Structural approach to nanoscience: a case study of complex and cluster formation in ZnBr₂–ZnCl₂ melts

Y. Iwadatea,⁎, K. Fukushimab, Y. Sekic, K. Itohc, T. Fukunagae, M. Misawad, H. Matsuurae, A. Kajinamif, N. Ohtorig, N. Umesakih, H. Kofujii, M. Myochinj

aGraduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan
bDepartment of Materials Technology, Chiba University, Chiba 263-8522, Japan
cResearch Reactor Institute, Kyoto University, Osaka 590-0494, Japan
dDepartment of Chemistry, Niigata University, Niigata 950-2102, Japan
eResearch Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Tokyo 152-8550, Japan
fGraduate School of Science and Technology, Niigata University, Niigata 950-2102, Japan
gJapan Synchrotron Radiation Research Institute, Hyogo 679-5198, Japan
hJapan Nuclear Cycle Development Institute, Ibaraki 319-1194, Japan

Received 17 December 2003; revised 22 March 2004; accepted 23 March 2004
Available online 1 September 2004

Abstract

Although the melt structure of glass-forming ZnCl₂ has so far been well studied, there exists quite little information on the structural change due to anion-substitution. In the present work, the short-range structure of ZnCl₂–ZnBr₂ mixture melts was analyzed systematically by time-of-flight pulsed neutron diffraction techniques, Raman spectroscopy, molecular orbital calculations, and molecular dynamics simulations. According to radial distribution analysis, it was found that there were tetrahedral structural units of ligand-substituted [ZnCl₄₋₄–Br₄Kₙ]₂⁻ (n = 0–4) in these melts, not implying the simple mixing of [ZnCl₄]²⁻ and [ZnBr₄]²⁻ units. Further detailed estimation indicated that the ligand-substituted complex anions were linked with each other by sharing a common anion.

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Keywords: Zinc halides; Raman spectroscopy; Molecular orbital calculation; Pulsed neutron diffraction; Molecular dynamics

1. Introduction

Zinc halides such as ZnCl₂ and ZnBr₂ are the typical compounds with tetrahedral coordination, being polymeric with not less than three modifications called α-form (tetragonal), β-form (monoclinic but pseudo-orthorhombic), and γ-form (like HgI₂) [1]. Glass-forming ZnCl₂ is a highly viscous liquid even at elevated temperature, resulting in an extremely low electrical conductivity. The structure of molten zinc halides and their mixtures with alkali halides has so far been studied by X-ray diffraction [2,3], high-energy photon diffraction [4], neutron diffraction [5–9], EXAFS [10], molecular dynamics (MD) simulations [11,12], and Raman spectroscopy [13,14]. It has been revealed by neutron diffraction experiments that the structure of ZnCl₂ glass comprises a distorted corner-sharing type network of ZnCl₄²⁻ tetrahedra [15], that of the corresponding melt was mainly composed of the bonding as mentioned above and probably a small portion of the edge-sharing [16], and also the structure of molten ZnCl₂–KCl system was pointed out to consist of a corner-sharing closest-packing type of ZnCl₄²⁻ tetrahedra [3]. Mackenzie et al. suggested that molten ZnCl₂ was an associated liquid with a low degree of association [17], and on the contrary, Biggin et al. analyzed the structure of molten ZnCl₂ by neutron diffraction and proposed a structural model of γ-type ZnCl₂ crystalline arrangement [6]. In spite of extensive attention to vitreous ZnCl₂, the structure of

⁎ Corresponding author. Tel.: +81-43-290-3433; fax: +81-43-290-3039.
E-mail address: iwadate@xtal.tf.chiba-u.ac.jp (Y. Iwadate).

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doi:10.1016/j.stam.2004.03.008
ZnCl$_2$–ZnBr$_2$ glasses has been studied only by Kinugawa et al. [18] and that of melts by some of the present authors [19].

The aims of the present work are to analyze the variation in short-range structure of ZnBr$_2$–ZnCl$_2$ mixture melts with composition by pulsed neutron diffraction (PND) techniques, Raman spectroscopy, molecular orbital (MO) calculations, and MD simulations.

2. Experimental

Since the reagent grade chemicals ZnBr$_2$ and ZnCl$_2$ were dehydrated at respective melting points for 8 h under reduced pressure and then purified by sublimation under the conditions of 10$^{-3}$ Pa, 753 K and 8 h.

Raman spectra and their depolarization ratios were measured using JASCO NR-1800 spectrophotometer with Ar$^+$ ion laser at the wavelength of 514.5 nm, which was employed as an excitation light source with continuous 200 mW output power. The detailed procedure on experiments and calculations is described elsewhere [19].

