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# Neutron Diffraction Study on the Structure of Highly Concentrated Aqueous LiBr Solutions

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Neutron diffraction measurements have been carried out on aqueous solutions with 20 mol% lithium bromide. The isotopic substitution technique was applied to lithium ions and hydrogen atoms of the water molecule. The measured results were used to determine the partial pair distribution functions $g_{\mathrm{LiO}}(r)$, $g_{\mathrm{LiH}}(r)$, and $g_{\mathrm{HH}}(r)$. The $\mathrm{Li}^+\cdots$water molecule configuration is characterized by the intermolecular distances $r_{\mathrm{LiO}}=1.96\pm0.02$ Å and $r_{\mathrm{LiH}}=2.60\pm0.02$ Å, and the tilt angle between the $\mathrm{Li}^+\cdots\mathrm{O}$ axis and the molecular plane of water molecule, $\phi=27\pm10°$. The mean coordination number of water molecules around $\mathrm{Li}^+$ is computed to be $3.9\pm0.5$. The hydrogen–hydrogen pair correlation function $g_{\mathrm{HH}}(r)$ obtained from observed cross sections of these solutions with different isotopic compositions exhibits that each hydrogen atom in a given water molecule is surrounded with $3.7\pm0.5$ hydrogen atoms of neighboring molecules located at $r_{\mathrm{HH}}=2.65\pm0.05$ Å. The hydrogen bond among water molecules may be considered to be markedly destroyed in the present concentrated LiBr solution, compared with that in pure liquid water.

The hydration structure of $\mathrm{Li}^+$ in aqueous solutions have long been matter of interest. It was very difficult in earlier X-ray diffraction studies[1—3] for concentrated aqueous solutions to determine the hydration number of $\mathrm{Li}^+$ from observed total distribution functions because of the small scattering power of $\mathrm{Li}^+$ and hence the much smaller contribution of $\mathrm{Li}^+\cdots\mathrm{O}$ pairs in the total diffraction pattern. Narten et al have investigated the hydration structure of $\mathrm{Li}^+$ in aqueous solutions of LiCl with a wide solute composition range using both neutron and X-ray diffraction techniques.[4] Their least square analysis of the structure function for $\mathrm{LiCl{\cdot}3H_2O}$ has pointed out the tetrahedral hydration model around $\mathrm{Li}^+$. This tetrahedral hydration model has also been reported by a time-of-flight neutron diffraction study for the more dilute LiCl solution.[5] On the other hand, the neutron first-order difference method involving $^6\mathrm{Li}/^7\mathrm{Li}$ isotopic substitution has been applied to 6.7 and 16.7 mol% LiCl heavy water solutions[6,7] in order to investigate the number of water molecules in the first coordination shell and the orientation of the water molecules with respect to $\mathrm{Li}^+$–O axis. The result obtained is considerably striking, that is to say, the hydration number of $\mathrm{Li}^+$ is strongly concentration dependent and the value 5.5 at 6.7 mol% LiCl solution decreases to 3.3 at 16.7 mol% LiCl solution. The coordination number $n(\mathrm{Li}^+\cdots\mathrm{O})=2.3$ has also been reported from the $^6\mathrm{Li}/^7\mathrm{Li}$ isotopic substitution experiments for highly concentrated 33 mol% LiCl solution.[8] Recent molecular dynamics (MD) calculations for this system seem to support this concentration dependent $n(\mathrm{Li}^+\cdots\mathrm{O})$.[9,10] In addition, MD calculations have also given the following predictions. There exists the $\mathrm{Li}^+\cdots\mathrm{Cl}^-$ ion pair contact in $\mathrm{LiCl{\cdot}3H_2O}$, and the significant deformation of the solvent structure occurs in $\mathrm{LiCl{\cdot}4H_2O}$[9] because the hydrogen bonds between water molecules become weaker. At any way, the experimental determination of the partial pair distribution functions $g_{\mathrm{OH}}(r)$ and $g_{\mathrm{HH}}(r)$ for another concentrated aqueous solution is needed at the present time to improve the unclear situation regarding to the hydration structure of $\mathrm{Li}^+$ in the system.

In this report we describe results of neutron diffraction measurements on five aqueous 20 mol% LiBr solutions in which the isotopic ratios of both $^6\mathrm{Li}/^7\mathrm{Li}$ and H/D have been changed. The hydration structure of $\mathrm{Li}^+$ is determined in terms of the partial pair correlation functions, $g_{\mathrm{LiO}}(r)$ and $g_{\mathrm{LiH}}(r)$. The information for the deformation of hydrogen bonded structure among water molecules, is also provided from the partial distribution function, $g_{\mathrm{HH}}(r)$, experimentally deduced.

