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Structural Analysis of Molten LiCl-$CaCl_2$ System by X-ray Diffraction†

Nobuya IWAMOTO*, Norimasa UMESAKI**, Tadashi ASAHINA*** and Mineo KOSAKA***

Abstract

The structures of molten system $(LiCl)_x - (CaCl_2)_{1-x}$, with x=1,2/3,1/2 and 0, are investigated by X-ray diffraction analysis. The obtained nearest neighbour coordination number $n_{Li/Cl}$ in molten LiCl is explained well with the volume expansion $\Delta V_f/V_s$ (=26.2%) on melting. In molten $CaCl_2$, the obtained distances and coordition numbers are close to those found in the crystalline form, which are consistent with the extraordinary small $\Delta V_f/V_s$ (=0.9%). $n_{Li/Cl}$ and $n_{Ca/Cl}$ in molten $LiCaCl_3$ or Li_2CaCl_4 are similar to those found in molten LiCl and $CaCl_2$, respectively. In addition, over the whole range of concentration in this system, the nearest neighbour distance $r_{Cl\text{-}Cl}$ appeares to show the linear dependence on the molar fraction.

These behaviors in this system are analized to be a result of the strong Coulombic attraction between Li^+ or Ca^{2+} and Cl^-, which implies the formation of $LiCl_4$ and $CaCl_6$ ionic groups. Our results by X-ray analysis do not give the evidence of the existence of some ionic complexes proposed previously being based on results of thermodynamical measurements.

KEY WORDS: (Calcium chloride) (Lithium chloride) (Liquid structure) (X-ray analysis)

1. Introduction

Radial distribution functions obtained by X-ray or neutron analyses are the most valuable data to know the structures of ionic liquids.The structural analyses of ionic liquids have been performed fruitfully on molten alkali halides, but scarcely on molten alkaline earth halides.

Recently, the existence of doubly charged cation in molten $BaCl_2$ was shown by the study of partial distribution functions obtained with a neutron diffraction analysis[1], though it was not consistent with the singly charged cation complex model proposed from the analysis of the electrical conductivity of molten alkaline earth halides.[2] But these experiments were performed on single salts and the structures of mixed molten systems of these salts have not been studied systematically.

The most remarkable difference in thermal properties between alkali halides and alkaline earth halides is the volume expansion $\Delta V_f/V_s$ (%) on melting. Though alkali halides have rather large values i.e. LiCl(26.2%),NaCl(25.0%) and KCl(17.3%), alkaline earth halides have pretty small values i.e. $CaCl_2$ (0.9%), $SrCl_2$ (4.2%) and $BaCl_2$ (3.5%). This behavior of alkaline earth halides accounts for the small changes of the coordination numbers and the little disordering on melting.[3]

Φye et al.[4] and Ejima et al.[5] measured thermal properties e.g. density, viscosity, surface tension, conductivity and ultrasonic propergation in molten ACl (A=Li, Na, K and Rb) $-BCl_2$ (B=Mg and Ca) systems and found the existence of complex anions in molten $MgCl_2$ but not in $CaCl_2$.

Emons et al.[6] also measured thermal properties e.g. EMF, mobility, density and conductivity in molten ACl (A=Li, Na, K, Rb and Cs) $-CaCl_2$ systems and proposed the existence of complex anions of $(CaCl_3)^-$ or $(CaCl_4)^{2-}$ types, which was not consistent with the models mensioned above. The formation of complexes in molten $MgCl_2$ was also supported by the results of Raman spectroscopy measurements[7], but not found in molten $CaCl_2$ yet.

Recently computer simulations of molten salts have been progressing very much and remarkably good agreements with experiments were reported, though most calculated systems were molten alkali halides where interionic potentials were known rather well.

The liquid structures of alkaline earth halides or mixed systems of them have less studied[9),10)] and less made clear yet. Though some models have been postulated in these systems as is mentioned above, it is necessary for the definite understanding of the liquid structure of these systems to study directly and

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systematically by X-ray or neutron diffraction analyses.

The authors have been studying the liquid structures of mixed alkali and alkaline earth chlorides by X-ray diffraction methods. In this paper, molten systems $(LiCl)_X$–$(CaCl_2)_{1-X}$ with x=1, 2/3, 1/2 and 0 were analyzed.

