Neutron Diffraction Study of Aqueous Hydrochloric and Hydrobromic Acid Solutions

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The structure factors $S_m(Q)$ over a wide range of Q (1.7—25 Å^{-1}) for aqueous solutions of DCl and DBr (*ca.* 1 M) at room temperature have been determined by means of LINAC-TOF neutron diffraction. The intramolecular structures of D_2O and D_3O^+ in the solutions are found to be identical with those in the "revised watery model" for water. Applying the subtraction method of analysis to diffraction data for the solutions, we have obtained the following results with respect to the structure of the nearest hydration shell around ions in the DCl and DBr solutions: (a) D_3O^+ is tetrahedrally coordinated with four water molecules and Cl^- and Br^- are octahedrally coordinated with six ones, (b) the O–O distances between the central oxygen atom and that of hydrated water molecules for D_3O^+ are 2.88±0.05 Å, (c) the anion-oxygen distances are 3.10±0.05 Å for Cl^- and 3.21±0.05 Å for Br^-, and (d) around cations (D_3O^+) water molecules take the configuration to orient the axis of one of the two lone-pair hybrids on a straight line joining an oxygen atom and the cation, while around anions (Cl^- and Br^-) those take the configuration to orient the vector which bisects the D–O–D angle on a straight line joining an oxygen atom and the cation.

With respect to the structural studies of aqueous ionic solutions, X-ray diffraction techniques have been widely used and a rather large amount of knowledge with respect to the structure of the hydration shell around ions have been accumulated. These X-ray results are summarized in recent review articles.[1,2] The results obtained, such as the coordination numbers, *etc.*, however, are diverse and no precise determination of the orientational configuration of hydrated water molecules has been made by the X-ray diffraction studies.

Then, the neutron diffraction method, which has a unique advantage for determination of the positions of light atoms such as hydrogen (deuterium) contained in the molecules within liquids,[3] has been applied to the study of aqueous solutions. Narten *et al.* carried out X-ray and neutron diffraction studies on aqueous LiCl[4] and DCl[5] solutions, and in the latter they used a well-known conventional method developed for steady state experiment at reactor. Enderby *et al.*, using the same reactor conventional method, investigated aqueous solutions of $NiCl_2$, NaCl, and $CaCl_2$.[2,6,7] The authors carried out studies on alkali chloride (LiCl, NaCl, KCl, and CsCl) solutions by the use of a TOF neutron diffraction method at LINAC.[8,9] These works have the following remarkable features. First, the resolving power of neutron diffraction in structural studies of aqueous solutions has turned out to be superior to that of X-ray diffraction.[1,2] The neutron studies are sufficiently effective to distinguish between various possible ion-water configurations. Second, for structural studies of liquids, the accuracy of a LINAC-TOF neutron diffraction method has been raised in comparison with that of the reactor conventional method.[8,9,10–14] Consequently, associated with the proposition of improved correction procedures for inelastic scattering, the authors' works for hydrogenous molecular liquids have made it possible to provide more detailed knowledge.[8,9,13,14]

Concerning neutron diffraction data of aqueous ionic solutions, there is no definite procedure for the analysis. Three procedures have been proposed recently: the near-neighbor model approach by Narten *et al.*,[4,5] the first- and second-order-difference spectroscopy by Enderby *et al.*,[2,6,7] and the subtraction method by the authors.[8,9] The subtraction method has been found to be useful in order to elucidate the structure of the nearest neighbor shell around ions in more dilute aqueous solutions,[8,9] while Enderby *et al.*'s method using isotopes is clearly restricted in its practical utility.[15] As regards the method of Narten *et al.* especially on the fundamental nature of the near-neighbor model itself, important criticism has been raised by several workers.[13,15,16]

In the present paper, the result of a neutron diffraction study on aqueous solutions of DCl and DBr at *ca.* 1 M is given. With respect to concentrated DCl solutions X-ray[17,18] and neutron[5] diffraction studies have been made recently. However, the diffraction study for its more dilute aqueous solutions has never been carried out, which is required for the elucidation of the fundamental structure of hydration. Then, in order to investigate the hydrated structures around ions in dilute solutions, we have made an experiment for *ca.* 1 M solutions of DCl and DBr.

