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The intra-molecular structure of a water molecule in hydrated and incompletely hydrated LiCl solutions

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Abstract. Time-of-flight neutron diffraction measurements were carried out on the hydrated and incompletely hydrated solutions $(\text{LiCl})_x(\text{D}_2\text{O})_{1-x}$ for $x = 0.20, 0.27, 0.32$ and 0.35 . The data for the high- Q region observed at the high scattering angle $2\theta = 91^\circ$ have been analysed in terms of intra-molecular interference, including an inelasticity correction, to determine the intra-molecular distances of a water molecule, r_{OD} and r_{DD} . The former shows no composition dependence within experimental error: the distance $r_{\text{OD}} = 0.970 \pm 0.006 \text{ \AA}$ is equal to that in pure D_2O . On the other hand, the distance $r_{\text{DD}} = 1.59 \pm 0.02 \text{ \AA}$ in the solutions with above 20 mol% LiCl is 0.04 \AA longer than that of liquid D_2O because of the strong interaction between the D_2O molecule and the ions. The conclusion reached in this work suggests that the results of the molecular dynamics simulation are not reasonable.

1. Introduction

In a highly dilute electrolyte solution, the solute ion is completely hydrated. Thus, the physical and chemical properties of the solution are mostly governed by the structure of this completely hydrated ion. The diffraction investigation showed that counter-ions shared water molecules in concentrated electrolyte or hydrated solutions. In the incompletely hydrated solutions with above 25 mol% salt (e.g., LiCl) each ion has insufficient water molecules to form the complete hydration sheath and both direct and indirect contacts between unlike ions occur.

An aqueous solution of LiCl is very useful in enabling one to study the solute–solvent and solute–solute interactions in a hydrated melt or an incompletely hydrated melt, because of the high solubility of LiCl in liquid water and the small ionic radius of lithium. The structure of a hydrated chloride ion in concentrated aqueous solutions with above 10 mol% LiCl has been investigated by using x-ray diffraction analyses (Brady 1958, Lawrence and Kruh 1967). Narten *et al* (1973) attempted to distinguish various possible ion–solvent configurations by carrying out x-ray and neutron diffraction measurements for the solutions with less than 25 mol% LiCl. Better neutron diffraction results can be achieved by using the method of isotopic substitution of Li and Cl nuclei in the solutions. The hydration number and the hydration geometry between a water molecule and a lithium or chloride ion have been determined for solutions with 7 mol% and 17 mol% LiCl (Soper *et al* 1977, Enderby and Neilson 1981, Newsome *et al* 1980, Newsome 1981). Direct and indirect correlations between Li^+ and Cl^- have been found by a TOF neutron diffraction study for the solutions with 33 mol% LiCl in D_2O by isotopic substitution of

Li (Ichikawa *et al* 1984). The direct correlation between Cl^- and Cl^- has been reported for 23 mol% LiCl in D_2O ; it was found using the Cl isotopes and the second-order difference method (Copestake *et al* 1985).

The intra-molecular structure of a water molecule in highly concentrated solution is very interesting, because its structure may be affected by a strong electrostatic field formed by the surrounding solute ions. However, the intra-molecular structure of a water molecule in hydrated and incompletely hydrated melts has not yet been determined with sufficient precision by such diffraction measurements. TOF neutron diffraction has the great advantage of being able to determine the precise molecular structure of liquid water, because of the availability of the structure factor in the high-momentum-transfer range up to about 50 \AA^{-1} (Kameda and Ichikawa 1986).

In this paper, we report the results of TOF neutron diffraction measurements on hydrated or incompletely hydrated $(\text{LiCl})_x(\text{D}_2\text{O})_{1-x}$ solutions, which are meant to clarify the effect of ion–water-molecule interaction on the intra-molecular structure of water molecules.

2. Experiment

Anhydrous LiCl of a guaranteed grade was used without further purification. Liquid heavy water was obtained from Merck Inc (99.75%D). The solutions of LiCl dissolved in heavy water were sealed *in vacuo* in a quartz cell (10 mm in inner diameter and 0.4 mm in thickness). The diffraction measurements were carried out at $125 \pm 10 \text{ }^\circ\text{C}$. The compositions of the sample were 20, 27, 32 and 35 mol% LiCl.