2. Experimental

The reagents LiCl and $CaCl_2$ (Rare Metallic Co., 99.9% purity) were treated previously by drying and melting in a vacuum. After being weighed and mixed throughly, the samples were melted under HCl or Ar atmospheres and purified.

The sample salt was placed on a flat Pt tray (35×25 ×3 mm^3) and melted in a furnace made of alumina and wound Pt wire under a He atmosphere in a brass chamber. The temperature was controlled to within a maximum error of 10°C throughout the measurement. The X-ray beam passed through a window of Ni foil of thickness 10 μm into the chamber.

The X-ray diffraction experiment was carried out with the use of a $\theta-\theta$ diffractometer with parafocusing reflection geometry and Mo K $\bar{\alpha}$ (λ =0.7107 $\times 10^{-1}$nm) radiation monochromatized by a curved graphite monochrometor mounted in the path of the diffracted beam. Slit systems of 1/2–1/2 and 1–1 degrees were employed for the low ($3° \leqq \theta \leqq 10°$)and high ($8° \leqq \theta \leqq 50°$) scattering angles, respectively, where θ is the scattering angle. The X-ray scattering intensities were measured at 0.25° intervals over the whole range of scattering angle using the step–scanning technique by means of a scintillation counter. Several runs were made in order to accumulate forty thousand counts per datum point for the whole range.

After the measured X-ray intensities were corrected for background, polarization and Compton scattering, they were scaled by means of the Krogh-Moe-Norman and the high angle methods to the theoretical intensities arising from independent atoms contained in the stoichiometric unit, and the total coherent scattering intensities I_{eu}^{coh} (S) were calculated.

The radial distribution function D(r), the correlation function G(r) and the reduced intensity function S·i(S) are gjven as

$$D(r)=4\pi r^2\rho_0\sum_{i=1}^{m}\overline{K}_i+\sum_{i=1}^{m}(\overline{K}_i)^2\frac{2r}{\pi}\int_0^{Smax} S\cdot i(S)\sin(Sr)dS \quad (1)$$

$$G(r)=1+\frac{\sum_{i=1}^{m}(\overline{K}_i)^2}{\sum_{i=1}^{m}\overline{K}_i 2\pi^2\rho_0 r}\int_0^{Smax} S\cdot i(S)\sin(Sr)dS \quad (2)$$

$$S\cdot i(S)=S\left(\frac{I_{eu}^{Coh}(S)}{\sum_{i=1}^{m}f_i(S)^2}-1\right) \quad (3)$$

where m is the number of atoms contained in the stoichiometric unit, $\bar{K}_i$ the effective electron number[12] of atom i, ρ_0 the mean electron density, $f_i(S)$ the independent atomic scattering factor[13] of atom i corrected for anomalus dispersion,[14] and S_{max} the maximum value of S ($=4\pi \sin\theta/\lambda$) reached in the diffraction experiment. The constants used in the calculations of eqs. (1) — (3) are given in **Table 1**. All calculations were carried out by the degital computer ACOS model 900 at the caculation center of Osaka University.

Table 1 Parameters used in the calculations of eqs. (1), (2) and (3).

	LiCl	Li_2CaCl_4	$LiCaCl_3$	$CaCl_2$
x	1.00	0.67	0.50	0.00
mp (°C)	612	524	559	774
Obs. temp. (°C)	650	570	607	800
Density (g/cm^3)[6]	1.49	1.78	197	2.07
ρ_0	0.0212	0.0191	0.0155	0.0112
Effective electron number				
$\bar{K}_{Li}$	2.33	2.21	2.19	
$\bar{K}_{Ca}$		20.74	20.57	20.29
$\bar{K}_{Cl}$	17.67	17.21	17.08	16.85
S_{max}($\times 10nm^{-1}$)	12.0	13.5	13.5	13.5

$(LiCl)_x - (CaCl_2)_{1-x}$; x: molar fraction

3. Results and Discussion

The reduced intensity functions of the molten $(LiCl)_X$–$(CaCl_2)_{1-X}$ system with x =1, 2/3, 1/2 and 0 are shown in **Fig.1**. This figure shows that the packing of ions in this system becomes less loose as the content of $CaCl_2$ increases, which corresponds to the continuity of the oscillation to higher S values. Then, the upper limits of the Fourier integral to calculate D(r) are chosen to be 12.0 × 10 nm^{-1} for LiCl and 13.5 × 10 nm^{-1} for others.

