Hydrogen-bonded Structure in Highly Concentrated Aqueous LiBr Solutions

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Neutron diffraction measurements were carried out for H/D isotopically substituted aqueous 10, 25 and 33 mol% LiBr solutions in order to obtain structural information on the intermolecular hydrogen bonds among water molecules in highly concentrated aqueous solutions. Observed scattering cross sections for D₂O (99.9 % D), 0 H₂O (35.9 % D) and ${}^{0-2}$ H₂O (68.0 % D) solutions were combined to deduce partial structure factors, $a_{\rm HH}(Q)$, $a_{\rm XH}(Q)$ and $a_{\rm XX}(Q)$ (X: O, Br and Li). The least squares fitting analysis was applied to the observed partial structure factors to determine the nearest neighbor interatomic distance, root-mean-square amplitude and coordination number. Intermolecular distances, $r_{\rm OH} = 1.91(1)$ Å, $r_{\rm HH} = 2.38(1)$ Å and $r_{\rm OO} = 3.02(1)$ Å, between the nearest neighbor water molecules, were obtained for the 10 mol% LiBr solution. On the other hand, the intermolecular O···H interaction was found to almost disappear in concentrated 25 and 33 mol% LiBr solutions. The result implies that the hydrogen-bonded network is completely broken in highly concentrated aqueous LiBr solutions.

KEYWORDS: H/D isotopic substitution, neutron diffraction, hydrogen-bonded structure, concentrated aqueous LiBr solution

§1. Introduction

The lithium halogenide (LiX) is one of the most suitable solute compounds for investigations on the solutesolvent and solute-solute interactions in the concentrated aqueous solution because of its high solubility to water. Recent neutron diffraction studies with ⁶Li/⁷Li isotopic substitution technique have proved that the hydration number of Li^+ is strongly concentration dependent.^{1,2)} In aqueous solutions with higher solute content above 25 mol% LiBr, an evidence for the $Li^+ \cdots Br^-$ contact ionpair formation has been found by neutron diffraction²) and Raman scattering³⁾ studies. The structural property of intermolecular hydrogen bonds in concentrated LiCl solutions has been investigated by neutron diffraction with H/D isotopic substitution method.⁴⁻⁶⁾ The results indicate that the hydrogen-bonded network among water molecules is maintained in the solute content up to 20 mol% LiCl. It is of considerable interest to investigate the hydrogen-bonded structure in solutions with extremely high solute content.

In this paper, we describe the results of neutron diffraction measurements on highly concentrated aqueous 25 and 33 mol% LiBr solutions in which H/D isotopic compositions have been changed. Partial structure factors $a_{\rm HH}(Q)$, $a_{\rm XH}(Q)$ and $a_{\rm XX}(Q)$ (X: O, Br and Li) have been derived from observed scattering cross sections. The same procedure has been adopted for aqueous 10 mol% LiBr solutions for the purpose of comparison.

§2. Experimental

⁷Li-enriched lithium bromide was prepared by reacting ⁷LiOH·H₂O (99.94 % ⁷Li, Tomiyama Chemical Co. Ltd.) with slightly excess amounts of the concentrated aqueous hydrobromic acid solution (Nacalai Tesque, Guaranteed grade). The product solutions were dehydrated by heating at 180 °C under vacuum. Weighed amounts of enriched anhydrous LiBr were dissolved into D₂O (99.8 % D, Aldrich Chemical Inc. Co.) or D₂O-H₂O mixtures to prepare three aqueous LiBr solutions, I (LiBr)_x(D₂O)_{1-x} (99.8 % D, $b_{\rm H} = 0.655 \times 10^{-12}$ cm), II (LiBr)_x(⁰H₂O)_{1-x} (35.9 % D, $b_{\rm H} = 0$), and III (LiBr)_x(⁰⁻²H₂O)_{1-x} (68.0 % D, $b_{\rm H} = 0.334 \times 10^{-12}$ cm). In order to reduce uncertainties arising from large incoherent scattering from H atom, the isotopic composition of the "null" mixture ($b_{\rm H} = 0$) was employed in this study.