## Theory

The observed total scattering cross section from a neutron diffraction experiment is divided into two parts corresponding to self and interference terms, the latter of which contains all the information concerning the liquid structure;[11]

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}} = (\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{self}} + (\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}}\,. \tag{1}$$

The self term can be wirtten as,

$$(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{self}} = \Sigma c_i\sigma_{\mathrm{s},i}/4\pi + \text{Correction terms arising from the inelasticity effect,} \tag{2}$$

where, $c_i$ and $\sigma_{\mathrm{s},i}$ denote the number of nucleus $i$ in the stoichiometric unit and the scattering cross section of nucleus $i$, respectively. The inelasticity contribution arises from mainly H and D nuclei which have a smaller effective mass. It is frequently pointed out that the serious distortion in the scattering cross section is observed due to this effect. For the purpose of the extraction of the interference term from the observed total scattering cross section, semi-empirical approaches using the polynominal functional form for the self scattering term have been employed in several hydrogenous systems.[12—15] More available expressions can be found in works by

Powles.[16,17] However, the functional form of his inelasticity correction is considerably complicated, involving the detector efficiency, $\alpha_d$, $Q$-dependent effective mass of constituent nuclei, $M_i^*$ and the molecular geometry. The magnitude of the correction term is roughly proportional to $1/M^*$ and $\sin^2\theta$.[16,17] To obtain the information on the hydration structure around a given ion, the first-order difference method[18] concerned with isotopic substitution technique, has been developed by the Bristol group, the main concept of which is the cancellation of inelasticity distortion arising from the hydrogen or deuterium atom contained in the solvent molecule. Then, we will apply this cancellation method to the present measured results and obtain the reliable information on the hydration structure around $Li^+$.

The observed interference term for the present system, scaled by a stoichiometric unit, $(LiBr)_x(H_2O)_{1-x}$, can be written as the weighted sum of ten partial structure factors;

$$\begin{aligned}(\mathrm{d}\sigma/\mathrm{d}\Omega)_{\mathrm{int}} &= x^2 b_{\mathrm{Li}}{}^2\,[a_{\mathrm{LiLi}}(Q)-1]\\ &+ x^2 b_{\mathrm{Br}}{}^2\,[a_{\mathrm{BrBr}}(Q)-1]\\ &+ 2x^2 b_{\mathrm{Li}} b_{\mathrm{Br}}\,[a_{\mathrm{LiBr}}(Q)-1]\\ &+ 2x(1-x) b_{\mathrm{Li}} b_{\mathrm{O}}\,[a_{\mathrm{LiO}}(Q)-1]\\ &+ 4x(1-x) b_{\mathrm{Li}} b_{\mathrm{H}}\,[a_{\mathrm{LiH}}(Q)-1]\\ &+ 2x(1-x) b_{\mathrm{Br}} b_{\mathrm{O}}\,[a_{\mathrm{BrO}}(Q)-1]\\ &+ 4x(1-x) b_{\mathrm{Br}} b_{\mathrm{H}}\,[a_{\mathrm{BrH}}(Q)-1]\\ &+ 4(1-x)^2 b_{\mathrm{O}} b_{\mathrm{H}}\,[a_{\mathrm{OH}}(Q)-1]\\ &+ 4(1-x)^2 b_{\mathrm{H}}{}^2\,[a_{\mathrm{HH}}(Q)-1]\\ &+ (1-x)^2 b_{\mathrm{O}}{}^2\,[a_{\mathrm{OO}}(Q)-1]\,, \qquad (3)\end{aligned}$$

where, $b_i$ stands for the mean coherent scattering length of nucleus $i$. The difference function, $\Delta_{\mathrm{Li}}(Q)$, between two solutions which are identical in all respect except for different isotopic states of Li, is expressed as follows,

$$\begin{aligned}\Delta_{\mathrm{Li}}(Q) &= A\,[a_{\mathrm{LiO}}(Q)-1] + B\,[a_{\mathrm{LiH}}(Q)-1]\\ &+ C\,[a_{\mathrm{LiBr}}(Q)-1] + D\,[a_{\mathrm{LiLi}}(Q)-1]\\ &+ \text{correction term}, \qquad (4)\end{aligned}$$

here,

$$\begin{aligned}A &= 2x(1-x)b_{\mathrm{O}}\left(b_{\mathrm{Li}} - b_{\mathrm{Li}}{}'\right)\\ B &= 4x(1-x)b_{\mathrm{H}}\left(b_{\mathrm{Li}} - b_{\mathrm{Li}}{}'\right)\\ C &= 2x^2 b_{\mathrm{Br}}\left(b_{\mathrm{Li}} - b_{\mathrm{Li}}{}'\right)\\ D &= x^2\left(b_{\mathrm{Li}}{}^2 - b_{\mathrm{Li}}{}'^2\right).\end{aligned}$$

Contributions from the atom pair which does not include $Li^+$ are completely canceled out in this $\Delta_{\mathrm{Li}}(Q)$. The distortion in self scattering term from the light nuclei, H or D, is also canceled out by taking the difference for two solutions and then, is not involved in $\Delta_{\mathrm{Li}}(Q)$. The correction term in Eq. 4 arises from the small difference in inelasticity contribution for the self term between $^6Li$ and $^7Li$, which can possibly be neglected.[7,18]