The distances r_{i-j} and coordination numbers $n_{i/j}$ of the nearest neighbour i–j ionic pairs are calculated by

adopting the following Debye scattering equation to the observed S·i(S) curves and shown in **Table 2.**

$$S\cdot i(S)\sum_{i=1}^{m} f_i(S)^2=\sum_{i=1}^{m}\sum_{j=1} n_{i/j} f_i(S)$$

$$f_j(S)\exp(-b_{i-j}S^2)\frac{\sin(S r_{i-j})}{r_{i-j}} \qquad (4)$$

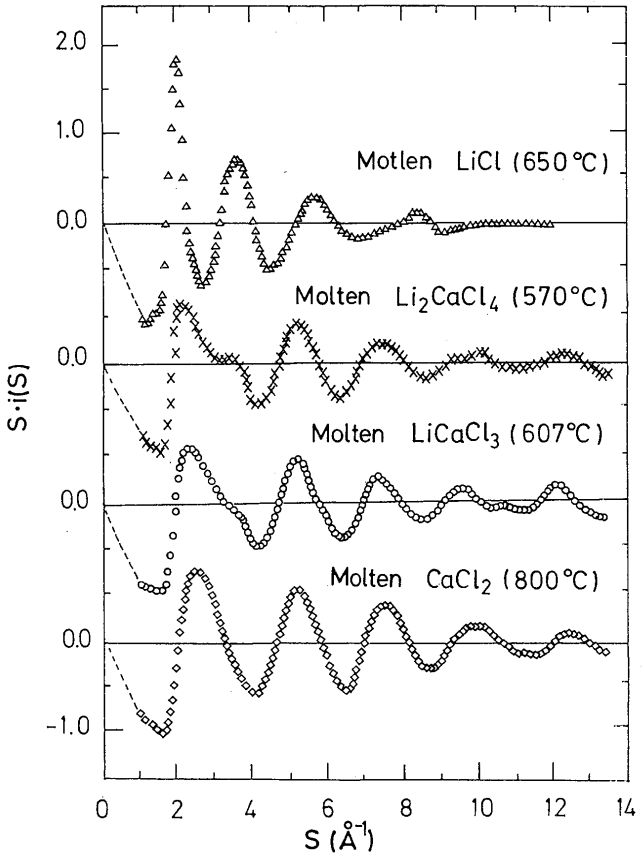

Fig. 1 Reduced intensity functions S·i(S) of molten system LiCl–$CaCl_2$.

Table 2 Observed distances r_{i-j} and coordination numbers $n_{i/j}$ of the nearest neighbour i – j ionic pairs in molten system $(LiCl)_x-(CaCl_2)_{1-x}$, with x=1, 2/3, 1/2 and 0.

Salts	i	j	r_{i-j} ($\times10^{-1}$nm)	$n_{i/j}$ (atoms)
LiCl	Li	Cl	2.45	4.1
	Cl	Cl	3.85	12.1
Li_2CaCl_4	Li	Cl	2.45	4.0
	Ca	Cl	2.72	5.8
	Cl	Cl	3.75	6.3
$LiCaCl_3$	Li	Cl	2.45	4.0
	Ca	Cl	2.73	5.9
	Cl	Cl	3.70	6.6
$CaCl_2$	Ca	Cl	2.72	5.5
	Cl	Cl	3.55	7.4

$r_{i-j}\pm0.01\times10^{-1}$nm, $n_{i/j}\pm0.1$ atoms

where b_{i-j} is half the mean-square variation of r_{i-j}.

