

Ionic Species and Linkage in Ligand-Substituted ZnCl₂-ZnBr₂ Melts

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The short range structure of ZnCl₂-ZnBr₂ melts was analyzed by time-of-flight pulsed neutron diffraction techniques and the structural change due to anion-substitution was also studied. According to radial distribution analysis, it is found that there are tetrahedral structural units of ligand-substituted [ZnCl_nBr_{4-n}]²⁻ (n=0-4) in these melts, not implying the simple mixing of [ZnCl₄]²⁻ and [ZnBr₄]²⁻ units. Further detailed estimation indicates that the ligand-substituted complex anions are linked with each other by sharing a common anion.

KEYWORDS: melt, zinc halide, ligand substitution, tetrahedron, complex

§1. Introduction

Zinc halides are the typical compounds with tetrahedral coordination, being polymorphic with not less than three modifications.¹⁾ The structure of molten zinc halides and their mixtures with alkali halides have so far been vigorously studied by X-ray diffraction,^{2,3)} high energy photon diffraction,⁴⁾ neutron diffraction,⁵⁻⁹⁾ EXAFS,¹⁰⁾ molecular dynamics simulation,^{11,12)} and Raman spectroscopy.^{13,14)} Although the obtained results have supported the tetrahedral coordination of halide atoms, in many cases chloride atoms, around a zinc atom and described some clustering among tetrahedra, there exist little information, except for the previous Raman spectroscopic study and molecular orbital calculation,¹⁵⁾ on what happens in ZnCl₂-ZnBr₂ melts and whether the ligand substitution occurs in tetrahedra of zinc halides. The aim of the present work is to analyze the variation in short range structure of ZnBr₂-ZnCl₂ melts with composition by pulsed neutron diffraction (PND) techniques, to determine the most probable structural model for these melts and to obtain the structural information on the possibility of ligand substitution as well as clustering and/or networking of tetrahedra.

§2. Experimental

The sample preparation has been described in detail in the previous work.¹⁵⁾ Pulsed neutron scattering experiments were performed at 773 K using the High Intensity Total scattering spectrometer (HIT) in the pulsed neutron source of High Energy Accelerator Research Organization, Neutron Science Laboratory at Tsukuba, Japan. The experimental details and the correction procedure have so far been reported elsewhere.^{9,16,17)} The coherent scattering lengths of Zn, Br, and Cl atoms with natural abundance were taken from the literature.¹⁸⁾

§3. Results

The structure factor, $S(Q)$, the reduced intensity function, $Q \cdot i(Q)$, the radial distribution function, $D(r)$ and

the correlation function, $G(r)$, are defined in the forms,

$$Q \cdot i(Q) = Q \cdot [S(Q) - 1] \quad (3.1)$$

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{Q_{max}} Q \cdot i(Q) \sin(Qr) dQ \quad (3.2)$$

$$G(r) = 1 + (2\pi^2 r \rho_0)^{-1} \times \int_0^{Q_{max}} Q \cdot i(Q) \sin(Qr) dQ \quad (3.3)$$

where ρ_0 is the number of stoichiometric units per unit volume, Q_{max} the maximum of Q reaching in this scattering experiment. The total structure factors, $S(Q)$'s, for the x ZnCl₂-(1-x)ZnBr₂ melts ($x=0.00, 0.25, 0.50, 0.75$ and 1.00) are shown in Fig. 1. The phase variation in $S(Q)$'s with x was small in the entire range of Q but the intensity variation in $S(Q)$'s was noticeable especially in the low Q region, indicating the changes in medium range structure of the melts with x . The so-called prepeak in $S(Q)$, characteristic of the diffraction patterns for glasses and liquids with medium range order, was recognized at around 1 \AA^{-1} for each mixture melt. According to the relation $Q_p \cdot r_p = 2\pi$ where Q_p and r_p are the momentum transfer and the correlation length corresponding to the prepeak, respectively, the r_p value was nearly equal to 6.3 \AA . Figure 2 depicts the variation of correlation functions $G(r)$'s with the composition x , in which tentative assignments of atomic pairs were made by consulting the ionic radii by Shannon,¹⁹⁾ the crystallographic data¹⁾ and the results of Zinc halides with alkali halides previously reported.²⁻¹⁴⁾ The typical peaks appeared at about $r=2.30-2.40 \text{ \AA}$ and $r=3.70-4.00 \text{ \AA}$. The first peaks were thought to be due to Zn-Cl and Zn-Br nearest neighbor correlations by considering the peak shift with x . The second peaks would be regarded as the contributions from Cl-Cl, Cl-Br, Br-Br, and Zn-Zn correlations. The shift of the second peaks in $G(r)$ with increasing x was also observed. Beyond $r=6 \text{ \AA}$, $G(r)$'s fluctuated monotonously in the very vicinity of unity.