Experimental

Procedures for Measurements. The experiment was performed by the TOF neutron diffraction method by LINAC at Hokkaido University. Details of the apparatus and procedures were reported.[13,19,20] Experimental accuracy has been raised to a more satisfactory level by recent improvements: the resolving powder $\Delta Q/Q$ of less than a few % and the statistical errors of smaller than 1% in the whole range of Q can be easily attained at present ($Q=(4\pi\sin\theta)/\lambda$)[19,20]

Measurements on the DCl and DBr solutions and pure

D_2O at room temperature (16 °C) were carried out at a scattering angle, $2\theta=90°$. Data for pure heavy water are required for analysis of the data of aqueous ionic solutions. The time-of-flight of neutrons was analyzed by a multichannel time analyzer with a channel width of 10 μs. Thin-walled cylindrical quartz vessels were used as a container of samples.

Samples. Two acid solutions were prepared by the addition of deuterated hydrochloric and hydrobromic acids with the purity of deuteration of 99% to heavy water. The concentration and density of the DCl solution at 25 °C were 1.097 M and 1.125 g cm^{-3}, and those of the DBr solution were 1.038 M and 1.160 g cm^{-3}.

Corrections and Calibrations of Raw Scattering Data. For the determination of the structure factor $S_m(Q)$, corrections for multiple scattering, absorption, background counting, and inelastic scattering are necessary and absolute normalization of data was performed by the use of the scattering data from a standard vanadium rod of the same shape and dimensions as those of the sample.[8,9,13,14] Above all the correction for the inelastic scattering of neutrons is the most important for hydrogenous molecular liquids including light nuclei like deuterium. In order to compensate for this effect, we can apply the correction method being used successfully in our recent studies on liquid D_2O and CD_3COCl.[13,14] In the present study the Placzek correction method[21] was used in a lower Q region and the Wick correction method[22] in a higher Q region.

Calibration of absolute values for high Q data was performed according to the limiting procedure that $S_m(Q)\rightarrow \sum b_n^2/(\sum b_n)^2$ as $Q\rightarrow\infty$, where n ranges over all the nuclei in a molecule. Calibration of low Q data was made by overlapping the $S_m(Q)$ curves in the range 6—10 Å^{-1} for the two corrected data.[14] Thus, combining the data sets, we obtained the final $S_m(Q)$ curve for a wide range of Q, 1.7—25 Å^{-1}. In Fig. 1, the $S_m(Q)$ curves of DCl and DBr solutions together with that of D_2O are given.

The resolving powder $\Delta Q/Q$ was 0.03 in the Q range 1—8 Å^{-1} and 0.04 in the range of Q greater than 10 Å^{-1}.

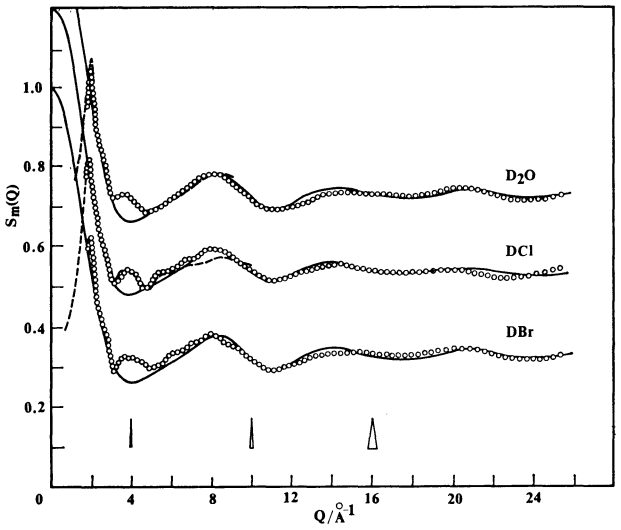

Fig. 1. Observed structure factors for DCl and DBr solutions at 1.10 M and 1.04 M, respectively, compared with the factor for D_2O.
○: $S_m(Q)$ observed, ----: $S_m(Q)$ observed previously (for D_2O by the authors[8,13] and for DCl solution by Triolo and Narten[5]), ——: $f_1^W(Q)$ for D_2O and $S_m^{(1)}(Q)$ for DCl and DBr solutions.

The magnitudes of resolution ΔQ are shown as triangles along the abscissa. The statistical error was found to be smaller than 1% in the whole range of Q.