Radial distribution function D(r), function D(r)/r and a correlation function G(r) of molten LiCl are presented in **Fig.2.** The first peak at 2.45×10^{-1} nm corresponds to the nearest Li–Cl ionic pair. The coordination number of this pair (4.1) can be compared with the calculated one (4.2) with the following equation[15] about the volume change on melting.

$$\frac{\Delta V_f}{V_s}=\frac{V_l-V_s}{V_s}=\frac{(r^s)^3}{(r^l)^3}\times\frac{n^l}{n^s} \qquad (5)$$

where V are molar volumes and subscripts s and l mean solid and liquid states at the melting point, respectively. The second peak at 3.85×10^{-1}nm corresponds to the nearest Cl–Cl ionic pair, the third around 5.5×10^{-1}nm to the second nearest Li–Cl pair and the fourth around 7.0×10^{-1}nm to the second nearest Cl–Cl pair.

In molten LiCl, a small Li^+ ion ($r_{Li^+}=0.60\times10^{-1}$nm) becomes stable by tightly attracting four large Cl^- ions ($r_{Cl^-}=1.81\times10^{-1}$nm). The volume expansion on the melting breakes the crystal structure of NaCl type and makes ionic tetrahedrons of Cl^- around Li^+. But this tetrahedron of Cl^- is not so permanent to be called a complex anion. Each Cl^- ion of the tetrahedron rearranges separately and a Li^+

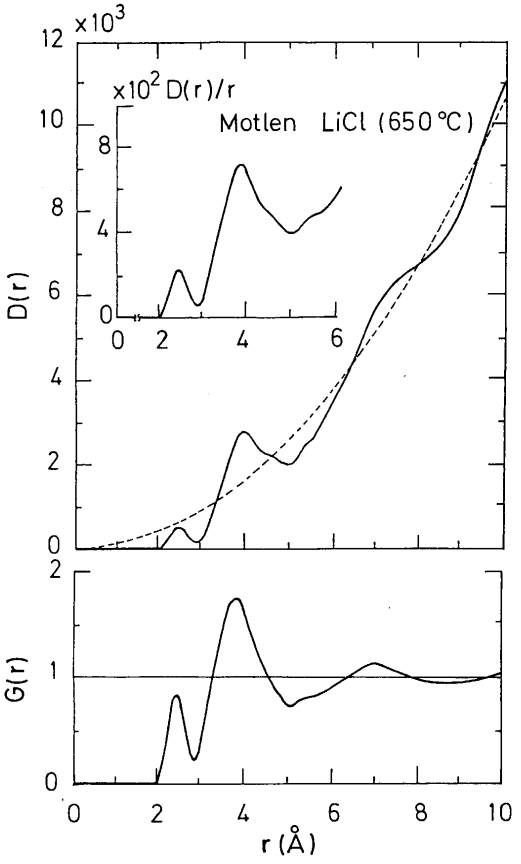

Fig. 2 Radial distribution function D(r), function D(r)/r and correlation function G(r) of molten LiCl (650°C).

ion has four nearest neighbour Cl^- ions on the time average.

Many measurements[16)-18)] and computer simulations[19)-21)] have already been performed on molten LiCl. These results are summarized in **Table 3**. The agreement of our results is fairly well.

The functions, D(r), D(r)/r and G(r) of molten $CaCl_2$ are presented in **Fig.3**. The first peak at 2.72×10^{-1}nm corresponds to the nearest Ca–Cl ionic pair, the second at 3.65×10^{-1}nm to the nearest Cl–Cl pair, the third around 5.5×10^{-1}nm to the nearest Ca–Ca pair and the fourth around 6.4×10^{-1} nm to the second nearest Ca–Cl and Cl–Cl ionic pairs. The observed coordination number $n_{Ca/Cl}$ (5.5) is close to the calculated one(5.8) from the volume expansion. Observed distances, r_{Ca-Cl} and r_{Cl-Cl} and coordination numbers,$n_{Ca/Cl}$ and $n_{Cl/Cl}$ are close to those found in the crystalline form, which are consistent with the extraordinary small value of $\Delta V_f/V_s$ on melting.

The crystal structure[22)] of $CaCl_2$ is composed of disordered $CaCl_6$ octahedrons which are made of the nearest Ca–Cl ionic pairs ($r=2.70\sim2.76\times10^{-1}$nm). These octahedrons are connected with common edges and the structure of ionic packing is fairly loose. Thus, the distances and the coordination numbers of nearest ionic pairs would not change on melting. Namely, in molten $CaCl_2$ Ca^{2+} ions are surrounded octahedrally by nearly $5.5 \sim 6.0$ Cl^- ions on an average,too.

