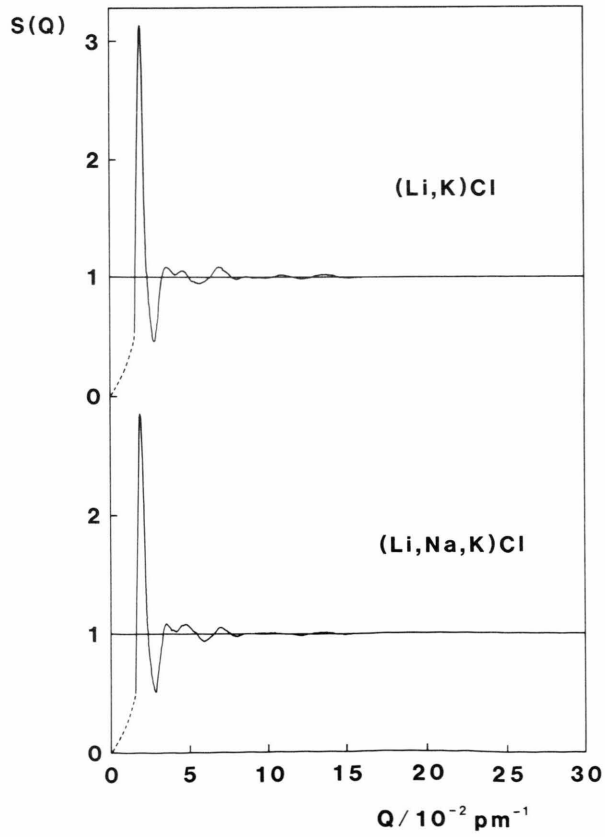

Fig. 2. The structure factors $S(Q)$.

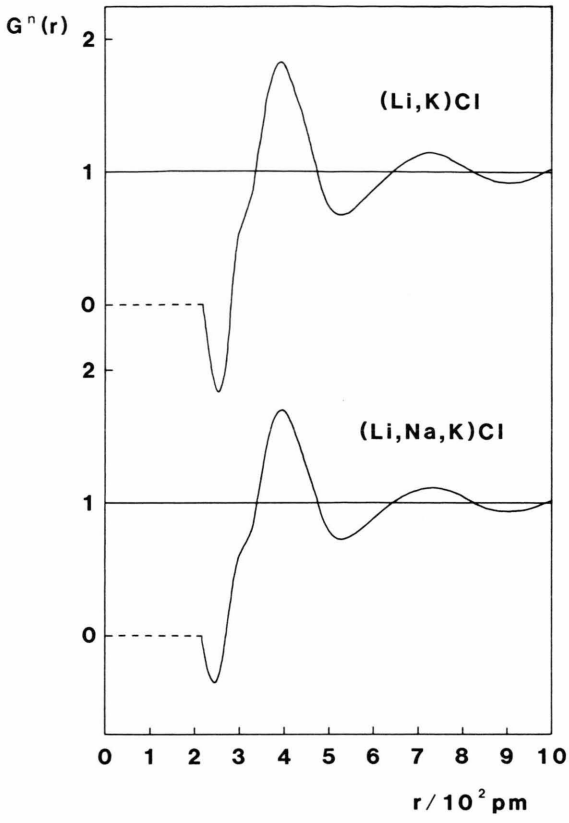

Fig. 3. The radial distribution functions $G^n(r)$.

where ϱ_0 denotes the number density of atoms, and Q_{max} is the upper limit of Q restricted under the experimental conditions.

Results and Discussion

The obtained $S(Q)$'s are shown in Figure 2. For the calculation of the $G^n(r)$'s, Q_{max}'s were 0.181 pm^{-1} for (^{7}Li, K)Cl and 0.182 pm^{-1} for (^{7}Li, Na, K)Cl. The $G^n(r)$'s are shown in Figure 3. In view of the previous results by MD simulation [1, 2], we have analysed the $G^n(r)$'s. As seen in Fig. 3, the first peak makes a negative contribution to the $G^n(r)$ around 240 pm for both melts, which should be referred to the Li^+-Cl^- interaction. The second peak appearing around 390 pm in both melts is assignable to the interaction between Cl^- ions coordinating to the central Li^+ ion. A discernible shoulder around 310 pm is ascribed to the K^+-Cl^- interaction. In the case of the X-ray diffraction measurements, this interaction has more clearly been observed [1, 2]. Thus, X-ray diffraction is superior to neutron diffraction to detect the K^+-Cl^- interaction. This fact is also clear from Fig. 1, since the weight of the K^+-Cl^- contribution to the total X-ray pattern is larger than that to the total neutron pattern. In the case of the (^{7}Li, Na, K)Cl mixture, the Na^+-Cl^- interaction cannot be observed in the present neutron diffraction measurement mainly because of the small mole fraction of sodium chloride.

Table 1 summarises the distances of the nearest neighbours (peak positions) between unlike ion pairs and between Cl^- ions determined from X-ray and neutron diffraction of the present mixtures and the pure melts. The distances between unlike ion pairs are almost the same in the present mixtures as in the pure melts, while those between Cl^- ions change on mixing.