Results. For the sake of comparison, the $S_m(Q)$ data for heavy water reported by the authors (dashed line)[8,13] are indicated in Fig. 1 overlapping the present data (open circles). Two sets of data agree fully with each other in the range of Q, 1.7—9 Å^{-1}, though slight differences in the main peak at 2 Å^{-1} and a broader peak at *ca.* 8 Å^{-1} are observed. Taking experimental uncertainties as well as the small difference in temperature into consideration, the $S_m(Q)$ data for D_2O are found to agree with other data (Page and Powles'[23] and Narten's[24] data at reactor, and the authors' at LINAC[8,13]). Thus, the reproducibility of the neutron data for D_2O is confirmed with sufficient accuracy.

Furthermore, the data for hydrochloric acid solution at *ca.* 1 M reported by Triolo and Narten (dashed line)[5] are indicated in Fig. 1 overlapping the present data (open circles). Their data in the figure are normalized to the value at the first peak of the structure factor obtained in the present work. A small deviation of Triolo and Narten's data from ours at 6—10 Å^{-1} is observed. Values of rms deviations for D_2O and D_3O^+ in their least-square analysis are, thus, supposed to be too large. Except for this point, their data are found to be essentially identical with our data in the range of Q, 1.7—6 Å^{-1}, and then the reproducibility of the data has been confirmed.

From the above-mentioned fact, reliability of the data required to elucidate the structure of the solutions is attained. Thus, with the help of the subtraction method in the analysis of lower Q data, the configurations of water molecules within the first hydration shell can be studied, and the molecular structure of D_2O and D_3O^+ within the solutions can be determined by the use of the $S_m(Q)$ data in a wide range of Q.[14]

Results and Discussion

Intramolecular Contribution to $S_m(Q)$. The structure factor $S_m(Q)$ for molecular liquids consists of an intramolecular contribution $S_m^{(1)}(Q)$ and an intermolecular one $S_m^{(2)}(Q)$, and is expressed as

$$S_m(Q) = S_m{}^{(1)}(Q) + S_m{}^{(2)}(Q). \quad (1)$$

Structure factors for higher Q region are dominated by the intramolecular contribution, *i.e.* $S_m(Q)\rightarrow S_m^{(1)}(Q)$. Then, the $S_m^{(1)}(Q)$ for the DCl and DBr solutions becomes

$$S_m{}^{(1)}(Q) = (1-x_+-x_-)f_1^W(Q)+x_+f_1^C(Q)+x_-f_1^A(Q). \quad (2)$$

$f_1^W(Q)$ is the intramolecular contribution from water molecules constituting a tetrahedral pentamer (the "revised watery model"[8,13]). $f_1^C(Q)$ and $f_1^A(Q)$ are the intramolecular contributions from the species constituting the first hydration shell around D_3O^+ and anions, respectively.[8] x_+ and x_- are mole fractions of D_2O molecules coordinated in the first shell around cations and anions.

The calculated curves $f_1^W(Q)$ for D_2O, $S_m^{(1)}(Q)$ for the DCl solution, and $S_m^{(1)}(Q)$ for the DBr solution are indicated in Fig. 1, in comparison with the observed data. The agreement between the calculated curves and the observed data at high Q region ($Q\gtrsim$ 8 Å^{-1}) is satisfactory. The agreement in our results is found to be over a wider range of Q (8—25 Å^{-1})

than that in Triolo and Narten's work (8—13 Å^{-1}).[5] Thus, it has been confirmed that the intramolecular structures of D_2O within liquid heavy water are specified by those in the revised watery model.[8,13] Likewise, the structures of D_2O and D_3O^+ in the DCl and DBr solutions at 1 M have been found to be identical with those in the revised watery model.[8,13,25]

Significant differences between the $S_m(Q)$ data of D_2O and those of DCl and DBr solutions in the lower Q region (<7 Å^{-1}) can be ascribed mainly to contributions from the ion-water and water-water interactions within the structure of the first hydrated shell around ions.

Structure of the First Hydration Shell around Ions. A determination of the structure of the nearest hydration shell around ions has been made by comparing calculated values with observed data according to the subtraction method described in the preceding paper.[8,9] The method was proposed for the analysis of the data of comparatively dilute aqueous solutions, and its availability for the determination of the structure was demonstrated.[8,9] The outline of the subtraction method is as follows.