The Fourier transform of $\Delta_{\mathrm{Li}}(Q)$ gives the distribution function $\overline{G}_{\mathrm{Li}}(r)$ around $Li^+$. $\overline{G}_{\mathrm{Li}}(r)$ is related to the weighted sum of partial distribution functions,

$$\begin{aligned}\overline{G}_{\mathrm{Li}}(r) &= \frac{1}{2\pi^2\rho r}\int_0^{Q_{\max}} Q\Delta_{\mathrm{Li}}(Q)\sin(Qr)\,\mathrm{d}Q\\ &= A\,[g_{\mathrm{LiO}}(r)-1] + B\,[g_{\mathrm{LiH}}(r)-1]\\ &+ C\,[g_{\mathrm{LiBr}}(r)-1] + D\,[g_{\mathrm{LiLi}}(r)-1]\,, \qquad (5)\end{aligned}$$

where, $\rho$ is the number density of the stoichiometric unit $(LiBr)_x(H_2O)_{1-x}$. The partial pair correlation function of $i$–$j$ pair, $g_{ij}(r)$, is defined as the Fourier transform of the partial structure factor $a_{ij}(Q)$ as given below,

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2\rho r}\int Q\,[a_{ij}(Q)-1]\sin(Qr)\mathrm{d}Q. \qquad (6)$$

The number of $\alpha$ atom around Li, $n_{\mathrm{Li}\alpha}$, is given by,

$$n_{\mathrm{Li}\alpha} = c_\alpha\int 4\pi\rho r^2 g_{\mathrm{Li}\alpha}(r)\mathrm{d}r. \qquad (7)$$

The Li–H partial structure factor, $a_{\mathrm{LiH}}(Q)$, is derived from the second order difference between two $\Delta_{\mathrm{Li}}(Q)$s, in which the isotopic composition of the hydrogen atom has been changed, that is to say,

$$\begin{aligned}&\Delta_{\mathrm{Li}}(Q) - \Delta'_{\mathrm{Li}}(Q)\\ &\quad = 4x(1-x)\left(b_{\mathrm{H}} - b'_{\mathrm{H}}\right)\left(b_{\mathrm{Li}} - b'_{\mathrm{Li}}\right)[a_{\mathrm{LiH}}(Q)-1]. \qquad (8)\end{aligned}$$

The H–H partial structure factor, $a_{\mathrm{HH}}(Q)$, is deduced directly from the combination of the observed cross sections for three solutions, namely, $(LiBr)_x({}'H_2O)_{1-x}$, $(LiBr)_x({}''H_2O)_{1-x}$, and $(LiBr)_x({}'''H_2O)_{1-x}$. In the third solution, the isotopic composition of hydrogen has been chosen to be the average value of the first and the second ones, i.e., $b'''_{\mathrm{H}} = (b'_{\mathrm{H}} + b''_{\mathrm{H}})/2$.

$$\begin{aligned}&(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\text{ (for solution 1)}\\ &\quad + (\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\text{ (for solution 2)}\\ &\quad - 2\,(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\text{ (for solution 3)}\\ &\quad = 2(1-x)^2\left(b'_{\mathrm{H}} - b''_{\mathrm{H}}\right)^2[a_{\mathrm{HH}}(Q)-1]. \qquad (9)\end{aligned}$$

The inelasticity distortion arising from H and D atoms can again be expected to be canceled out by the same procedure as described for the structure determination of pure liquid water by Soper.[19,20]

## Experimental and Data Analysis

**Materials.** $^6Li$- and $^7Li$-enriched lithium bromides were respectively prepared by reacting $^6Li_2CO_3$ (95.45% $^6Li$) and $^7LiOH \cdot H_2O$ (99.94% $^7Li$), obtained form Tomiyama Chemical Co., Ltd., Tokyo, with slightly excess amount of concentrated aqueous hydrobromic acid solution. The dehydration of the product solution was achieved by heating at 180°C under vacuum for two days. The weighted amount of enriched anhydrous LiBr was dissolved into $D_2O$ (99.9% D, CIL Co., Ltd.) or $D_2O$–$H_2O$ mixtures to prepare five aqueous 20 mol% LiBr solutions with different isotopic compositions of both lithium and hydrogen atoms. The sample parameters are listed up in Table 1. In order to reduce uncertainties in the data correction procedure arising form

Table 1. The Isotopic Compositions, Mean Scattering Lengths $b_{\mathrm{Li}}$ and $b_{\mathrm{H}}$ for Lithium and Hydrogen Atoms, Mean Scattering and Absorption Cross Sections and the Number Density Scaled in the Stoichiometric Unit $(\mathrm{LiBr})_{0.2}(\mathrm{H_2O})_{0.8}$, $\sigma_{\mathrm{s}}$, $\sigma_{\mathrm{a}}$, and $\rho$, Respectively, for Sample Solutions Used in This Study