But if the freedom of ions in liquid states is considered the octahedron in molten $CaCl_2$ must be symmetrical as is shown in **Fig.4** which is different from the disordered one found in solid $CaCl_2$. The reduced intensity functions for these two octahedrons are calculated and compared with the observed S·i(S) in **Fig.5**. The observed S·i(S) agrees pretty well with the calculated one for the symmetrical octahedron

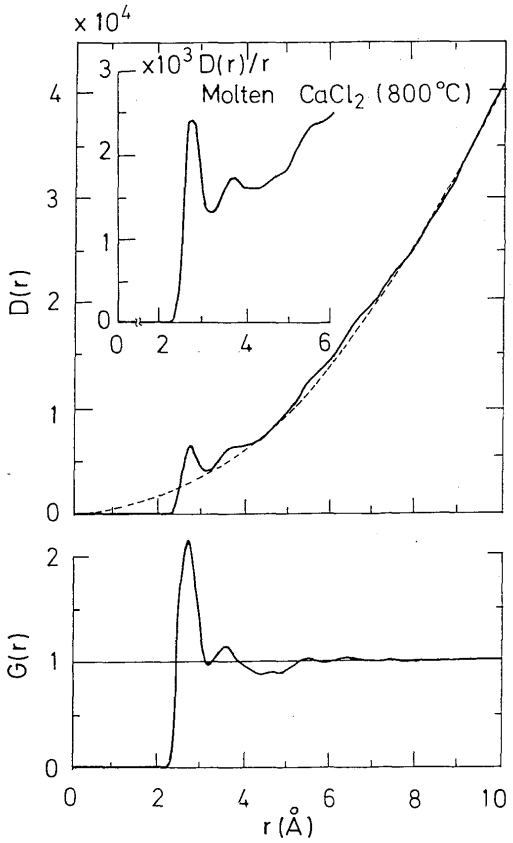

Fig. 3 Radial distribution function D(r), function D(r)/r and correlation function G(r) of molten $CaCl_2$ (800°C).

Table 3 Distances and coordination numbers of nearest neighbour Li-Cl and Cl-Cl ionic pairs in molten LiCl as compared with the previous experimental and computed values.

References	Li-Cl		Cl-Cl		
	r_{Li-Cl} ($\times10^{-1}$nm)	$n_{Li/Cl}$ (atoms)	r_{Cl-Cl} ($\times10^{-1}$nm)	$n_{Cl/Cl}$ (atoms)	
This work	2.45	4.1	3.85	12.1	X-ray
H.Ohno et al.[16)]	2.40	4.0	3.86	12.0	X-ray
H.A.Levy et al.[17)]	2.47	4.0	3.86	12.0	X-ray
H.A.Levy et al.[17)]	2.45	3.5	3.80	12.0	Neutron
J.Zarzycki et al.[18)]	2.00	3.7	3.75		X-ray
J.Zarzycki et al.[18)]	2.55	4.1	3.90	12.0	X-ray
R.Takagi et al.[19)]	2.03	3.8	3.53	9.5	MD (900K)
R.Takagi et al.[19)]	2.01	4.0	3.4	12.1	MD (1200K)
J.W.Lewis et al.[20)]	2.00		3.55		MD (1273K)
J.Krogh-Moe et al.[21)]	2.40	4.1	4.10	11.1	MC (1073K)

MD: Molecular dynamics calculation, MC: Monte Carlo calculation

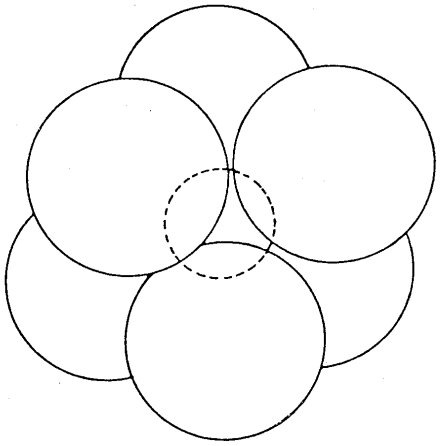

Fig. 4 Symmetrical $CaCl_6$ octahedron present in molten $CaCl_2$.