Determination of $\Delta S_m(Q)_{obsd}$: This factor is obtained by subtracting the structure factor $S_m(Q)_{D_2O}$ of D_2O multiplied by an appropriate fraction from the observed total structure factor $S_m(Q)_{total}$ for solution. Thus, in an aqueous solution as dilute as 1 M, the remaining factor for the hydrated structure $\Delta S_m(Q)_{obsd}$ becomes

$$\Delta S_m(Q)_{obsd} = S_m(Q)_{total} - (1-x)S_m(Q)_{D_2O} - axS_m(Q)_{D_2O}, \quad (3)$$

where x is the mole fraction of D_2O molecules coordinated in the first hydration shell, $x=c(n_+ + n_-)/55.3$: n_+ and n_- are the coordination numbers around cations and anions, respectively, and c is the concentration in M. The second term in Eq. 3 is the contribution from bulk water outside of the hydration shell, and the third one that from pairs between the molecules within the shell and bulk water molecules. The magnitude of a was estimated to be 1/2 in a preceding paper.[9]

Calculation of $\Delta S_m(Q)_{calcd}$: The structure of the hydration shell is specified by several parameters, such as coordination numbers, ion-oxygen distances, O–D···O distances, and orientational arrangements of water molecules around ions. Coordination numbers and ion-oxygen distances reported so far are given in Table 1 (see also Tables 1 and 2 in Ref. 8). As regards the configuration of water molecules around ions, two forms, "linear" and "bifurcated,"[8] are assumed for cations where lone-pair electrons are located in the vicinity of ions (Figs. 5(a) and (b) in Ref. 8), and also for anions where deuterium atoms in the vicinity of the ions (Figs. 5(c) and (d) in Ref. 8).

We calculated $\Delta S_m(Q)_{calcd}$ for a number of structure models in which the magnitudes of parameters were varied (Table 2). The expression for $\Delta S_m(Q)_{calcd}$ is given Eq. 4 of Ref. 9.

For each of the DCl and DBr solutions, 42 different types of structures with respect to varieties of coordination numbers and orientational configurations are assumed. In the case of D_3O^+, for the tetrahedral configuration three cases were taken into consideration: 1) all peripheral water molecules take the linear con-

TABLE 1. COORDINATION NUMBERS, O-O DISTANCES, AND ION-OXYGEN DISTANCES FOR D_3O^+, PROTON (H_3O^+), AND Br^- DETERMINED FROM X-RAY (X) AND NEUTRON (N) DIFFRACTION STUDIES AS WELL AS FROM MOLECULAR DYNAMICS (MD) CALCULATION

Ion	Coordination number	O-H···O distance/Å	Solute	Concentration	Method	Reference
D_3O^+	4	2.52	HCl, DCl	0.58—13.9 m	X, N	i[a]
Proton		2.56—2.75	HCl	2—6 M	X	ii
(H_3O^+)		2.5—2.6	HCl	7.48—12.28 M	X	iii
Ion	**Coordination number**	**Ion-oxygen distance/Å**	**Solute**	**Concentration**	**Method**	**Reference**
Br^-	6.6—8.9	3.37—3.43	LiBr	2.5—10 m	X	iv
		3.36	NH_4Br	7.3 m	X	v
	7.4—9.5	3.40	LiBr	3.80 M	X	vi
		3.40	NaBr	3.65 M		
	6	3.287—3.293	LiBr	2.1—5.6 M	X	vii
	6, 8	3.316—3.342	$CaBr_2$	1.2—2.0 M	X	viii
		3.14±0.1	$CuBr_2$	0.056 m	X	ix
		3.14±0.1	NaBr			
	5				MD	x
		3.5	$LaBr_3$	2.26, 2.95 m	X	xi

i) Ref. 5. ii) Ref. 17. iii) Ref. 18. iv) R. M. Lawrence and R. F. Kruh, *J. Chem. Phys.*, **47**, 4758 (1967). v) I. M. Shapovalov and I. V. Radchenko, *J. Struct. Chem.*, **10**, 804 (1969). vi) G. Licheri, G. Piccaluga, and G. Pinna, *J. Appl. Crystallogr.*, **6**, 392 (1973). vii) G. Licheri, G. Piccaluga, and G. Pinna, *Chem. Phys. Lett.*, **35**, 119 (1975). viii) G. Licheri, G. Piccaluga, and G. Pinna, *J. Chem. Phys.*, **63**, 4412 (1975). ix) P. Eisenbager and Kincaid, *Chem. Phys. Lett.*, **36**, 134 (1975). x) C. L. Briant and J. J. Burton, *J. Chem. Phys.*, **64**, 2888 (1976). xi) L. S. Smith and D. L. Wertz, *J. Inorg. Nucl. Chem.*, **39**, 95 (1977).