| Samples | $^6$Li/% | $^7$Li/% | H/% | D/% | $b_{\mathrm{Li}}/10^{-12}$ cm[a)] | $b_{\mathrm{H}}/10^{-12}$ cm[a)] | $\sigma_{\mathrm{s}}$/barns[b)] | $\sigma_{\mathrm{a}}$/barns[c)] | $\rho/\text{Å}^{-3}$ |
|---|---|---|---|---|---|---|---|---|---|
| $(^7\mathrm{LiBr})_{0.2}(\mathrm{D_2O})_{0.8}$ | 0.1 | 99.9 | 0.1 | 99.9 | −0.220 | 0.666 | 11.32 | 0.92 | 0.0302 |
| $(^0\mathrm{LiBr})_{0.2}(\mathrm{D_2O})_{0.8}$[d)] | 54.1 | 45.9 | 0.1 | 99.9 | 0 | 0.666 | 11.27 | 63.06 | |
| $(^7\mathrm{LiBr})_{0.2}(^0\mathrm{H_2O})_{0.8}$ | 0.1 | 99.9 | 64.1 | 35.9 | −0.220 | 0 | 41.58 | 1.13 | |
| $(^0\mathrm{LiBr})_{0.2}(^0\mathrm{H_2O})_{0.8}$ | 54.1 | 45.9 | 64.1 | 35.9 | 0 | 0 | 41.53 | 63.24 | |
| $(^7\mathrm{LiBr})_{0.2}(^{0-2}\mathrm{H_2O})_{0.8}$ | 0.1 | 99.9 | 32.0 | 68.0 | −0.220 | 0.333 | 26.45 | 1.02 | |

a) Taken from Ref. 21. b) Calculated using total cross sections for $\mathrm{D_2O}$ and $\mathrm{H_2O}$.[11,22)] c) For the incident neutron wavelength of 1.102 Å. d) The superscript 0 denotes an isotopic mixture with $b=0$.

the extremely large absorption and incoherent scattering of $^6$Li and H nuclei, respectively, the isotopic composition of "null mixture", in which the mean scattering length of both lithium and hydrogen atoms are zero, was employed in this study. Another merit of the "null mixture" is that the interpretation of the resultant distribution function becomes much simplified since no contribution from Li–X or H–X (X=Br, O, H or Li) pairs is expected to appear in the distribution function.

**Neutron Diffraction Measurements.** The sample solutions were sealed in vacuo into a cylindrical quartz sample cell (11.4 mm in inner diameter and 1.2 mm in thickness). Neutron diffraction measurements were carried out at 25°C using 4G diffractometer installed at JRR-3 research reactor operated at 20 MW, in Japan Atomic Energy Research Institute, Tokai, Japan. The incident neutron wavelength was found to be $\lambda=1.102\pm0.004$ Å, which was determined by the Bragg reflections from KCl powder. Collimations used were 40′-40′-40′ in going from the reactor to the detector. The aperture of the colimated beam was 20 mm in width and 41 mm in hight. The scattered neutrons from the sample solution were collected over the angular range of $3<2\theta<118°$, which corresponds to $0.30<Q<9.77$ Å$^{-1}$ ($Q=4\pi\sin\theta/\lambda$). In the region of $3<2\theta<40°$ and $41<2\theta<118°$, the step interval was chosen to be $\Delta 2\theta=0.5°$ and 1°, respectively. The preset time was 300 s for the samples with high $^6$Li content and 240 s for the other ones. The measurement of scattering intensities was also made for a vanadium rod (10 mm in diameter), an empty cell and a background.

Measured scattering data were corrected for the background intensity, the absorption of both the sample and cell[23)] and multiple scattering.[24)] The obtained count rate for the sample was converted to the absolute scale by the use of intensity data from the vanadium rod. Much attention was paid to the calculation of the absorption and multiple scattering correction coefficients for the sample containing $^6$Li and H, which have large absorption and scattering cross sections. The method by Paalman and Pings[23)] was applied for the absorption correction. Scattering cross sections for H and D atoms within the water molecules, $\sigma_{\mathrm{s,H}}=33.55$ barns and $\sigma_{\mathrm{s,D}}=4.04$ barns, were employed for both the absorption and multiple scattering corrections in this work. These values have been successfully applied for the data corrections of aqueous $\mathrm{NiCl_2}$ solutions in $\mathrm{H_2O}$.[22)] Absorption correction coefficients $A_{\mathrm{s,sc}}$ and $A_{\mathrm{c,sc}}$[23)] were calculated integrating numerically over the whole range of the scattering angle, $3<2\theta<120°$. Then, the angular dependence of $A_{\mathrm{s,sc}}$ and $A_{\mathrm{c,sc}}$ was determined through the least square fit to the polynominal function,

$$A_{\mathrm{s,sc}}(2\theta)\ \text{or}\ A_{\mathrm{c,sc}}(2\theta)=\sum_{i=1}^{3}R_i(2\theta)^{i-1}. \tag{10}$$

The multiple scattering intensity was estimated through the method by Brech and Averbach.[24)] The calculated ratio of the multiple scattering intensity to the observed total scattering intensity for the present five samples were between 0.1034 (for $^0$LiBr–$\mathrm{D_2O}$ solution) and 0.4733 (for $^7$LiBr–$^0\mathrm{H_2O}$ solution), suggesting that the uncertainty derived by the multiple scattering correction is not significant.