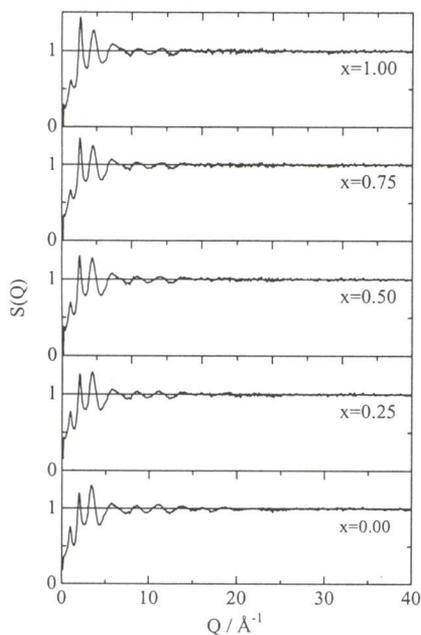


Fig. 1. Total structure factor $S(Q)$ of $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melt.

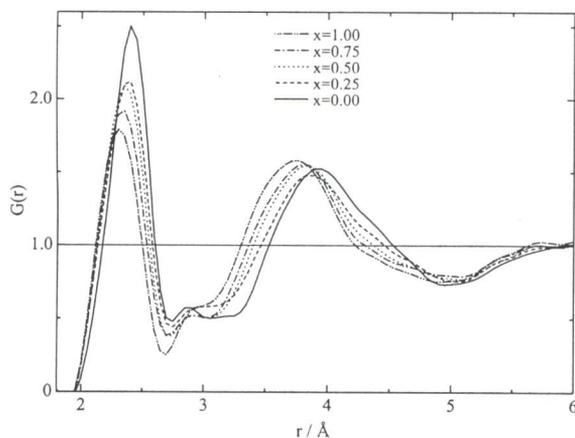


Fig. 2. Correlation function $G(r)$ of $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melt.

§4. Discussion

In the analysis of the radial distribution function $D(r)$, the scaled function defined by $D(r)/r$ is also incorporated since it is essentially expressed as a sum of unique Gaussian-type functions corresponding to individual pair correlations.²⁰ The near neighbor coordination number was roughly calculated from $D(r)$ to be 4 in each melt if the ligands around one Zn atom are Cl and Br atoms in proportion to melt composition. In fact, the first peaks in $D(r)$ and/or $D(r)/r$ are asymmetrical except for pure melts. As described before, the first peaks in $G(r)$ shifted gradually with increasing x . If the discrete $[\text{ZnCl}_4]^{2-}$ and $[\text{ZnBr}_4]^{2-}$ complexes are formed in $\text{ZnCl}_2\text{-ZnBr}_2$ melts, the first peak in $D(r)$ should be described by the simple sum of the contributions from Zn-Cl in $[\text{ZnCl}_4]^{2-}$ and those from Zn-Br in $[\text{ZnBr}_4]^{2-}$. This outlook is not applicable to the experimental $G(r)$'s. The

first peaks shifted to the direction of large r , perhaps having distortions on the tetrahedra, with increasing x . Raman spectroscopic measurements and molecular orbital calculations¹⁵⁾ have pointed out that ligands such as Cl^- and Br^- can be substituted for each other according to the melt compositions, that is, the first coordination shells in these melts consist of tetrahedrally ligand-substituted $[\text{ZnCl}_n\text{Br}_{4-n}]^{2-}$ ($n=0-4$), neither $[\text{ZnCl}_4]^{2-}$ nor $[\text{ZnBr}_4]^{2-}$ units, being in good agreement with the present study.