a) Triolo and Narten's "structure parameters for the hydrated ions were those found for the most concentrated solutions" (Ref. 5) in their study,

TABLE 2. RANGE OF PARAMETERS FOR STRUCTURE MODELS

Ion	Coordination number, n	O-O distance/Å	Type of configuration around ion (Hydrogen-, Non-hydrogen-bonded)
D_3O^+	4 (Tetrahedral)	2.70—2.94 (Interval of 0.03)	(Linear, Linear) (Linear, Bifurcated) (Bifurcated, Linear)
	3 (Pyramidal, Planar)		
Ion	**Coordination number, n**	**Ion-oxygen distance/Å**	**Type of configuration around ion**
Cl^-	4 (Tetrahedral) 6 (Octahedral) 8 (Cubic)	3.00—3.20 (Interval of 0.05)	Linear, Bifurcated
Br^-	4 (Tetrahedral) 6 (Octahedral) 8 (Cubic)	3.15—3.50 (Interval of 0.05)	Linear, Bifurcated

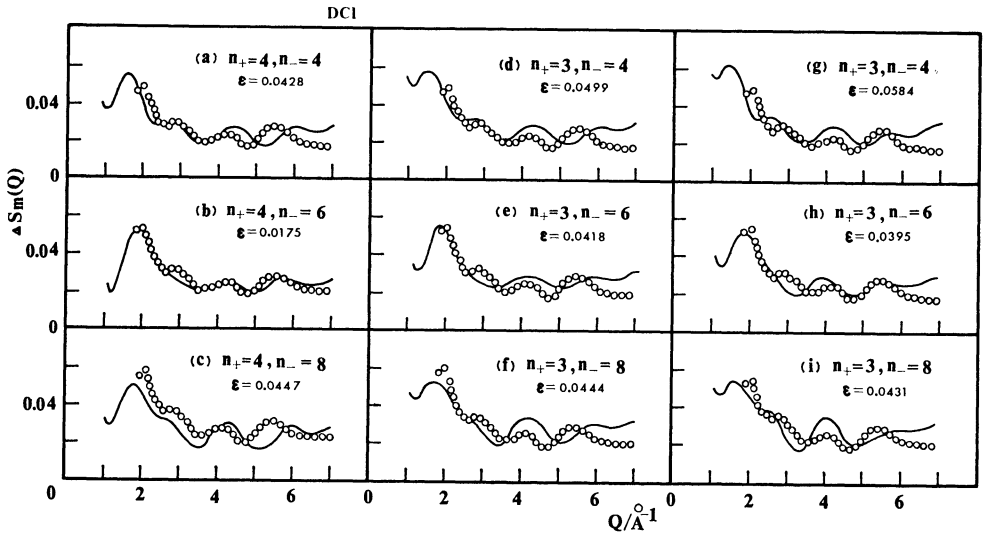

Fig. 2. Changes in the $\Delta S_m(Q)_{calcd}$ with variation of the coordination number for DCl solution. O: $\Delta S_m(Q)_{obsd}$, ——: $\Delta S_m(Q)_{calcd}$, tetrahedral ($n_+=4$): (a) $n_-=4$, (b) $n_-=6$, and (c) $n_-=8$, pyramidal ($n_+=3$): (d) $n_-=4$, (e) $n_-=6$, and (f) $n_-=8$, planar ($n_+=3$): (g) $n_-=4$, (h) $n_-=6$, and (i) $n_-=8$.

figuration, 2) all those take the bifurcated one, and 3) one non-hydrogen-bonded molecule takes the bifurcated one and others the linear, and also for the pyramidal and/or planar configurations, two cases, 1) and 2), were taken. Distances were varied successively at intervals of 0.03 Å for the O–O distances and 0.05 Å for other ion-oxygen ones. As a whole, we calculated the $\Delta S_m(Q)_{calcd}$ curves for 516 different structure models of the first hydration shell in the DCl solution and those for 625 different models in the DBr solution, and then determined the best structure model by the comparison of $\Delta S_m(Q)_{calcd}$ with $\Delta S_m(Q)_{obsd}$ for both solutions.