In MO calculations, the semi-empirical MO calculation program, called MOPAC [20], was used to obtain the information concerning the structure and nature of ionic species in molten ZnBr$_2$–ZnCl$_2$ and to assign the vibrational modes. The initial value of the interatomic distance was determined from the ionic radii by Shannon [21].

Pulsed neutron scattering experiments were performed at 773 K using the High Intensity Total scattering spectrometer (HIT), which is designed to measure the structure factor $S(Q)$ at high rate of data collection over a wide range of momentum transfer $Q$ (from 0.5 to 50 Å$^{-1}$ in this work) and installed in the pulsed neutron source of High Energy Accelerator Research Organization, Neutron Science Laboratory at Tsukuba, Japan. The procedure of data correction has so far been reported in detail elsewhere [22,23]. The coherent scattering lengths of Zn, Br, and Cl atoms with natural abundance were taken from the literature [24].

In MD Simulations, the pair potential employed was of the Born-Mayer-Huggins type used by Woodcock et al. [25] without the dispersion terms. The potential parameters used were the same as in the papers [26,27], which reproduced the interference function $Q(i(Q))$ and especially the near neighbor distances by XRD [28]. The condition of constant temperature was achieved according to Nosé’s method [29]. The cell lengths were determined from the experimental molar volume data, and 480 ions in all were contained in the cubic cell.

3. Results and discussion

3.1. Raman spectroscopy and MO calculations

Since tetrahedral structure such as ZnCl$_4^-$ and ZnBr$_4^-$ has four vibrational modes, one can see four peaks (totally symmetric stretching vibration $\nu_1$, bending vibration $\nu_2$ and $\nu_4$, stretching vibration $\nu_3$) in each spectrum. Since the excited vibrations of ions in melts became more vigorous with increasing temperature, each peak was broadened and its intensity tended to gradate. The strong peaks were strongly polarized, but weak peaks were depolarized. The polarized bands were assigned to the totally symmetric stretching vibration $\nu_1$. As mentioned in Ref. [19], each peak for this band in each spectrum was asymmetric and it was found to overlap more than or equal to two contributions. Each peak was resolved into two vibrational contributions by reference to Raman spectra of ZnCl$_2$–ZnBr$_2$ binary glasses [18]. The resolved peak positions are listed in Table 1.

Two resolved peaks in $\nu_1$ were suggested to be due to the symmetric stretching modes of ligand substituted species. Kinugawa et al. [18] discussed the ‘bridging’ and ‘non-bridging’ of anions. The bridging anion was bonded to two Zn$^{2+}$ ions (A-type), while the non-bridging anion was bonded to only one Zn$^{2+}$ ion (B-type). The band at 224 cm$^{-1}$ in molten ZnCl$_2$ might be due to the Zn–Cl stretching in the ZnCl$_4^-$ tetrahedra, corresponding to the bridging Cl$^-$ ions of A-type [18]. On the other hand, the band at 248 cm$^{-1}$ was attributed to the Zn–Cl stretching of B-type in ZnCl$_4^-$ tetrahedra by Aliotta et al. [30]. The polarized bands at 147 cm$^{-1}$ and 169 cm$^{-1}$ in molten ZnBr$_2$ belonged to A-type and B-type, respectively [31]. By consulting the spectra of ZnBr$_2$ glass, two weak peaks may be assigned to $\nu_2$ and $\nu_4$, respectively [31]. In the ZnBr$_2$–ZnCl$_2$ glasses, two polarized bands were observed and assigned to the symmetric stretching modes of Zn–Cl and Zn–Br, respectively. The Zn–Cl mode shifted to higher wavenumber and Zn–Br mode shifted to the lower wavenumber as the amount of ZnBr$_2$ increased. In melts, the similar phenomena were observed except for the concentration of 75 and 87.5 mol% of ZnCl$_2$. X-ray diffraction and Raman spectroscopy have so far been carried out for single ZnCl$_2$ and ZnBr$_2$ melts, in which the coordination number of Cl$^-$ around Zn$^{2+}$ was estimated at about 3.82, that of Br$^-$ around Zn$^{2+}$ being about 4.10 in terms of X-ray diffraction [3,16]. Those data supported that