As seen from Table 1, the Li^+-Cl^- distance obtained in the previous studies [1, 2] of a combination of X-ray and MD-simulation is smaller than that obtained in the present neutron diffraction experiments. In these previous studies the $G^X(r)$'s obtained by X-ray diffraction were analysed by MD simulations. In these simulations the Tosi-Fumi potentials and the combination rule for mixtures presented by Larsen et al. [9] were used with a small modification; that is, the softness parameter common for all the ion pairs was multiplied by 0.92, so that the $G^X(r)$ and $s \cdot i(s)$ obtained by the MD simulation should well agree with the corresponding data obtained by the X-ray diffraction. Since the contribution of Li^+-Cl^- pairs to the total $G^X(r)$ or $s \cdot i(s)$ is relatively small, the MD-results based on these $G^X(r)$ or $s \cdot i(s)$ could not necessarily yield very accurate values. As for the Li^+-Cl^- pair, the present data can therefore be considered to be more accurate than those previously obtained by a combination of the X-ray diffraction and the MD simulation.

This appreciable discrepancy suggests that the combination rule of using a common value as the softness parameter in the pair potentials is not suitable for reproducing structure very accurately by MD or Monte Carlo simulation.

We have interpreted the mechanism of electric conductivity in the present systems from the structural aspect [6, 7, 10]. In [7] and [10], we have explained the experimental results by using simplified potential profiles for cations located between two Cl^- ions separated by the distance determined on the assumption of the simple cubic arrangement. For the explanations,

Table 1. Distances of the nearest neighbours (peak positions) between unlike ion pairs and between Cl^- ions determined by means of X-ray and neutron diffraction. Parentheses mean that the peak positions have not distinctively been detected.

Salt	Method	T	Li–Cl	Na–Cl	K–Cl	Cl–Cl	Ref.
		K	pm				
(Li, K)Cl	neutron	668	240		(310)	390	this work
	X-ray + MD	668	231		308	385	[1]
(Li, Na, K)Cl	neutron	625	240		(310)	390	this work
	X-ray + MD	625	231		307	375	[2]
LiCl	X-ray	923	240			386	[11]
NaCl	X-ray	1083		273			[12]
	neutron	1148		278		391	[13]
KCl	X-ray	1173			305		[14]
	neutron	1073			306	482	[15]

changes in the distance between Cl^- ions on mixing and with temperature have to be invoked. The results of the present investigation corroborate our interpretation of the mechanism of electric conductivity in the present systems.

In conclusion, the nearest neighbour distance between Li^+ and Cl^- ions in the mixtures could be determined more accurately by the present neutron diffraction experiments than by the X-ray diffraction measurements. The distance is determined to be 240 pm in both mixtures. This value is much the same as that in pure molten LiCl, irrespective of the temperature difference.

The expenses of this work were partly defrayed by the Grant-in-Aids for Scientific Research (No. 63470008) and for International Joint Research (No. 63044040) from the Ministry of Education, Science and Culture, Japan.

[1] I. Okada, H. Okano, H. Ohtaki, and R. Takagi, Chem. Phys. Lett. **100,** 436 (1983).
[2] A. Endoh, T. Yamaguchi, I. Okada, and H. Ohtaki, Nippon Kagaku Kaishi **1986,** 1492 (in Japanese).
[3] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25,** 45 (1964).
[4] T. Yamaguchi, Y. Tamura, I. Okada, H. Ohtaki, M. Misawa, and N. Watanabe, Z. Naturforsch. **40a,** 490 (1985).
[5] V. F. Sears, Thermal Neutron Scattering Lengths and Cross Sections for Condensed Matter Research, Atomic Energy of Canada Limited Report No. AECL-8490, 1984.
[6] A. Lundén and I. Okada, Z. Naturforsch. **41a,** 1034 (1986).
[7] A. Endoh and I. Okada, Z. Naturforsch. **43a,** 638 (1988).
[8] Y. Ishikawa, N. Watanabe, Y. Endoh, N. Niimura, and J. M. Newsome, Ed., Proceedings of the Fourth Meeting of International Collaboration on Advanced Neutron Source (ICANS-IV), KEK-Report II, KEK, Tsukuba, 1981.
[9] B. Larsen, T. Førland, and K. Singer, Mol. Phys. **26,** 1521 (1973).
[10] I. Okada, Z. Naturforsch. **42a,** 21 (1987).
[11] H. Ohno, M. Yoroki, K. Furukawa, Y. Takagi, and T. Nakamura, J. Chem. Soc. Faraday Trans. I **74,** 1861 (1978).
[12] H. Ohno and K. Furukawa, J. Chem. Soc. Faraday Trans. I **77,** 1981 (1981).
[13] S. Biggin and J. E. Enderby, J. Phys. C: Solid State Phys. **15,** L305 (1982).
[14] R. Takagi, H. Ohno, and K. Furukawa, J. Chem. Soc. Faraday Trans. I **75,** 1477 (1979).
[15] J. Y. Derrien and J. Dupuy, J. Phys. Paris **36,** 191 (1975).