Determination of the Best Fit Model: The procedure for determination of the best fit structure model is as follows. First the $\Delta S_m(Q)_{calcd}$ calculated by the above-mentioned procedures were compared by a rough estimation with the $\Delta S_m(Q)_{obsd}$ in the range of Q, 2—5 Å^{-1} and the models which gave appreciable deviations of the $\Delta S_m(Q)_{calcd}$ curves from the $\Delta S_m(Q)_{obsd}$ were excluded. Next, for the remaining $\Delta S_m(Q)_{calcd}$ curves, we calculated the deviations expressed as

$$\varepsilon = \{\sum_{i=1}^{N}[\Delta S_m(Q_i)_{obsd} - \Delta S_m(Q_i)_{calcd}]^2\}^{1/2} / \sum_{i=1}^{N}[\Delta S_m(Q_i)_{obsd}], \quad (4)$$

where N is the number of data points in the fitting region, and used ε as a measure for the fitness of the model. In the present study, the fitting region with respect to $\Delta S_m(Q)$ is taken to be Q=2—7 Å^{-1}.

In Figs. 2 and 3, the $\Delta S_m(Q)_{calcd}$ for different sets of coordination numbers are compared with the $\Delta S_m(Q)_{obsd}$ data for the DCl and DBr solutions. The values of ε calculated for each case are indicated. The ε_{min} is 0.0175 and 0.0347 for the DCl and DBr solutions, respectively. Thus, the best fit curve with $\Delta S_m(Q)_{obsd}$ is obtained in the case of $n_{D_3O^+}=4$ and $n_{Cl^-}=6$ for the DCl solution (Fig. 2(b)) and also obtained in the case of $n_{D_3O^+}=4$ and $n_{Br^-}=6$ for the DBr solution (Fig. 3(b)). The curves other than the best fit one deviate appreciably from the $\Delta S_m(Q)_{obsd}$ ($\varepsilon > \varepsilon_{min}$). In the case of $n_{D_3O^+}=3$, all curves are found to deviate from the observed ones ($\varepsilon > \varepsilon_{min}$) appreciably, and, thus, the structure models with

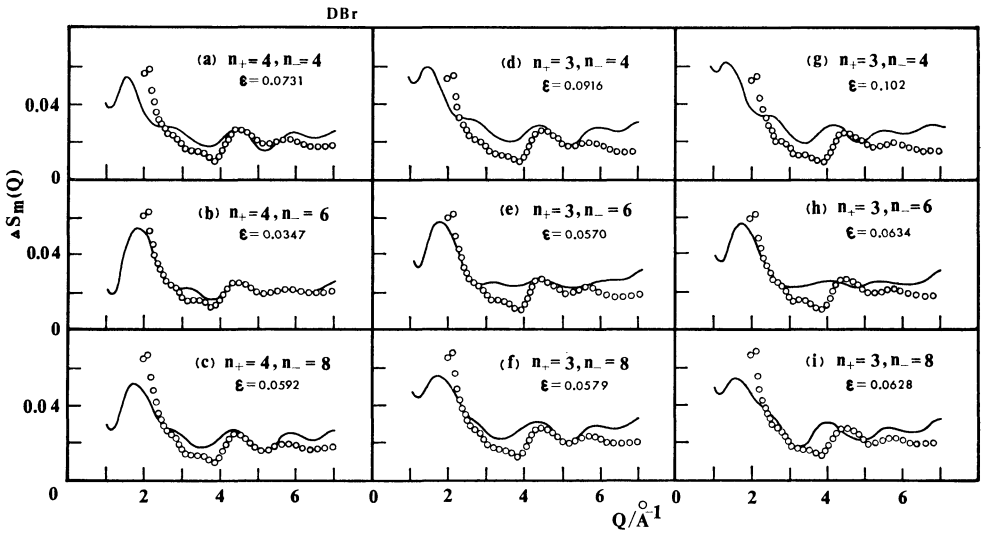

Fig. 3. Changes in the $\Delta S_m(Q)_{calcd}$ with variation of the coordination number for DBr solution. ○: $\Delta S_m(Q)_{obsd}$, ——: $\Delta S_m(Q)_{calcd}$, tetrahedral ($n_+=4$): (a) $n_-=4$, (b) $n_-=6$, and (c) $n_-=8$, pyramidal ($n_+=3$): (d) $n_-=4$, (e) $n_-=6$, and (f) $n_-=8$, planar ($n_+=3$): (g) $n_-=4$, (h) $n_-=6$, and (i) $n_-=8$.