Neutron diffraction measurements on sample solutions sealed into a cylindrical quartz cell were carried out using the ISSP diffractometer (PANSI) installed at the JRR-2 research reactor operated at 10MW in JAERI, Tokai, Japan. The incident neutron wavelength, $\lambda = 1.008\pm0.003$ Å, was employed. Diffraction measurements were carried out at 25 °C for 10 mol% LiBr solutions, at 100 °C for 25 mol% LiBr solutions, and at 130 °C for 33 mol% LiBr solutions, respectively. Scattered neutrons were collected over the angular range of $3 \leq 2\theta \leq 102^{\circ}$, corresponding to $0.32 \leq Q \leq 9.69$ Å⁻¹ ($Q = 4\pi \sin \theta/\lambda$). Scattering intensities were measured in advance for a vanadium rod (10 mm in diameter), empty cell and background.

After corrections for the background and absorption of both sample and cell,⁷⁾ the observed count rate for the sample was converted to the normalized cross section scaled at the stoichiometric unit, $(\text{LiBr})_x(^*\text{H}_2\text{O})_{1-x}$, by the use of scattering intensities from the vanadium rod. Details of the data correction and normalization procedure have already been described in our previous papers.^{8,9)}



Fig.1. Total scattering cross sections observed for aqueous 10, 25 and 33 mol% LiBr solutions (a, b and c, respectively) with different H/D isotopic ratios (circles). Contributions from the self and intramolecular interference terms are indicated by solid lines.

§3. Results and Discussion

The observed cross sections, $(d\sigma/d\Omega)^{obs}$, for the 10, 25 and 33 mol% LiBr solutions with different H/D isotopic ratios are shown in Fig. 1a–c, respectively. The decrease in the intensity of $(d\sigma/d\Omega)^{obs}$ at a larger-Q range due to the inelasticity effect, becomes more pronounced for solutions with higher-H content. The observed intermolecular interference term, $(d\sigma/d\Omega)^{inter}$, was obtained by subtracting the self scattering term, $(d\sigma/d\Omega)^{self}$, and the intramolecular interference term for the *H₂O molecule. The self term involving coherent, incoherent, and multiple scattering contributions is evaluated by an empirical method of the polynomial expansion which has been successfully adopted for D₂O and H₂O-D₂O mixtures,^{9,10}

$$(d\sigma/d\Omega)^{self} = A + BQ^2 + CQ^4 + DQ^6 + EQ^8.$$
 (3.1)

Coefficients A—E were determined by the least-squares fit to the observed total scattering cross section in the range of $3.00 \le Q \le 9.69$ Å⁻¹.

H—H, X—H and X—X intermolecular partial structure factors, $a_{\rm HH}(Q)$, $a_{\rm XH}(Q)$ and $a_{\rm XX}(Q)$ (X: O, Br and Li), were derived from the combination of the intermolecular interference terms for three sample solutions (I, II and III) as follows:

$$(d\sigma/d\Omega)^{\text{inter}}(\text{for I}) + (d\sigma/d\Omega)^{\text{inter}}(\text{for II}) -2(d\sigma/d\Omega)^{\text{inter}}(\text{for III}) = 2(1-x)^2 b_D^2[a_{\text{HH}}(Q) - 1], \qquad (3.2) 4(d\sigma/d\Omega)^{\text{inter}}(\text{for III}) - (d\sigma/d\Omega)^{\text{inter}}(\text{for I}) -3(d\sigma/d\Omega)^{\text{inter}}(\text{for II}) = 4(1-x)\{x(b_{\text{Li}} + b_{\text{Br}}) + (1-x)b_O\}b_D[a_{\text{XH}}(Q) - 1], \qquad (3.3)$$

$$(d\sigma/d\Omega)^{\text{inter}}(\text{for II}) = \{x(b_{\text{Li}} + b_{\text{Br}}) + (1-x)b_{\text{O}}\}^2 [a_{\text{XX}}(Q) - 1].$$
(3.4)

Prior to evaluation of $a_{ij}(Q)$, contributions from intermolecular nearest neighbor $\mathrm{Li}^+ \cdots \mathrm{O}$ and $\mathrm{Li}^+ \cdots \mathrm{D}(\mathrm{H})$ interactions were subtracted from the observed $(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{inter}}$ to reduce the number of atom pairs in the least squares analysis of $a_{ij}(Q)$ as described below. Structural parameters for the nearest neighbor $Li^+ \cdots O$ and $Li^+ \cdots D(H)$ were taken from those obtained in our previous neutron diffraction study with ⁶Li/⁷Li isotopic substitution method.²)

The observed partial structure factors $a_{ij}(Q)$ for the 10, 25 and 33 mol% LiBr solutions are represented in Fig. 2. Although data points are somewhat scattered due to statistical uncertainties involved in the neutron count rate, the oscillational feature is clearly evidenced in present $a_{ij}(Q)$ functions.