| Table 1: Deconvolution of Raman bands in molten ZnCl$_2$–ZnBr$_2$ |
|--------------------------|----------|----------|----------|----------|
| ZnCl$_2$ (mol%) | $\nu_1$ (cm$^{-1}$) | $\nu_2$ (cm$^{-1}$) | $\nu_3$ (cm$^{-1}$) | $\nu_4$ (cm$^{-1}$) |
| 100.0 | 226.6 | 266.0 | 68.0 | 108.1 |
| 87.5 | 159.9 | 192.7 | 59.1 | 95.3 |
| 75.0 | 145.2 | 169.1 | 52.5 | 84.3 |
| 62.5 | 174.9 | 230.8 | 59.8 | 108.3 |
| 50.0 | 170.3 | 228.2 | 59.3 | 94.7 |
| 37.5 | 156.9 | 186.5 | 55.2 | 92.2 |
| 25.0 | 155.2 | 178.2 | 59.7 | 98.1 |
| 12.5 | 153.3 | 183.1 | 57.4 | 93.9 |
| 0.0 | 147.1 | 173.9 | 58.0 | 92.4 |

The superscripts of $b$ and $nb$ refer to bridging and non-bridging, respectively [18].
the basic structure in each melt was of tetrahedral configuration and two structural units shared one ion (Cl\(^-\) or Br\(^-\)) at the corner and polymerize. Triolo et al. [2] showed that Zn–Cl distance was 2.3 Å and Cl–Cl distance was 3.7 Å by X-ray diffraction. Tetrahedral coordination of the Cl\(^-\) ions around Zn\(^{2+}\) was assumed, since the ratio of the above two distances was close to the value \(\sqrt{8/3}\). Biggin et al. [6] showed that Cl\(^-\) ions occupied tetrahedral sites for Zn\(^{2+}\) ion. Moreover, it has been reported that the [ZnCl\(_4\)]\(^2-\) units \((n = 0–4)\) were expected to be in the ZnCl\(_2–ZnBr_2\) glasses [3]. As for ZnCl\(_2–ZnBr_2\) melts, each Raman spectrum could not be expressed by the simple sum of the contributions from unique ZnCl\(_4\)\(^2-\) and ZnBr\(_4\)\(^2-\). This implies that there are any units other than ZnCl\(_4\)\(^2-\) and ZnBr\(_4\)\(^2-\) in melt. That is, the coexistence of the tetrahedral [ZnCl\(_4\)]\(^2-\) and ZnBr\(_4\)\(^2-\) units \((n = 0–4)\) or more complex ions might be taken into account also in ZnCl\(_2–ZnBr_2\) melts. Consequently, the splitting in \(v_1\) mode and the variation in \(v_1\) shift were thought to be interpreted by the bridging or non-bridging anions and the ligand substitution, respectively. Due to the exchange of ligands, asymmetry of tetrahedral units increased in molten ZnCl\(_2–ZnBr_2\) in comparison with the case of pure melts, probably resulting in the break-out of the network.

3.2. PND

The structure factors \(S(Q)\) was estimated by the intensity data over the entire range of \(Q\), from which the reduced intensity function \(Q \cdot i(Q)\) was derived. The total pair distribution function, sometimes called the correlation function, \(G(r)\), was calculated by Fourier transformation of the \(Q \cdot i(Q)\) [22,23]. The phase variation in \(S(Q)\)'s with the mole fraction of ZnBr\(_2\), \(x\), was small in the entire range of \(Q\) but the intensity variation in \(S(Q)\)'s was noticeable especially in the low \(Q\) region with ease, 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 Å\(^{-1}\) for each mixture melt. According to the relation \(Q_p, r_p = 2\pi/Q_p\) where \(Q_p\) are the momentum transfer and the correlation length corresponding to the prepeak, respectively, the \(r_p\) value was nearly equal to 6.3 Å. The interpretation of the prepeaks would be discussed later.