$n_{D_3O^+}=3$ are rejected.

For $n_+=4$ and $n_-=6$, the $\Delta S_m(Q)_{calcd}$ curves with various magnitudes of the distances (r_{O-O}, r_{Cl^--O}, and r_{Br^--O}) are shown in Figs. 4(a)—(d), together with the parabolic curves in Figs. 4(a')—(d') required for locating the value of ε_{min}. For the distance r_{O-O} the ε_{min} exists at $r_0=2.88$ Å in both solutions, and that for r_{Cl^--O} and r_{Br^--O} exists at $r_0=3.10$ Å and $r_0=3.21$ Å in the DCl and DBr solutions, respectively. If we can introduce a range of allowance for ε, variations of distances can be determined. Then, taking account of the experimental errors, we set up the range, $\varepsilon<0.02$ for the DCl solution and $\varepsilon<0.035$ for the DBr solution. As a result, the deviations are found to be ±0.05 Å for all the distances.

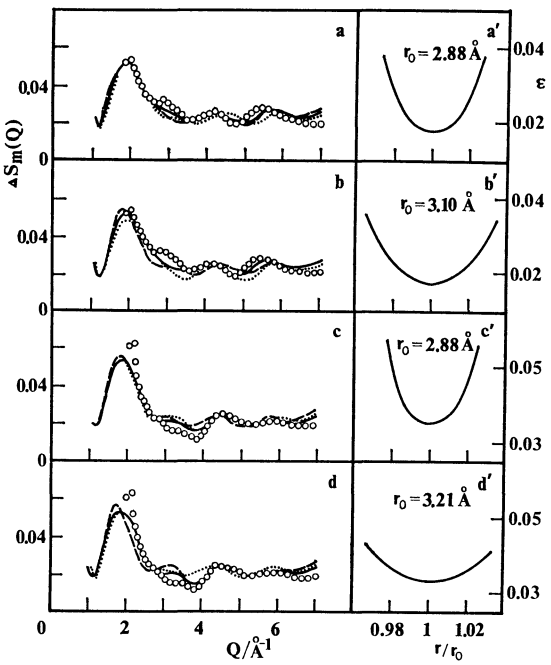

Fig. 4. Changes in the $\Delta S_m(Q)_{calcd}$ with variation of the O–O distance and the ion-oxygen distance for DCl (a, b) and DBr (c, d) solutions, and variation of ε with distances (a'—d').
○: $\Delta S_m(Q)_{obsd}$, (a), (c) r_{O-O} (all other parameters are identical with those given in Table 3), ……: 2.82 Å, ——: 2.88 Å, ----: 2.94 Å, (b) r_{Cl^--O} (all other parameters are identical with those given in Table 3), ……: 3.00 Å, ——: 3.10 Å, ----: 3.20 Å, (d) r_{Br^--O} (all other parameters are identical with those given in Table 3), ……; 3,15 Å, ——: 3.25 Å, ----: 3.35 Å.

In Figs. 5(a)—(d), the $\Delta S_m(Q)_{calcd}$ curves with various orientational configurations for the same set of coordination numbers ($n_+=4$ and $n_-=6$) are shown. Applying the same criterion ($\varepsilon<0.02$ for the DCl solution and $\varepsilon<0.035$ for the DBr solution) to these cases, linear configurations for D_3O^+ and bifurcated ones for anions are accepted as the best fit for both solutions.

The $\Delta S_m(Q)_{calcd}$ curves of the best models thus determined are given in Figs. 2(b) and 3(b) for the DCl and DBr solutions, respectively. The magnitudes of parameters and orientational configurations for the best fit models of the first hydration shell are given in Table 3.