## Results and Discussion

**The Hydration Structure around Li$^+$.** Observed scattering cross sections for five aqueous LiBr solutions are shown in Fig. 1. A remarkable change in the diffraction patterns is obviously found among these solutions with different isotope ratios of $^6$Li/$^7$Li and H/D. The decrease in the intensity of $(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}$ curves at a larger $Q$ side arising from the inelasticity effect, becomes more pronounced for the solutions with higher H content. Two $\Delta_{\mathrm{Li}}(Q)$s were derived from a numerical difference between the scattering cross sections for the solutions with the same isotopic state for hydrogen atoms and the different one for lithium atoms, as followings,

$$\begin{aligned}
{}^{\mathrm{D}}\Delta_{\mathrm{Li}}(Q) &= (\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\left(\text{for }{}^0\text{Li–D}\right)\\
&\quad-(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\left(\text{for }{}^7\text{Li–D}\right),\\
{}^{0\mathrm{H}}\Delta_{\mathrm{Li}}(Q) &= (\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\left(\text{for }{}^0\text{Li–}{}^0\text{H}\right)\\
&\quad-(\mathrm{d}\sigma/\mathrm{d}\Omega)^{\mathrm{obsd}}\left(\text{for }{}^7\text{Li–}{}^0\text{H}\right),
\end{aligned} \tag{11}$$

where, the superscript 0 denotes the isotopic composition of the null mixture. The coefficients for respective partial structure factors contained in these difference functions are listed in Table 2. It can be seen that the weighting coefficients for Li–Br and Li–Li pairs are small compared with those for Li–O and Li–H ones, hence these $\Delta_{\mathrm{Li}}(Q)$s are dominated by the terms concerning with the hydration structure of Li$^+$. Since there is no contribution from the Li–H pair, the information on the Li–O partial pair distribution function is accessible from $^{0\mathrm{H}}\Delta_{\mathrm{Li}}(Q)$ and its Fourier transform, $^{0\mathrm{H}}\overline{G}_{\mathrm{Li}}(r)$. The Li–H partial structure factor,

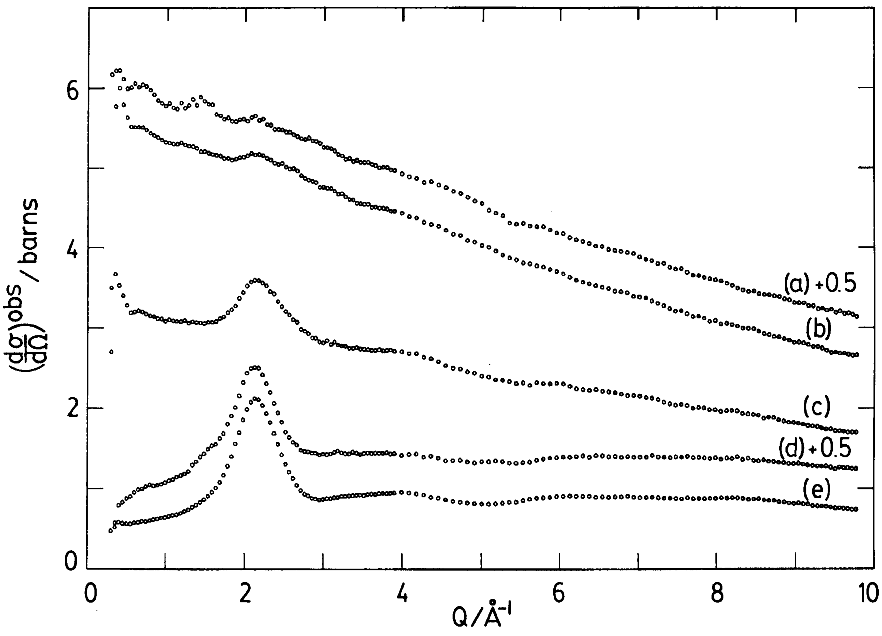

Fig. 1. Observed scattering cross sections $(d\sigma/d\Omega)^{\mathrm{obsd}}$ for aqueous 20 mol% LiBr solutions with different isotope ratios of $^6$Li/$^7$Li and H/D. (a) $^0$Li–$^0$H. (b) $^7$Li–$^0$H. (c) $^7$Li–$^{0-2}$H. (d) $^0$Li–D. (e) $^7$Li–D. The superscript 0 denotes an isotopic mixture in which the mean scattering length is null.