For better understanding the melt structure, the structural parameters for each atomic pair are needed to be refined by the correlation method in the $(Q, Q \cdot i(Q))$ space, using the non-linear least squares regression of Eq. (4.1)

$$Q \cdot i(Q) = \frac{\left[\sum_i \sum_j n_{ij} b_i b_j \exp(-B_{ij} Q^2) \sin(Q r_{ij}) / r_{ij} \right]}{\left(\sum_i b_i \right)^2} \quad (4.1)$$

where n_{ij} , r_{ij} , and B_{ij} refer to the average coordination number, the average interatomic distance, and the temperature factor for the atomic pair i - j , respectively. The optimized short range structural parameters for $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melts ($x=0.00, 0.25, 0.50, 0.75$ and 1.00) were listed in Table I, where the statistical errors in n_{ij} , r_{ij} , b_{ij} , and $\Delta r_{ij}^2 / 2$ were estimated at ± 0.2 , ± 0.01 Å, $\pm 0.5 \times 10^{-4}$ Å², and ± 0.01 Å, respectively. Allen *et al.*⁷⁾ have analyzed pure ZnBr_2 melt at 693 K with the aid of pulsed neutron diffraction in which the distances of Zn-Br and Br-Br pairs and the coordination number of nearest neighbours are computed to be 2.41 Å, 4.08 Å, and 3.9, respectively. The results of pure ZnBr_2 melt tabulated in Table I are in quantitatively good agreement with the previous work. The Zn-Br separation, 2.40 Å, is smaller by over 0.1 Å than the sum of ionic radii of constituent ions,¹⁹⁾ 2.56 Å, implying the existence of strong covalent bond between Zn and Br. Taking the Raman spectra of ZnBr_2 melt into consideration²¹⁾ and consulting with the results of pure ZnCl_2 melt,²²⁾ it is confirmed that there exist stable tetrahedra $[\text{ZnBr}_4]^{2-}$ and their linkage through a common Br atom, that is, clustering of tetrahedra or networking in pure ZnBr_2 melt to some extent. As for mixture melts, the total coordination numbers of near neighbors, that is, the sum of the numbers of Cl and Br atoms existing around a Zn atom in the first coordination shell, were computed to be 3.45, 3.61, 3.63, 3.85, and 3.59, for the $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melts ($x=0.00, 0.25, 0.50, 0.75$ and 1.00), respectively. Anyway, the coordination numbers of near neighbors were almost equal to 4, being characteristic of the tetrahedral species. These findings as well as Raman spectroscopic work¹⁵⁾ reveal the existence of tetrahedral configurations such as ligand-substituted $[\text{ZnCl}_n\text{Br}_{4-n}]^{2-}$ ($n=0-4$) in these melts, not implying the simple mixing of $[\text{ZnCl}_4]^{2-}$ and $[\text{ZnBr}_4]^{2-}$ units.

As far as the clustering or the networking in $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melts is concerned, the nearest Zn-Zn correlation reflecting the clustering or the networking should