TOF neutron diffraction measurements were carried out using a high-intensity total scattering (HIT) spectrometer (Watanabe *et al* 1980) installed at a pulsed spallation neutron source (the National Laboratory for High Energy Physics, Tsukuba, Japan). The exposure time was about 2 h for each sample. The measurements were also made for a vanadium rod (10 mm in diameter), an empty cell and a background.

3. Theory

The theory of neutron diffraction for molecular liquids has been presented in detail in our previous work (Kameda and Ichikawa 1986). The observed total scattering cross section can be divided into a self-term and an interference term, $(d\sigma/d\Omega)_{\text{self}}$ and $(d\sigma/d\Omega)_{\text{int}}$. The self-term, scaled by a molecule formulated as $(\text{LiCl})_x(\text{D}_2\text{O})_{1-x}$, can be given by

$$(d\sigma/d\Omega)_{\text{self}} = x(\sigma_{s,\text{Li}} + \sigma_{s,\text{Cl}})/4\pi + (1-x)(2\sigma_{s,\text{D}} + \sigma_{s,\text{O}})/4\pi \quad (1)$$

where $\sigma_{s,i}$ stands for the total scattering cross section for nucleus i . The interference term includes all the information about the liquid structure and consists of two contributions, an intra-molecular and an inter-molecular part, $(d\sigma/d\Omega)_{\text{int}}^{\text{intra}}$ and $(d\sigma/d\Omega)_{\text{int}}^{\text{inter}}$.

The intra-molecular interference function, which represents the scattering from an isolated water molecule associated with harmonic oscillation can be expressed as

$$(d\sigma/d\Omega)_{\text{int}}^{\text{intra}}/(1-x)^2 = 4b_{\text{O}}b_{\text{D}} \exp(-l_{\text{OD}}^2 Q^2/2) \sin Qr_{\text{OD}}/Qr_{\text{OD}} \\ + 2b_{\text{D}}^2 \exp(-l_{\text{DD}}^2 Q^2/2) \sin Qr_{\text{DD}}/Qr_{\text{DD}} \quad (2)$$

where $Q = (4\pi/\lambda) \sin \theta$ and b_i stands for the coherent scattering length of nucleus i ; l_{ij} and r_{ij} are the RMS amplitude and inter-nuclear distance of the nuclear pair i - j , respectively.

3.1. Inelasticity correction in the TOF neutron diffraction method

A large inelasticity effect should occur in neutron scattering from molecules that contain light nuclei such as deuterium (Powles 1973a). One must take account of the inelasticity correction for the total cross sections observed at the high scattering angle 2θ , because the magnitude of this effect is proportional to $\sin 2\theta$. The self-term of the nucleus i , including the inelasticity correction in the TOF experiment, can be written as follows (Powles 1973b, Matsumoto 1979):

$$\left(\frac{d\sigma}{d\Omega}\right)_i^{\text{self}} \left| (\sigma_{s,i}/4\pi) = 1 - 2 \frac{\sin^2 \theta}{M_i^*} \left(2(1 - \gamma) + (1 - \gamma) \frac{d \ln \varepsilon}{d \ln k} \right) \right|_{k=k_e} - \gamma \frac{d \ln \varphi}{d \ln k_0} \Big|_{k_0=k_e} \quad (3)$$

and

$$M_i^* = M_i/[1 - \alpha_i + \exp(-\beta_i Q^2)] \quad (4)$$

where γ is equal to $l/(l_0 + l)$ with the incident and scattered neutron flight paths l_0 and l , ε is the detector efficiency, φ the incident neutron spectrum, k_0 and k the wavenumbers of incident and scattered neutrons, k_e the wavenumber for elastic scattering, M^* the effective mass of nucleus i for self-scattering, and α_i and β_i the constants calculated by using the molecular geometry and vibrational frequencies (Powles 1981).