Table 2. Values of the Coefficients of $a_{ij}(Q)$ in Eq. 4

| Difference function | $A$/barns | $B$/barns | $C$/barns | $D$/barns |
|---|---|---|---|---|
| $^{\mathrm{D}}\Delta_{\mathrm{Li}}(Q)$ | 0.0408 | 0.0938 | 0.0119 | −0.0019 |
| $^{0\mathrm{H}}\Delta_{\mathrm{Li}}(Q)$ | 0.0408 | 0 | 0.0119 | −0.0019 |

$a_{\mathrm{LiH}}(Q)$, may be determined by taking the second order difference between $^{\mathrm{D}}\Delta_{\mathrm{Li}}(Q)$ and $^{0\mathrm{H}}\Delta_{\mathrm{Li}}(Q)$. $^{\mathrm{D}}\Delta_{\mathrm{Li}}(Q)$, $^{0\mathrm{H}}\Delta_{\mathrm{Li}}(Q)$ and $a_{\mathrm{LiH}}(Q)$, and corresponding distribution functions, $^{\mathrm{D}}\overline{G}_{\mathrm{Li}}(r)$, $^{0\mathrm{H}}\overline{G}_{\mathrm{Li}}(r)$ and $g_{\mathrm{LiH}}(r)$ obtained in this work are represented in Figs. 2 and 3, respectively. The upper limit $Q_{\mathrm{max}}$ for the Fourier integral in Eq. 5 is taken as 9.77 Å$^{-1}$ for all distribution functions. The truncation effect due to $Q_{\mathrm{max}}=9.77$ Å$^{-1}$ and minute scatterings of the data points, particularly, at high $Q$ region in the intensity function cause serious ripples at small $r$ region and high frequency periodic oscillations in the distribution function. Then, we needed to smooth the intensity functions by using the spline function before the Fourier transform without loosing the feature of the data points themselves. In addition, unphysical ripples below the first peak appeared in two $\overline{G}_{\mathrm{Li}}(r)$s and $g_{\mathrm{LiH}}(r)$ were eliminated by setting these functions to $-(A+B+C+D)$ or to zero, respectively. After these corrections, $\overline{G}_{\mathrm{Li}}(r)$s and $g_{\mathrm{LiH}}(r)$ were back transformed to obtain the corrected two $\Delta_{\mathrm{Li}}(Q)$s and $a_{\mathrm{LiH}}(Q)$ as represented by the solid line in Fig. 2. The present $^{\mathrm{D}}\overline{G}_{\mathrm{Li}}(r)$ exhibits the common overall feature which can be seen in earlier works for aqueous LiCl[6,7,25] and LiNO$_3$[26] solutions, i.e., well resolved Li–O and Li–D peaks suggesting the distinct first hydration shell around Li$^+$ with a stable orientational correlation between Li$^+$ and water molecules. It is surprising that the well defined hydration structure around Li$^+$ is kept even in a highly concentrated solution such as 20 mol% LiBr, where at most four water molecules can contact with each Li$^+$. It appears obviously that oxygen atoms of the water molecule in the first hydration shell are directly facing toward Li$^+$ from the comparison between $^{\mathrm{D}}\overline{G}_{\mathrm{Li}}(r)$ and $^{0\mathrm{H}}\overline{G}_{\mathrm{Li}}(r)$, because the peak located at $r=2.6$ Å in $^{\mathrm{D}}\overline{G}_{\mathrm{Li}}(r)$ is absent in $^{0\mathrm{H}}\overline{G}_{\mathrm{Li}}(r)$. Contributions from Li–O and Li–Br pairs are dominant in $^{0\mathrm{H}}\overline{G}_{\mathrm{Li}}(r)$, hence the significant peak at $r=2.0$ Å can be assigned to the nearest neighbor Li···O interaction. The interatomic distance

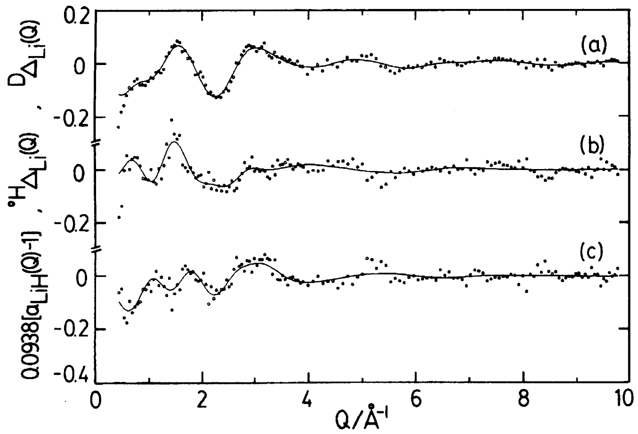

Fig. 2. Observed difference functions (a) $^{\mathrm{D}}\Delta_{\mathrm{Li}}(Q)$, (b) $^{0\mathrm{H}}\Delta_{\mathrm{Li}}(Q)$, and (c) the partial structure factor $a_{\mathrm{LiH}}(Q)$ for aqueous 20 mol% LiBr solution (dots). Solid lines are given by the inverse Fourier transform of the solid line in Fig. 3.