be interpreted and discussed precisely. As given in Table I, the Zn-Zn distance ranged from 4.31 Å to 4.58 Å in spite of the variation of x , the difference of which is well understood according to ionic sizes of Cl⁻ (1.81 Å) and Br⁻ (1.96 Å)¹⁹ and the fact that the halide ligand always lies between two Zn atoms. The coordination numbers of Zn-Zn pair were not changed very much with the variation of x , 3.42 to 4.03 in the whole range of x . This means that almost all of the four ligands in one tetrahedron are combined with Zn in the adjacent tetrahedron, that is, the highly ordered networking is formed in the melts. In the ZnCl₂-type crystals,¹⁾ Zn-ligand-Zn is calculated to be 109.47° which is the same as the tetrahedral angle. In mixture melts, the corresponding angle is evaluated to be about 140° on the average on the basis of distances $r(\text{Zn-Zn})$ and $r(\text{Zn-Cl or Zn-Br})$. This fact implies that there exists something of distortion in linkage of two [ZnCl_{*n*}Br_{4-*n*}]²⁻ tetrahedra with a common ligand. For further interpretation of networking in the melts, the origins of prepeaks are discussed. The position of prepeak in $S(Q)$ of ZnBr₂ melt has been recognized at 0.943 Å⁻¹ by Allen et al.,⁷⁾ which is equivalent to $r_p = 6.66$ Å. As illustrated in Fig. 1, Q_p 's of $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melts were evaluated to be about 1.0 Å⁻¹, the corresponding r_p 's being 6.3 Å. If Q_p 's originated from some linkage of two [ZnCl_{*n*}Br_{4-*n*}]²⁻ tetrahedra with a common ligand, r_p 's should correlate with the Zn-Zn distances listed in Table I. Unfortunately, r_p 's do not correlate directly with near neighbor Zn-Zn distances. This r_p value appears to be due to the second neighbor Zn-Zn correlation, if distortions of linkage among tetrahedra and rotation of tetrahedra along the Zn-ligand-Zn axes are taken into account. In this case the networking and/or clustering is meant to develop considerably in spite of the difference in the sum of ionic radii between 2.30 Å for ZnCl₂ and 2.41 Å for ZnBr₂, since the prepeaks exist in the entire range of x . Another possibility might originate from the correlations of vacant sites caused by the above distortions. However, it is of much difficulty to obtain the information regarding the prepeaks in $S(Q)$'s of $x\text{ZnCl}_2-(1-x)\text{ZnBr}_2$ melts.

Acknowledgements

The authors deeply appreciate that a part of the present work has been financially supported by a research contribution from KATO Science Advancement Foundation.

Table I. Least-squares fitted structural parameters of ZnCl₂-ZnBr₂ melts (a: pure ZnCl₂, b: ZnCl₂ 75mol%, c: ZnCl₂ 50mol%, d: ZnCl₂ 25mol%, e: pure ZnBr₂).

<i>ij</i>	<i>n_{ij}</i>	<i>r_{ij}</i> (Å)	<i>b_{ij}</i> (Å ²)	$\langle \Delta r_{ij}^2 \rangle^{1/2}$ (Å *)	
Zn-Cl	a	3.586	2.301	0.0132	0.163
	b	2.803	2.307	0.0137	0.166
	c	1.828	2.309	0.0131	0.162
	d	1.390	2.290	0.0159	0.178
	e	-	-	-	-
Zn-Br	a	-	-	-	-
	b	1.043	2.402	0.0137	0.166
	c	1.802	2.425	0.0147	0.171
	d	2.220	2.412	0.0159	0.178
	e	3.449	2.400	0.0138	0.166
Cl-Cl	a	8.996	3.698	0.0508	0.319
	b	4.180	3.621	0.0349	0.264
	c	2.793	3.651	0.0283	0.238
	d	1.401	3.604	0.0297	0.244
	e	-	-	-	-
Cl-Br	a	-	-	-	-
	b	2.793	3.880	0.0349	0.264
	c	2.793	3.873	0.0320	0.253
	d	2.781	3.699	0.0298	0.244
	e	-	-	-	-
Br-Br	a	-	-	-	-
	b	1.397	3.941	0.0349	0.264
	c	2.784	3.850	0.0349	0.264
	d	4.098	3.924	0.0298	0.244
	e	6.284	3.895	0.0470	0.307
Zn-Zn	a	4.026	4.317	0.0509	0.319
	b	3.417	4.410	0.0370	0.272
	c	3.417	4.306	0.0350	0.264
	d	3.491	4.398	0.0307	0.248
	e	3.604	4.579	0.0471	0.307

$$*) \langle \Delta r_{ij}^2 \rangle^{1/2} = (2b_{ij})^{1/2}$$

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