The observed intra-molecular interference function $(d\sigma/d\Omega)_{\text{int}}^{\text{intra}}$ for a water molecule can be expressed as

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{int}}^{\text{intra}} / (1 - x)^2 = A \left[4 \left(\frac{d\sigma}{d\Omega}\right)_{\text{intOD}}^{\text{intra}} + 2 \left(\frac{d\sigma}{d\Omega}\right)_{\text{intDD}}^{\text{intra}} \right] \quad (5)$$

where the partial intra-molecular interference term for the nuclear pair i - j including the inelasticity correction can be written as follows:

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{\text{int}ij}^{\text{intra}} / b_i b_j &= \exp\left(\frac{-l_{ij}^2 Q^2}{2}\right) \frac{\sin Qr_{ij}}{Qr_{ij}} - 2 \frac{\sin^2 \theta}{M_{ij}^*} \\ &\times \left[2 \left(2(1 - \gamma) + (1 - \gamma) \frac{d \ln \varepsilon}{d \ln k} \Big|_{k=k_e} - \gamma \frac{d \ln \varphi}{d \ln k_0} \Big|_{k_0=k_e} \right) \frac{\sin Qr_{ij}}{Qr_{ij}} \right. \\ &\left. + (1 - 2\gamma) \left(\cos Qr_{ij} - \frac{\sin Qr_{ij}}{Qr_{ij}} \right) \right] \exp(-\kappa_{ij} Q^2) \quad (6) \end{aligned}$$

and A is the overall normalisation factor. Here M_{ij} stands for the effective mass for interference scattering, κ_{ij} is the damping factor calculated by using the molecular geometry and the vibrational frequencies (Powles 1981). The correction term, which corresponds to the second term on the RHS, decreases the amplitude of oscillation and gives rise to the phase shift in the interference term.

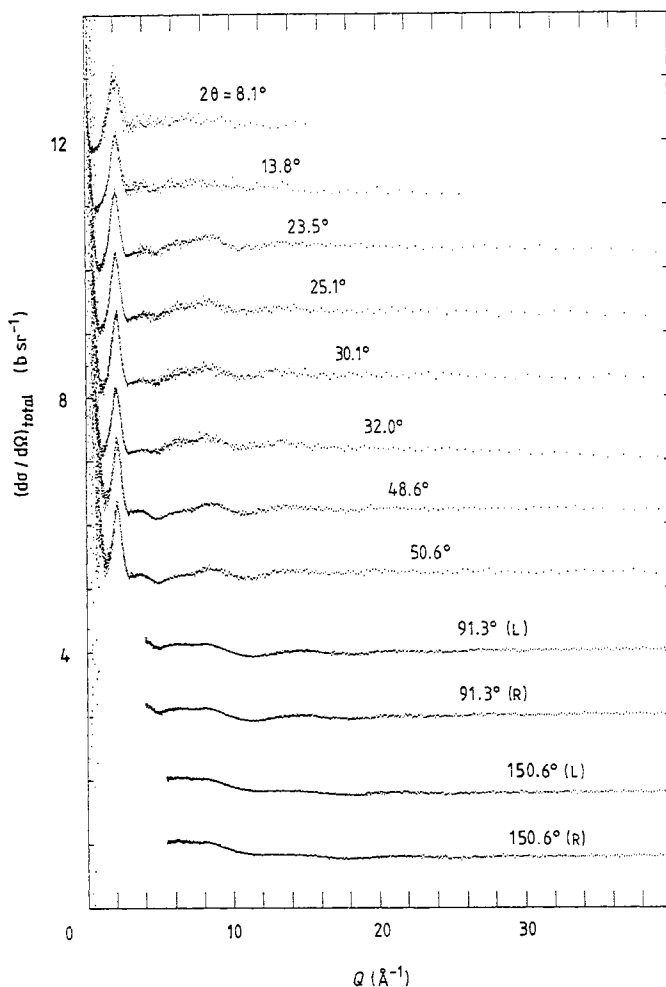


Figure 1. Total differential scattering cross sections for 20 mol% LiCl in liquid D_2O at $125 \pm 10^\circ C$. R and L denote the detectors that were located at the right- and left-hand sides of the incident neutron beam.