The partial distribution function, $g_{ij}(r)$, was derived by the Fourier transform of observed $a_{ij}(Q)$,

$$g_{ij}(r) = 1 + (2\pi^2 \rho r)^{-1} \\ \times \int_0^{Q_{max}} Q[a_{ij}(Q) - 1] M(Q) \sin(Qr) \, dQ, (3.5)$$

where, ρ denotes the number density. The modification function, $M(Q) = \exp(-0.018Q^2)$, was introduced to reduce spurious ripples arising from the truncation error associated with relatively small Q_{max} values (9.69 Å⁻¹) employed in this study.

Quantitative analysis of $a_{ij}(Q)$ was carried out using the following model function including contributions from the short- and long-range interactions,^{11,12}

$$a_{ij}(Q) = \sum \beta_{ij} n_{ij} \exp(-l_{ij}^2 Q^2/2) \sin(Qr_{ij}) / (Qr_{ij}) + 4\pi \rho (-l_0^2 Q^2/2) [Qr_0 \cos(Qr_0) - \sin(Qr_0)] Q^{-3},$$
(3.6)

where, n_{ij} , l_{ij} and r_{ij} denote the coordination number, rms amplitude and internuclear distance, respectively. β_{ij} is the weighting factor of the partial structure factor. Parameters l_0 and r_0 describe behavior of the long-range random distribution of atoms.

Composition dependence of the partial distribution function, $g_{ij}(r)$, is represented in Fig. 3. The first peak at r = 2.4 Å observed in $g_{\rm HH}(r)$ for 10 mol% LiBr solution, attributable to the hydrogen-bonded H···H interaction, which is disappeared in $g_{\rm HH}(r)$ for 33 mol% LiBr solution. The nearest neighbor H···H distances determined from the least-squares fit for the 10, 25 and 33 mol% LiBr solutions were 2.38(1) Å, 2.37(1) Å and 2.50(1) Å, respectively. The nearest neighbor hydrogen-bonded



Fig.2. Partial structure factors, a) $a_{HH}(Q)$, b) $a_{XH}(Q)$ and c) $a_{XX}(Q)$ (X: O, Br and Li), observed for aqueous 10, 25 and 33 mol% LiBr solutions (dots). The best-fit of calculated interference terms are shown by solid lines.



Fig.3. Partial distribution functions, a) $g_{\rm HH}(r)$, b) $g_{\rm XH}(r)$ and c) $g_{\rm XX}(r)$ (X: O, Br and Li), observed for aqueous 10, 25 and 33 mol% LiBr solutions (solid lines). Calculated contributions from the short- and long-range interatomic interactions are denoted by dotted and broken lines, respectively.

O···H interaction, appearing as a well resolved first peak in $g_{\rm XH}(r)$ for 10 mol% LiBr solution $(r_{\rm OH} = 1.91(1) \text{ Å})$, seems to be completely diminished in $g_{\rm XH}(r)$ for 25 and 33 mol% LiBr solutions. These observations suggest that the intermolecular hydrogen-bonded network remaining in the 10 mol% LiBr solution is completely broken in extremely high solute concentration above 25 mol% LiBr.

On the other hand, the nearest neighbor $Br^- \cdots H$ and $Br^- \cdots O$ interactions are found to present for all the three compositions $(r_{BrH} = 2.22(1) \text{ Å and } r_{BrO} = 3.30(1) \text{ Å for 10 mol\% LiBr}, r_{BrH} = 2.33(1) \text{ Å and } r_{BrO} = 3.12(2) \text{ Å for 25 mol\% LiBr, and } r_{BrH} = 2.33(1) \text{ Å and } r_{BrO} = 3.16(4) \text{ Å for 33 mol\% LiBr solutions, respectively}}. The hydration number of <math>Br^-$ is determined to 5.5(1), 4.3(1) and 3.8(1) for the 10, 20 and 33 mol\% LiBr solutions, respectively. These results suggest that the ion-water interaction is much stronger than the hydrogen bonds among the solvent water molecules in extremely concentrated aqueous solutions. The structural transition of the intermolecular hydrogen-bonded network is considered to occur at higher solute concentration above 25 mol\% LiBr.

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