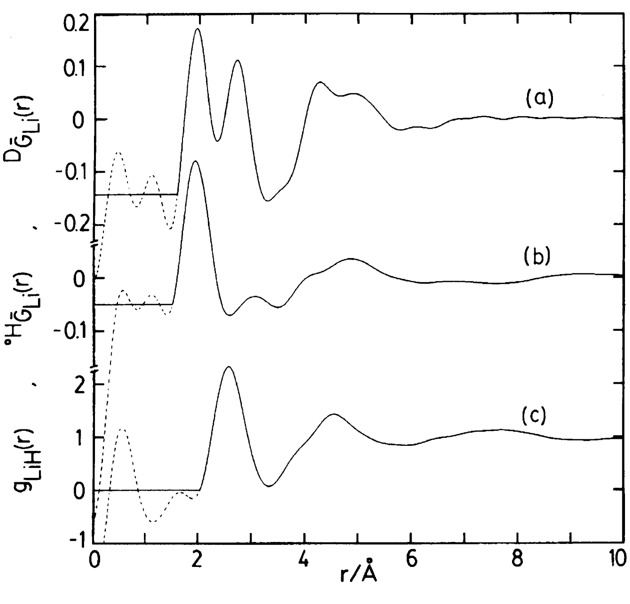

Fig. 3. The distribution functions around $Li^+$ (a) $^{D}\overline{G}_{Li}(r)$, (b) $^{0H}\overline{G}_{Li}(r)$, and (c) the partial pair correlation function $g_{LiH}(r)$ for aqueous 20 mol% LiBr solution.

$r_{LiO}$ and the coordination number $n_{LiO}$ for this peak are determined to $r_{LiO}=1.96\pm0.02$ Å and $n_{LiO}=3.9\pm0.5$, respectively, through the least square fitting of $r\cdot{}^{0H}\overline{G}_{Li}(r)$ curve to the Gaussian function. The hydration number of $Li^+$ is close to the ratio of the number of both $Li^+$ and water molecule in this solution, 1 : 4, implying that the $Li^+$ hydration occurs more preferently compared with that of $Br^-$. The value $r_{LiO}$ determined in this work is in good agreement with the result for aqueous LiCl solution of the comparable concentration reported by means of the neutron first order difference method,[6,7] which indicates that the nature of $Li^+\cdots O$ bond in the first hydration shell of $Li^+$ in aqueous lithium halogenide solutions is anion-independent.

The first peak in $g_{LiH}(r)$, corresponding to the 2.6 Å peak in $^{D}\overline{G}_{Li}(r)$, is reasonably ascribed to the nearest neighbor interaction between $Li^+$ and hydrogen atoms of the water molecule within the first hydration shell. The values $r_{LiH}$ and $n_{LiH}$ are obtained to be $2.60\pm0.02$ Å and $7\pm1$, respectively, from the Gaussian fitting of $r\cdot g_{LiH}(r)$ curve. If the contact ion pair $Li^+\cdots Br^-$ may exist in this solution, the $Li^+\cdots Br^-$ distance is expected to fall around $r=2.5$ Å, according to the sum of ionic radii for $Li^+$ and $Br^-$. However, any indication for this pair cannot be observed in the present $^{0H}\overline{G}_{Li}(r)$. The fact that $n_{LiH}\simeq 2n_{LiO}$ and the nearly symmetrical shape of $Li^+\cdots O$ peak found in $^{0H}\overline{G}_{Li}(r)$ also denotes the absence of $Br^-$ within the first hydration shell of $Li^+$. The tilt angle $\phi$ between the $Li^+\cdots O$ axis and the molecular plane of the water molecule is estimated to be $27\pm10°$ with the help of the knowledge of intramolecular structural parameters of a $D_2O$ molecule in the liquid state ($r_{OD}=0.97$—$0.98$ Å, $r_{DD}=1.55$—$1.59$ Å[17,27,28]. This value of $\phi$ in the present LiBr solution is much smaller than that of $52\pm5°$ reported for 16.7 mol% LiCl solution.[6,7]

It may be expected to contain considerable uncertainties on the determination of the coordination number in the present data analysis because of the truncation effect at $Q_{max}=9.77$ Å$^{-1}$. However, it seems that this effect is relatively small in the present distribution functions, because the values of full width at half maximum for the nearest neighbour Li–O and Li–H peaks, $w_{LiO}=0.4$ Å and $w_{LiH}=0.6$ Å, obtained from the present $^{H}\overline{G}_{Li}(r)$ and $g_{LiH}(r)$, are in good agreement with those reported for $\overline{G}_{Li}(r)$, truncated at $Q_{max}=16$ Å$^{-1}$ by Newsome[7] ($w_{LiO}=0.4$ Å, $w_{LiD}=0.6$ Å and $w_{LiO}=0.3$ Å, $w_{LiD}=0.5$ Å for 3.37 and 9.95 m LiCl solutions, respectively).

The peaks concerning the second coordination shell around $Li^+$ can be observed in the region of $4<r<6$ Å in $^{D}\overline{G}_{Li}(r)$ function. The second peak in $g_{LiH}(r)$ is ascribed to the hydrogen atoms in the second hydration shell. The second peak located at $r=4.5$ Å in $^{0H}\overline{G}_{Li}(r)$ is considered to include both $Li^+\cdots O$ and $Li^+\cdots Br^-$ contributions, although the unique decomposition of this peak is not possible at present.