4. Analyses and results

After corrections were made for background and absorption (Paalman and Pings 1962), multiple scattering (Blech and Averbach 1965, Bertagnolli and Cieux 1984) and neutron emission time for the observed TOF spectra, the spectra were converted to the total scattering cross sections using the vanadium rod data. Figure 1 shows the total scattering cross section for 20 mol% LiCl for each of the scattering angles. The term $d \ln \sigma / d \ln k$, which appears in the inelasticity correction, has been determined from the intensity of scattering from the vanadium rod, as shown in figure 2, since the coherent scattering length of vanadium is nearly zero and hence there are no Bragg peaks due to its crystal structure. The term $d \ln \epsilon / d \ln k$ has been evaluated from the absorption coefficients calculated for He gas at 20 atm by using the method devised by Paalman and Pings (1962); see figure 2. Figure 3 shows the self-scattering cross section calculated by using

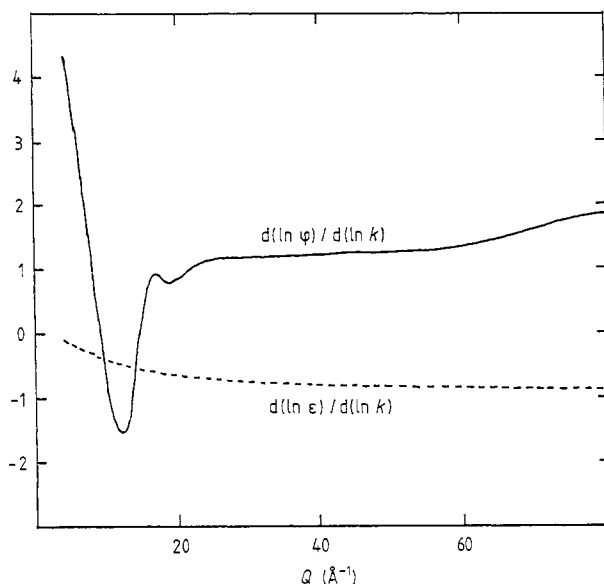


Figure 2. The logarithmic derivatives of the incident neutron spectrum φ (full curve) and detector efficiency ε (broken curve) at $2\theta = 91.3^\circ$ with respect to the wavenumbers of the incident and scattered neutrons.

equation (3) (full curve) and the total scattering cross section for pure D_2O at the scattering angle of 91° (dots). The constants α_i and β_i in equation (4) were taken from the literature (Powles 1981). The hollow around 10 \AA^{-1} in the total scattering cross sections at $2\theta = 150^\circ$ and 91° (see figure 1) is well represented by equation (3).

The amplitude of the inter-molecular interference function reaches zero rapidly in a region of relatively low Q , up to about 10 \AA^{-1} , because of the large RMS displacement l_{ij} and the large inter-nuclear distance r_{ij} . Because of this, we can estimate each of the amplitudes for all the inter-molecular interference functions for the nuclear pair $i-j$ by using the usual Debye equation including the parameters r_{ij} , l_{ij} and the coordination number, which are obtained in the neutron diffraction studies (Newsome 1980, Kameda and Ichikawa 1986, Ichikawa and Kameda 1988). In a region of sufficiently high Q ($40 > Q > 10 \text{ \AA}^{-1}$) the total interference cross section can be regarded as a contribution from the intra-molecular interference function, which determines the structure of a molecule. The diffraction data for a large scattering angle have a great advantage because of their wide Q -range. A least-squares fit to the experimental total interference cross section of (5) gives two intra-molecular distances r_{OD} and r_{DD} . Since the observed total scattering cross section includes uncertainties in the evaluation of the multiple-scattering correction and the overall normalisation factor, it is difficult to obtain the interference term by subtracting the calculated self-term from the total scattering cross section. The interference term was obtained by following the procedure described below.

(i) Calculate approximate values of $(d\sigma/d\Omega)_{\text{int}}^{\text{intra}}$ from (5) and (6) by using the initial approximate values of r_{OD} , r_{DD} and A (see (5)). The normalisation constant A has been chosen to normalise the observed intra-molecular interference function to give proper coordination values and proper values of b_i for the water molecule, in (5) and (6). The other parameters in (5), such as l_{OD} and l_{DD} , are taken from the spectroscopic data for