Fig. 1 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 [21], the crystallographic data [1] and the results of Zinc halides with alkali halides previously reported [2–14]. The typical peaks appeared at around \(r = 2.30–2.40\) Å and \(r = 3.70–4.00\) Å. 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, being probably caused by the same reason as the first peaks. Beyond \(r = 6\) Å, \(G(r)\)'s fluctuated monotonously in the very vicinity of unity. If the discrete [ZnCl\(_4\)]\(^2-\) and [ZnBr\(_4\)]\(^2-\) complexes are formed in ZnCl\(_2–ZnBr_2\) melts, the first peak in \(G(r)\) should be described by the simple sum of the contributions from Zn–Cl in [ZnCl\(_4\)]\(^2-\) and those from Zn–Br in [ZnBr\(_4\)]\(^2-\). This outlook is not applicable to the interpretation of experimental \(G(r)\)'s. The first peaks shifted to the direction of large \(r\), perhaps having distortions on the tetrahedra, with decreasing \(x\). Consulting the previous work on the short range structure of ZnCl\(_2–ZnBr_2\) mixture melts [19], Raman spectroscopic measurements and MO calculations 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 [ZnCl\(_n\)Br\(_{4–n}\)]\(^2-\) \((n = 0–4)\), neither [ZnCl\(_4\)]\(^2-\) nor [ZnBr\(_4\)]\(^2-\) units. The present diffraction study was in good agreement with the results by Raman spectroscopy and MO calculation. As for the stability of first coordination shell sometimes defined by the ratio of the first maximum to the first minimum in \(G(r)\), pure ZnCl\(_2\) or ZnBr\(_2\) melt is thought to be superior to \(x\)ZnCl\(_2–(1–x)\)ZnBr\(_2\) melts since the ligand-substituted [ZnCl\(_n\)Br\(_{4–n}\)]\(^2-\) complexes would become much distorted in terms of the size effect in ligand. Furthermore, this size effect makes the ligand substitution easier, and it compels [ZnCl\(_n\)Br\(_{4–n}\)]\(^2-\) complexes to live short. The peaks, the shoulders and/or small oscillations in and after the second peak were thought to be ascribed to the contributions of Cl–Cl, Cl–Br, Br–Br, Zn–Zn pairs.

For better understanding the melt structure, the structural parameters for each atomic pair in \(x\)ZnCl\(_2–(1–x)\)ZnBr\(_2\) melts \((x = 0.00, 0.25, 0.50, 0.75\) and 1.00\) were refined by the correlation method in the \((Q, Q \cdot i(Q))\) space [9,28] within the statistical errors in the average coordination number \(n_{ij}, ± 0.2\), the average interatomic distance \(r_{ij}, ± 0.01\) Å, the temperature factor \(b_{ij}, ± 0.5 \times 10^{-4}\) Å\(^2\), and the root mean squares displacement \((\Delta r_{ij})^{1/2}, ± 0.01\) Å, for the atomic pair \(i–j\), respectively.
Preliminary XRD results on the short-range structure of molten pure ZnBr$_2$ have been reported by some of the present authors [32]. The coordination number of the nearest neighbor Zn–Br pair was evaluated to be about 4 and the atomic distances of Zn–Br and Br–Br pairs were 2.47 and 3.96 Å, respectively. The atomic distance ratio $r_{\text{Br-Br}}/r_{\text{Zn-Br}}$ was thus calculated to be 1.60, which was close to that characteristic of tetrahedral geometry, $\sqrt{3}/3$. In the same manner, Allen et al. [7] have analyzed pure ZnBr$_2$ melt at 693 K with the aid of PND in which the distances of nearest neighbors were computed to be 2.41 Å, 4.08 Å, and 3.9 Å, respectively. The results of pure ZnBr$_2$ melt were in quantitatively good agreement with the previous works. The Zn–Br separation, 2.40 Å, was smaller by over 0.1 Å than the sum of ionic radii of constituent ions [21], 2.56 Å, implying the existence of strong covalent bond between Zn and Br. Taking the Raman spectra of ZnBr$_2$ melt into consideration [33] and consulting with the results of pure ZnCl$_2$ melt [34], it was confirmed that there exist stable tetrahedra ZnBr$_2^{2-}$ and their linkage through a common Br atom, that is, clustering of tetrahedra or networking in pure ZnBr$_2$ melt to some extent.

On the contrary, the structural parameters of the individual pairs within the first coordination shell were drastically changed by mixing with ZnCl$_2$ melt. 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, however, computed to be 3.45, 3.61, 3.63, 3.85, and 3.59, for the $x$ZnCl$_2$–(1–$x$)ZnBr$_2$ melts ($x$=0.00, 0.25, 0.50, 0.75 and 1.00), respectively. Anyways, the coordination numbers of nearest neighbors were almost equal to 4, being characteristic of the tetrahedral species. These findings as well as Raman spectroscopic work [19] reveal the existence of tetrahedral configurations such as ligand-substituted [ZnCl$_{n}$Br$_{4-n}$]$^{2-}$ ($n$=0–4) in these melts, not implying the simple mixing of [ZnCl$_2$]$^{2-}$ and [ZnBr$_2$]$^{2-}$ units, by taking into account the gradual variation of $G(r)$’s with composition $x$.