**H–H Partial Pair Correlation Function.** Figure 4 shows the hydrogen–hydrogen partial structure factor, $a_{HH}(Q)$, obtained by the Eq. 9 in the previous section and its Fourier transform, $g_{HH}(r)$, truncated at $Q_{max}=9.77$ Å$^{-1}$. The first peak located at $r=1.5$ Å in $g_{HH}(r)$ is apparently due to the intramolecular H–H distance in the water molecule. The second peak at ca. 2.7 Å can be ascribed to the intermolecular nearest

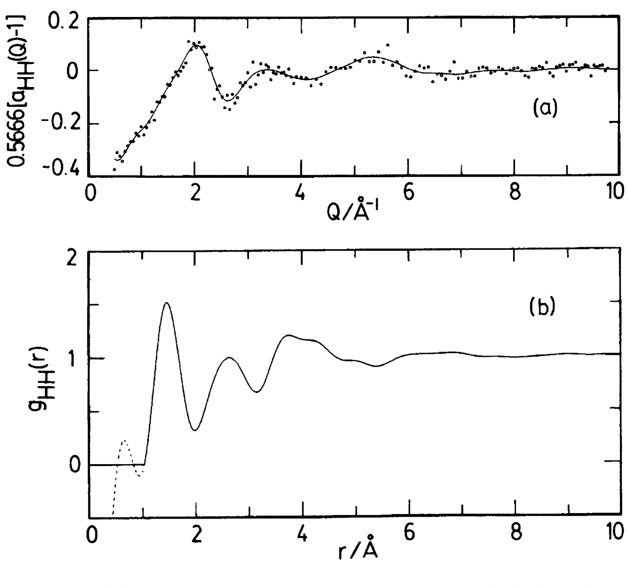

Fig. 4. (a) The partial structure factor, $a_{HH}(Q)$, (dots) and (b) the partial pair correlation function $g_{HH}(r)$ for aqueous 20 mol% LiBr solution. The solid line in (a) is given by the inverse Fourier transform of the solid line in (b).

neighbor H–H interaction. Another structural evidence is found around $r \approx 4$ Å. The peak position $r_{\mathrm{HH}}$ and the coordination number $n_{\mathrm{HH}}$ for the first two peaks, are determined to be $r_{\mathrm{HH}}=1.52\pm0.02$ Å, $n_{\mathrm{HH}}=1.1\pm0.2$ and $r_{\mathrm{HH}}=2.65\pm0.05$ Å, $n_{\mathrm{HH}}=3.7\pm0.5$, respectively, from the Gaussian fitting of $r \cdot g_{\mathrm{HH}}(r)$ function. The former peak position is slightly lower than the value reported for the water molecule in pure liquid water ($r_{\mathrm{DD}}=1.55$ Å)[17,27,28] or that found in highly concentrated aqueous LiCl solutions ($r_{\mathrm{DD}}=1.58$—$1.59$ Å).[27] This shorter D–D intramolecular distance in the present work may result mainly from the effect of the limited $Q$ range in the Fourier transform. The coordination number $n_{\mathrm{HH}}=1.1$, which corresponds well to the hypothetical value $n_{\mathrm{HH}}=1.0$ within the experimental error, may confirm that present data correction and normalization procedures are reasonably performed. The intermolecular nearest neighbor H–H distance obtained from the second peak position of the present $g_{\mathrm{HH}}(r)$ is sufficiently longer than the value found in pure liquid water,[19,20] in which the water molecules take locally a tetrahedral configuration due to the hydrogen bonds. The intermolecular nearest neighbor coordination number $n_{\mathrm{HH}}=3.7$, is also different from the value $n_{\mathrm{HH}} \approx 6$ reported for pure liquid water.[19,20] These results clearly indicate that the hydrogen bonded structure among the water molecules is considerably destroyed in the 20 mol% LiBr solution in comparison with the case in pure liquid water. The broad maximum observed in the present $g_{\mathrm{HH}}(r)$ at $r \approx 4$ Å may be ascribed to the H–H correlation between water molecules which are bonded to a common $\mathrm{Li}^+$. The distribution of atoms appears to be almost random in the region with $r>6$ Å.

In summary, the following conclusions can be drawn from the present experimental results for aqueous 20 mol% LiBr solutions. In this solution, $\mathrm{Li}^+$ is surrounded by about four water molecules with a steady configuration in which the oxygen atom of each water molecule is facing towards $\mathrm{Li}^+$. The tilt angle $\phi$ between $\mathrm{Li}^+ \cdots \mathrm{O}$ axis and the molecular plane of water molecule is obtained to be 27±10°. There is no indication of the presence of $\mathrm{Br}^-$ in the first hydration shell of $\mathrm{Li}^+$, suggesting the ion contact of $\mathrm{Li}^+\mathrm{Br}^-$ does not occur in this solute concentration. The intermolecular hydrogen bonded structure among water molecules seems to be significantly destroyed in this concentrated solution.

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