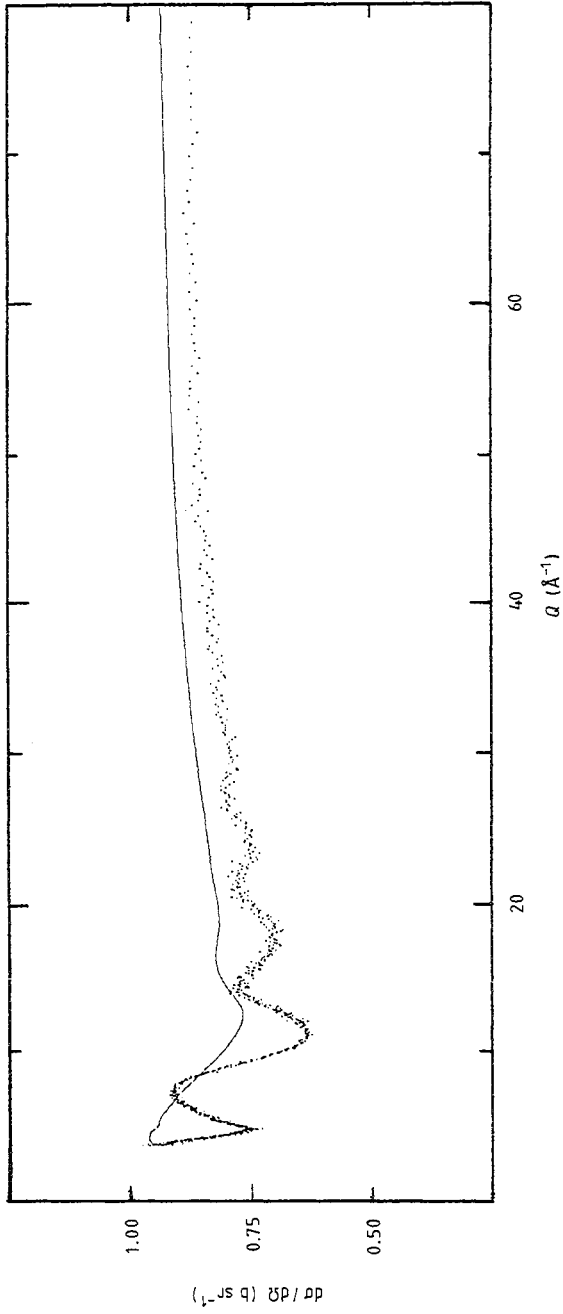


Figure 3. A typical self-scattering cross section calculated by using equations (1), (3) and (4) (full curve) and the total scattering cross section (dots) at $2\theta = 91.3^\circ$ for pure liquid D_2O .