As for negatively charged ion pairs such as Cl–Cl, Cl–Br, and Br–Br, the mean values of their near neighbor distances were in good order of the effective ionic radii [21]. The interatomic distances of Zn–Cl and Zn–Br pairs were determined to be 2.3–2.4 Å, respectively. If the tetrahedral arrangement of atoms is assumed as a complex species, the distances of negatively charged like ion pairs are estimated at about 3.7–3.9 Å. This finding supports the tetrahedral configuration of complex species in the melts.

As far as the clustering or the networking in $x$ZnCl$_2$–(1–$x$) ZnBr$_2$ melts is concerned, the nearest Zn–Zn correlation reflecting the clustering or the networking should be interpreted and discussed precisely. The Zn–Zn distance ranged from 4.31 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) [21] as well as considering 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 $x$, being 3.42–4.03 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 ZnCl$_2$-type crystals [1], the angle Zn–ligand–Zn is calculated to be 109.47° which is the same as the tetrahedral angle. In the mixture melts, the corresponding angle is evaluated at about 140° on the average. 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 desired to be discussed. The position of prepeak in $S(Q)$ of ZnBr$_2$ melt has been recognized at 0.943 Å$^{-1}$ by Allen et al. [7], which is equivalent to $r_p$ = 6.66 Å. $Q$’s of $x$ZnCl$_2$–(1–$x$)ZnBr$_2$ melts were evaluated to be about 1.0 Å$^{-1}$, the corresponding $r_p$’s being 6.3 Å. If $Q$’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. 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. 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 $x$ZnCl$_2$–(1–$x$)ZnBr$_2$ melts, and the small angle scattering experiments with high accuracy are desired to be carried out so as to check this problem.

### 3.3. MD simulations

According to the analyses of pair distribution functions $g_x(r)$’s derived from MD simulations, the following numerical results on the first peak positions and the corresponding average coordination numbers in individual $g_x(r)$’s were obtained as listed in Table 2. It was important to develop considerable. 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 $x$ZnCl$_2$–(1–$x$)ZnBr$_2$ melts, and the small angle scattering experiments with high accuracy are desired to be carried out so as to check this problem.

| Table 2 | First peak positions and average coordination numbers for molten ZnBr$_2$–ZnCl$_2$ system |
|---------|--------------------------------------------------------------------------------|
| $x$ZnBr$_2$ (mol%) | 100 | 75 | 50 | 25 | 0 |
| **First peak position (nm)** | | | | | |
| Zn–Br | 0.243 | 0.251 | 0.253 | 0.251 | – |
| Zn–Cl | – | 0.219 | 0.221 | 0.221 | 0.221 |
| Zn–Zn | 0.469 | 0.467 | 0.433 | 0.433 | 0.427 |
| Br–Cl | 0.387 | 0.397 | 0.399 | 0.397 | – |
| Br–Br | – | 0.379 | 0.383 | 0.383 | – |
| **Average coordination number** | | | | | |
| Zn–Br | 3.9 | 3.9 | 3.9 | 3.9 | – |
| Zn–(Br+Cl) | 3.9 | 3.9 | 3.9 | 4 | 3.9 |
| Zn–Zn | 3.8 | 3.9 | 3.9 | 4.1 | 3.8 |
that the peak positions were definitely affected by the difference in anionic radii, and the coordination number of Br around Zn was nearly proportional to the composition of ZnBr₂ in mixture melts but the total coordination number of anions around Zn was almost equal to 4. The angular distributions of A–Zn–A (A=Br, Cl) at the different concentration of ZnBr₂ are depicted in Fig. 2, all the peaks of which are centered around 110°, but the tail-end of angular distribution of A–Zn–A in higher angles contained the second distribution. These findings led to the conclusions that the tetrahedral chemical species of the type [ZnBr₄₋ₙCl₄₋ₙ]²⁻ (ₙ=0–4) were formed in the melts, almost all of which were combined with each other by sharing a common Br or Cl atom, that is called the corner-sharing, and formed highly ordered network structure.

4. Conclusions

It was found from Raman spectroscopy, MO calculations and PND structural analyses that there were tetrahedral structural units of ligand-substituted [ZnCl₄₋ₙBr₄₋ₙ]²⁻ (ₙ=0–4) in xZnCl₂–(1–x)ZnBr₂ melts, not necessarily the simple mixing of [ZnCl₄]²⁻ and [ZnBr₄]²⁻ units. It was also deduced from MD simulations that the ligand-substituted tetrahedra were combined with each other by sharing a common halide.

Acknowledgements

The neutron facilities made available to us from High Energy Accelerator Research Organization, Neutron Science Laboratory at Tsukuba are gratefully acknowledged.

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