Concerning the configurations of water molecules within the first hydration shell around D_3O^+, it is

TABLE 3. COORDINATION NUMBERS, O-O DISTANCES, ION-OXYGEN DISTANCES, AND ORIENTATIONAL CONFIGURATIONS AROUND IONS DETERMINED IN THE PRESENT STUDY

Ion	Coordination number	O-O and ion-oxygen distance/Å	Configuration around ion
D_3O^+	4	O-O: 2.88±0.05	Linear
Cl^-	6	Cl^--O: 3.10±0.05	Bifurcated
Br^-	6	Br^--O: 3.21±0.05	Bifurcated

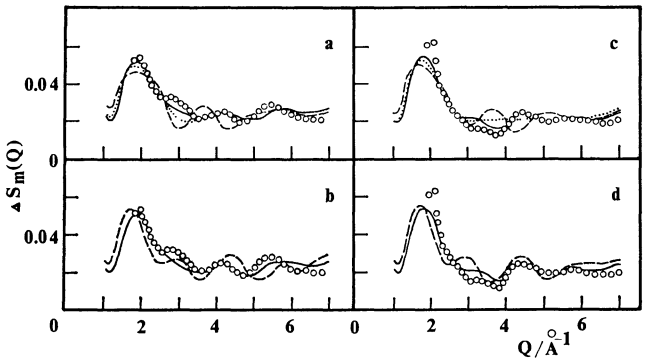

Fig. 5. Changes in the $\Delta S_m(Q)_{calcd}$ with variation of orientational configurations around ions for DCl (a, b) and DBr (c, d) solutions. ○: $\Delta S_m(Q)_{obsd}$, (a) confifurations around D_3O^+ (all other parameters are identical with those in Table 3), ·····: one non-hydrogen-bonded water molecule takes the bifurcated configuration and others are the linear (ε=0.0252), ——: all peripheral water molecules take the linear configuration (ε=0.0175), ----: all peripheral water molecules take the bifurcated configuration (ε=0.0351), (b) configurations around Cl^- (all other parameters are identical with those given in Table 3), ——: bifurcated (ε=0.0175), ----: linear (ε=0.0432), (c) configurations around D_3O^+ (all other parameters are identical with those given in Table 3), ·····: one non-hydrogen-bonded water molecule takes the bifurcated configuration and others are the linear (ε=0.0376), ——: all peripheral water molecules take the linear configuration (ε=0.0347), ----: all peripheral water molecules take the bifurcated configuration (ε=0.0507), (d) configurations around Br^- (all other parameters are identical with those given in Table 3), ——:bifurcated (ε=0.0347), ----: linear (ε=0.0554).

concluded that the "linear" type[8,9] of all water molecules is predominant for both solutions (Figs. 5(a) and (c)). On the other hand, with respect to the configurations around anions, it is concluded that the "bifurcated" type[8,9] is predominant for both solutions (Figs. 5(b) and (d)). The structure of the first shell around Cl^- in the DCl solution is found to be identical with those in aqueous alkali chloride solutions previously determined by the authors.[8,9] With respect to the coordination number around Cl^-, Triolo and Narten assigned the value of n_{Cl^-}=4 in their analysis (Ref. 5). However, as clearly seen in Figs. 2(a), (d), and (g), the tetrahedral coordination for Cl^- is rejected and n_{Cl^-}=6 is assigned. This difference between our results and those by Triolo and Narten is attributed to the difference in the concentration of solution.

In the present application of the "subtraction method" by using Eq. 3 we have taken the magnitude of

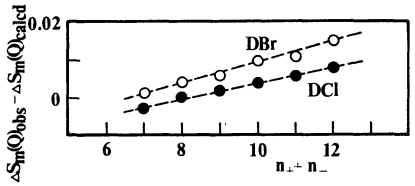

Fig. 6. $\Delta S_m(Q)_{obsd} - \Delta S_m(Q)_{calcd}$ plotted against $(n_+ + n_-)$.

a for 1/2 described above. In Fig. 6, the differences $\Delta S_m(Q)_{obsd} - \Delta S_m(Q)_{calcd}$[9] are plotted again against $(n_+ + n_-)$. The differences are substantially zero within the maximum range of 0.01. This supports the adequacy of the assignment of a as 1/2 (see Fig. 8 in Ref. 9).

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