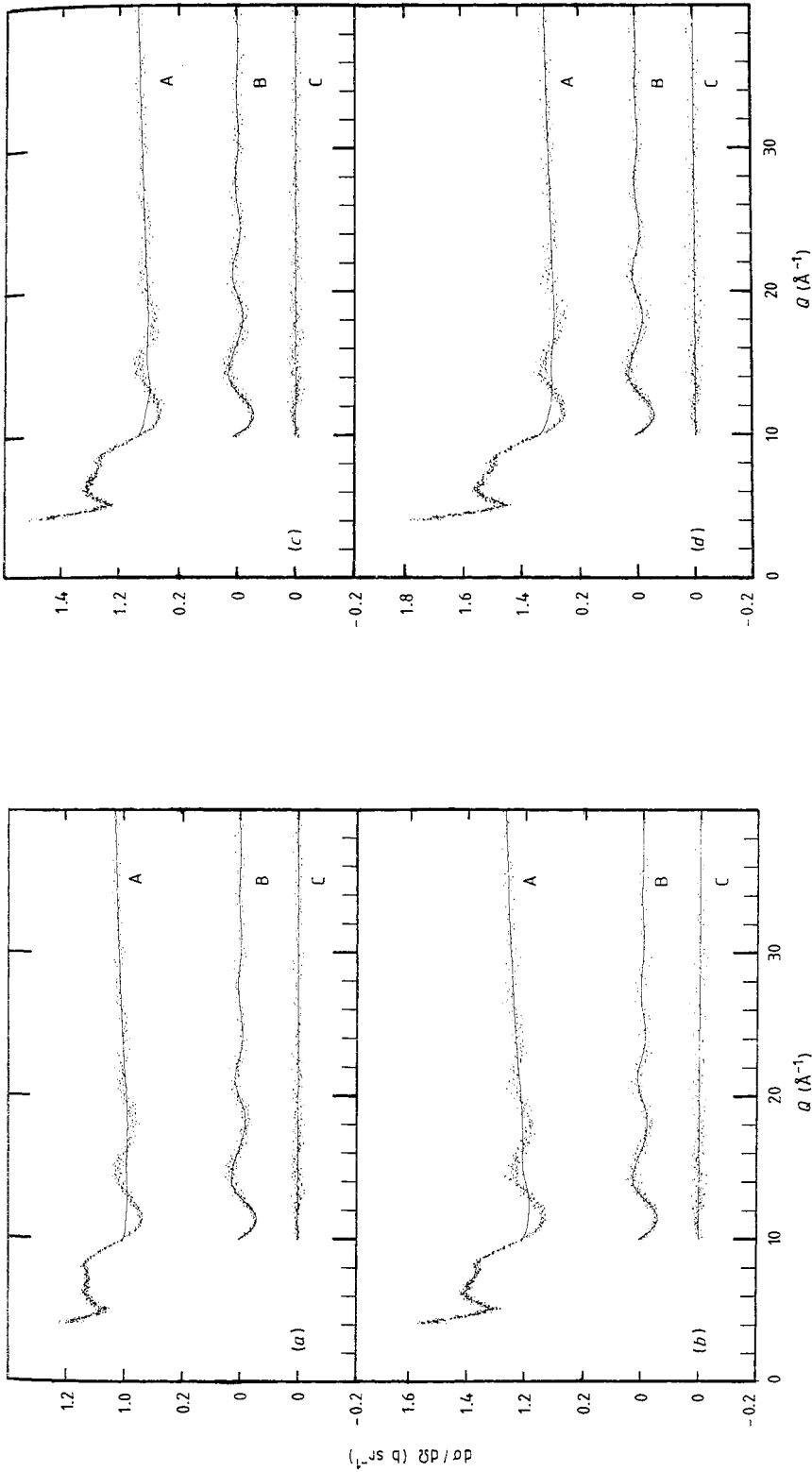


Figure 4. Curves A: the total scattering cross sections (dots) and self-scattering contribution (full curve) at (a) 20, (b) 27, (c) 32 and (d) 35 mol% LiCl. Curves B: the subtraction of self-term from the total scattering cross section yields the measured intra-molecular interference function (dots). The best fit (full curve) with the intra-molecular interference term was carried out by using equations (5) and (6). Curves C: fitting curves; the residual functions $\delta(Q)$ are shown as dots.

pure D₂O (Powles 1981). This is because the O–H stretching frequency and the H–H bending frequency of the water molecule in concentrated LiCl solutions do not differ significantly from those in pure water (Kanno and Hiraishi 1987).

(ii) Subtract $(d\sigma/d\Omega)_{\text{int}}^{\text{intra}}$ from the observed total scattering cross section to yield the difference $\Delta(Q)$.

(iii) Smooth the $\Delta(Q)$ obtained in (2) to remove all the oscillation associated with high frequency, resulting from uncertainty in the parameters r_{OD} , r_{DD} and A . The smoothed $\Delta(Q)$ can be regarded as the self-term because of the very small contribution from $(d\sigma/d\Omega)_{\text{int}}^{\text{inter}}$ in the high- Q region.

(iv) Subtract $(d\sigma/d\Omega)_{\text{self}}$ obtained in (3) from the total scattering cross section to obtain $(d\sigma/d\Omega)_{\text{int}}^{\text{intra}}$ for $40 > Q > 10 \text{ \AA}^{-1}$.

(v) Determine r_{OD} , r_{DD} and A from a least-squares fit of (5) (Nakagawa and Oyanagi 1980). Repeat the procedures from (i) to (v) until there is no change in the parameters and the square sum of the residue is minimised.

The best-fit results for the intra-molecular interference terms are shown in figure 4. The self-terms evaluated are sufficiently smooth for our purposes and do not show any oscillations. An excellent agreement between the experimental and calculated intra-molecular interference terms for 20, 27, 32 and 35 mol% LiCl proves the validity of our inelasticity correction evaluation using (5). The table shows the composition dependence of the final structural parameters of D₂O molecules determined by a least-squares fit. Here it has been concluded that the inelasticity correction causes the increase in r_{OD} and r_{DD} . The values r_{OD} and r_{DD} remain unchanged as concentration is varied in the range between 20 and 35 mol% LiCl, within experimental error: $r_{\text{OD}} = 0.970 \pm 0.006 \text{ \AA}$ and $r_{\text{DD}} = 1.59 \pm 0.02 \text{ \AA}$. The limits of error are estimated to be 2.58 times the standard deviation (cited in table 1) in least-squares fitting.