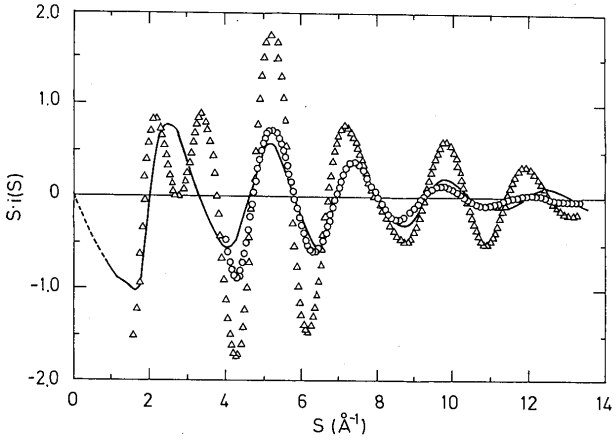

Fig. 5 Comparison of observed (solid line) and calculated (○: symmetrical $CaCl_6$ octahedron, △: disordered $CaCl_6$ octahedron in $CaCl_2$ crystal) reduced intensity functions S·i(S) of molten $CaCl_2$.

except at very high S values, but not with the one for the disordered octahedron where the first positive peak splits into two and many peaks shift to lower S values than those of the observed S·i(S).

The symmetrical $CaCl_6$ octahedron in molten $CaCl_2$ must have common vertexes with neighbour $CaCl_6$ octahedrons because the distance of the nearest Cl–Cl ionic pair (3.55×10^{-1}nm) is very close to the diameter of Cl^- ions (3.62×10^{-1}nm). Our results would be consistent with the models neither of $(CaCl)^+$ proposed by Bockris et al.[2] nor of $(CaCl_3)^-$ or $(CaCl_4)^{2-}$ by Emons et al.[6]

Figure 6 shows the correlation functions of the molten LiCl–$CaCl_2$ system. Both curves of Li_2CaCl_4 and $LiCaCl_3$ show no peak which corresponds to the nearest Li–Cl ionic pair. It is deduced that the peak of the Li–Cl pair is hidden by the peak of the nearest Ca–Cl pair because the effecttive electron number of Ca ($\bar{K}_{Ca}$=20.57 ~ 20.74) is greater than that of Li ($\bar{K}_{Li}$=2.19 ~ 2.21). Therefore the distance and the

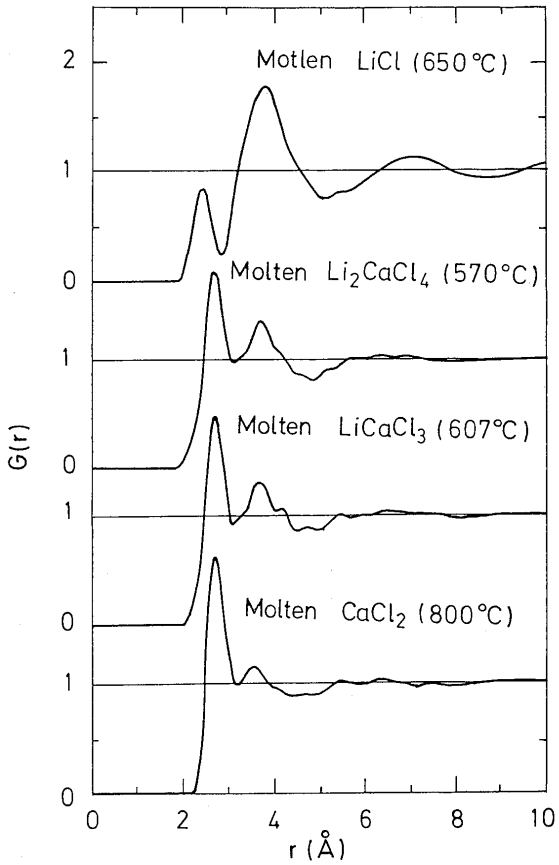

Fig. 6 Correlation functions G(r) of molten system LiCl–$CaCl_2$.