Table 1. Intra-molecular distances of a D₂O molecule in (LiCl)_x(D₂O)_{1-x} solutions. (The values in parentheses stand for the limits of the standard deviation.)

X	0.20	0.27	0.32	0.35
$r_{\text{OD}} (\text{\AA})$	0.970(2)	0.971(2)	0.970(2)	0.971(2)
$r_{\text{DD}} (\text{\AA})$	1.59(1)	1.58(1)	1.59(1)	1.58(1)
$A (\text{b sr}^{-1})$	0.40(1)	0.41(1)	0.39(1)	0.40(1)

5. Discussion

5.1. The molecular structure of D₂O in pure liquid D₂O

The inter-nuclear distances $r_{\text{OD}} = 0.971 \pm 0.003 \text{ \AA}$ and $r_{\text{DD}} = 1.55 \pm 0.02 \text{ \AA}$ at room temperature have been determined in our previous work (Kameda and Ichikawa 1986). On the other hand, at 100 °C and 150 °C both r_{OD} and r_{DD} have been determined as $0.969 \pm 0.003 \text{ \AA}$ and $1.55 \pm 0.02 \text{ \AA}$ in unpublished work (Ichikawa *et al* 1988). The limits of error are estimated to be 2.58 times the standard deviation. They can be compared with those of Powles, i.e. $r_{\text{OD}} = 0.983 \pm 0.008 \text{ \AA}$, $r_{\text{DD}} = 1.55 \pm 0.02 \text{ \AA}$, which were

obtained by using the inelasticity correction to the steady-state reactor data (Powles 1981). The OD inter-nuclear distance in the gas phase, determined by a microwave or electron diffraction study, is 0.9668 Å (Benedict *et al* 1956) or 0.970 Å (Shibata and Bartell 1965). As the OD stretching frequency is known to decrease by $20000 \text{ cm}^{-1} \text{ \AA}^{-1}$ with increasing separation r_{OD} (Placa *et al* 1973), the increase of 0.004 Å from 0.967 Å in the gas phase to 0.971 Å in the liquid phase determined in previous work (Kameda and Ichikawa 1986) corresponds to the decrease of 80 cm^{-1} in the OD stretching frequency. The small red shift is consistent with the experimental results obtained by Raman or by infrared spectroscopy (Eisenberg and Kauzmann 1969, Kanno and Hiraishi 1987). The TOF neutron diffraction measurements show that the inter-nuclear distances r_{OD} and r_{DD} in pure water are independent of temperature between room temperature and 150 °C (Ichikawa *et al* 1988). This conclusion is consistent with that from Raman spectroscopic experiments, because a red shift in the OD stretching frequency of D₂O molecules in pure water is observed up to about 80 cm^{-1} from room temperature to 100 °C (Walrafen 1967); the red shift of 80 cm^{-1} indicates an increase in r_{OD} by 0.004 Å.

5.2. The effect of ion–water-molecule interaction on the intra-molecular structure of water molecules

We have concluded (i) that the OD inter-nuclear distance remains constant in any concentrated solution and is equal to that in pure D₂O; (ii) that the inter-nuclear distance r_{DD} in the solutions for concentrations above 20 mol% LiCl is 0.04 Å longer than in pure D₂O, and that an increase of about 4° can thus be concluded for the bond angle DOD in a D₂O molecule.

The molecular dynamics (MD) simulation of a solution with 20 mol% LiCl showed an increase of 0.014 Å in r_{OH} and a decrease of about 4° in the bond angle HOH in comparison with the values for pure water (Probst *et al* 1984, Bopp *et al* 1985). The increase in r_{OH} corresponds to a red shift of about 280 cm^{-1} in OH stretching frequency in comparison with the value for pure liquid H₂O. The Raman spectroscopic results showing a blue shift of about 20 cm^{-1} (Sokolowska and Kecki 1983, Kanno and Hiraishi 1987), however, corresponds to a very small decrease in r_{OH} (i.e. about 10^{-3} \AA) for the solution with 20 mol% LiCl. Conclusion (i) is almost entirely consistent with the vibrational spectra results. In a highly concentrated electrolyte solution, the situation where two ions share one water molecule will occur. The increase in DOD may be explained in terms of a decrease in the repulsion between the two lone-pair electrons of an oxygen atom of a water molecule.

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