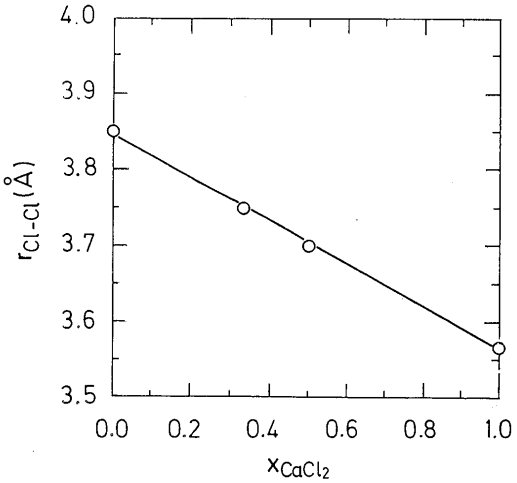

Fig. 7 Observed distances r_{Cl-Cl} of nearest neighbour Cl–Cl ionic pair in molten system LiCl–$CaCl_2$.

coordination number of the nearest Li–Cl ionic pair cannot be measured from the first peak of D(r) curves, they are calculated by adapting the equation (4) to the observed S·i(S). These results are also listed in Table 2. It is indicated that the numbers of nearest Cl^- ions around Ca^{2+} or Li^+ ions would not change even in these mixed systems from those in the single salts.

Both cations in the molten LiCl–$CaCl_2$ system

chain Cl^- ions with strong attractive force because of its smallness of the ionic radius (Li^+) or its double charge (Ca^{2+}). Thus even in the mixed molten system Li^+ ion has four and Ca^{2+} ion has six Cl^- ions around them on an average as is same in the single salts.

Because the distance of the nearest Cl–Cl ionic pair appears to show the additivity in this mixed system as is shown in **Fig.7**, this distance can be written with the distances of Cl–Cl ionic pairs in CaCl ($r_{Cl-Cl}^{CaCl_2} = 3.55\times10^{-1}$nm) and in LiCl ($r_{Cl-Cl}^{LiCl} = 3.85\times10^{-1}$nm) as follows.

$$r_{Cl-Cl}^{mix} = x_{LiCl}\cdot r_{Cl-Cl}^{LiCl} + (1-x_{LiCl})\cdot r_{Cl-Cl}^{CaCl_2}$$
$$= 0.30\ x_{LiCl} + 3.55\times10^{-1}\text{nm} \quad (6)$$

where x_{LiCl} is the molar fraction of LiCl. The reason for this system to follow the additivity is, in short that the coordination numbers of the nearest Cl^- ions around Li^+ or Ca^{2+} are the same as in their single salts and the structures of the mixed system are averages of LiCl and $CaCl_2$.

This behavior is similar to that of the excess molar volume ΔV^E of the molten LiCl–$CaCl_2$ system, where ΔV^E is much smaller than those of other alkali halide–$CaCl_2$ systems. The excess molar volume is a well-known parameter to reflect the condition of ionic packings.

The authors have performed the X–ray structural analysis and shown no trace of the existence of rigid anion complexes in this system. Hence it is also effective for the determination of this problem to use spectroscopic methods, the Raman spectropy measurement is in progress,too.

4. Conclusions

The obtained results can be summarized as follows.
(1) Li^+ ion is surrounded by four nearest Cl^- ions like a tetrahedron in molten LiCl. Observed distances and coordination numbers of the nearest ionic pairs, Li–Cl and Cl–Cl, can be explained well with the volume expansion on melting.
(2) Ca^{2+} ion is surrounded by six nearest Cl^- ions like a symmetrical octahedron in molten $CaCl_2$. Observed distances and coordination numbers of the nearest ionic pairs, Ca–Cl and Cl–Cl, are consistent with the small expansion on melting.
(3) The numbers of the nearest Cl^- ions around Li^+ and Ca^{2+} in molten Li_2CaCl_4 or $LiCaCl_3$ are nearly the same as those found in molten LiCl and $CaCl_2$, respectively. The distances of the nearest Cl–Cl ionic pair show linear dependence on the molar fraction in the mixed system.
(4) These behaviours can be analyzed to be a result of strong attractive force between ions. Our results give no evidence of the existence of some ionic complexes previously proposed.

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