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Neutron Diffraction Study of Aqueous Ionic Solutions. I. Aqueous Solutions of Lithium Chloride and Caesium Chloride

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The structure factors $S_m(Q)$ for aqueous solutions of LiCl and CsCl at room temperature, including those for heavy water, have been determined by means of the time-of-flight (TOF) neutron diffraction method using an electron linear accelerator (LINAC). Analysis of the diffraction data has been carried out for the aqueous ionic solutions as well as for pure heavy water. The following results were obtained with respect to the structure of the nearest hydration shell: (a) the coordination numbers are 4 for Li^+ and 6 for Cl^- in the LiCl solution, and 8 for Cs^+ and 6 for Cl^- in the CsCl solution, (b) the average ion-oxygen distances are 1.90±0.05 Å for Li^+, 2.95±0.10 Å for Cs^+ and 3.10±0.05 Å for Cl^-, and (c) around cations water molecules take the configuration to orient the axis of one of two lone-pair hybrids on a straight line joining an oxygen atom and a cation.

Since the work of Bernal and Fowler in 1933,[1] many X-ray diffraction studies have been carried out for clarification of the liquid structure of ionic solutions. Lawrence and Kruh made a comprehensive X-ray diffraction study on ionic solutions.[2] In the last decade neutron diffraction studies have appeared as a new means for giving basic data such as the number of hydrated water molecules in the first shell (coordination number), the ion-oxygen distances, and the orientational arrangements within the shell. The results obtained so far, such as on the coordination number, were found to be greatly diverse, as pointed out by Hinton and Amis.[3] A more precise determination of these quantities is desirable.

The first application of the neutron diffraction method to aqueous electrolyte (LiCl) solutions was attempted by Narten *et al.*,[4] who analyzed their data of aqueous LiCl solutions on the basis of their "near-neighbor model" for water. Licheri *et al.* carried out studies on aqueous solutions of electrolytes along the same line.[5–11] However, the present authors have shown that the structure model of water of Narten *et al.* used as a basis for their analysis is physically unacceptable.[12] Soper *et al.* in another approach by means of the neutron diffraction method have given an ion-water configuration using their "first-order difference spectroscopy".[13]

Many problems remain unsolved with respect to the hydrated structure within ionic solutions, but the neutron diffraction method is becoming one of the most powerful means for its elucidation. We have carried out studies on aqueous ionic solutions by means of the method for which neutron diffraction data of heavy water are required. Since there are small discrepancies in the structure factor curves for heavy water given by us,[12] by Page and Powles[14] and by Narten,[15] measurement on heavy water (D_2O) was carried out again.

Measurements were carried out for aqueous solutions of LiCl and CsCl, the former for observing the pronounced effects of Li^+ on the configuration of water molecules in the first hydration sphere due to the small size of the ion, and the latter in view of the different behavior of Cs^+ expected in water as compared with Li^+. The results obtained by means of TOF neutron diffraction are reported, together with the new results for heavy water.

Apparatus and Procedures

Details of the apparatus and procedure have been reported.[12,16] The neutron diffraction experiment was performed by means of the TOF diffraction method using pulsed neutrons produced by LINAC. Thin-walled cylindrical vanadium and quartz were used as container of samples. Measurements were made at room temperature and at the scattering angle $2\theta = 45°$.

All the data were smoothed out according to the usual least-square fitting procedure and corrections (multiple scattering, absorption, background counting and Placzek corrections) were made for the smoothed spectrum. Absolute calibration was then performed by comparison of the count rate time-spectrum from the sample with that from a polycrystalline vanadium rod of the same shape and dimension as the sample.[12]

Results and Analysis of Heavy Water

Neutron diffraction data for heavy water are required for analysis of the data of aqueous ionic solutions.

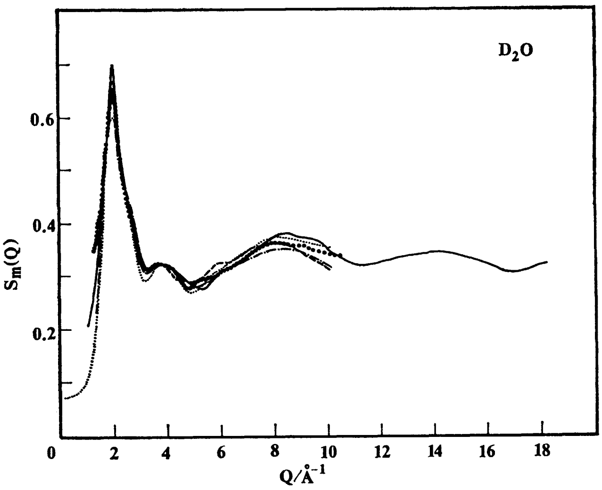

Fig. 1. Observed structure factors for D_2O.
• : $S_m(Q)$ by the authors (14 °C), ——: $S_m(Q)$ by the authors (17 °C),[12] ——: $S_m(Q)$ by the authors (25 °C), —·—: $S_m(Q)$ by Page and Powles (22 °C), ······: $S_m(Q)$ by Narten (25 °C).

Measurements for D_2O (99.75% D) were carried out at room temperature (14, 18, and 25 °C).

The absolute structure factors $S_m(Q)$ obtained for liquid heavy water are shown in Fig. 1, together with reported factors for the sake of comparison.[12,14,15] All five curves agree as a whole. The two curves except for the authors' were obtained by the conventional steady-state experiment using reactors as neutron sources. The accuracy of the present TOF experiment using LINAC ($2\theta=45°$) as a neutron source is as follows: the statistical errors are 0.5—0.6% in the Q range 2—5 $Å^{-1}$ and 0.9% at about 8 $Å^{-1}$.

We proposed the "revised watery model" as a structure model for liquid water and made an analysis by means of the formula[12]

$$S_m(Q) = f_1(Q) + f_{2c}(Q)[(S_c(Q) - 1]. \qquad (1)$$

A further slight refinement of the model was performed as follows. (a) The rotational angle ξ[17] is taken to be 60°. (b) Concerning the factor $[S_c(Q)-1]$, we used the values obtained according to the procedure of Page and Powles[14] starting from the X-ray data of Narten instead of the direct use of Narten's value of $[S_c(Q)-1]$.[18] (c) The intramolecular contribution $f_1(Q)$ has been taken to be the weighted average value of three varieties of the intramolecular factors, which correspond to the three groups of water molecules in the tetrahedral pentamer according to the manner of hydrogen-bonding (Fig. 5, Ref. 12).[19] This improves the agreement between the calculated and observed curves in the high Q region ($Q \gtrsim 8$ $Å^{-1}$). The $S_m(Q)$ for the present "revised watery model" is given in Fig. 2 and is compared with the calculated factors for other models, the "uncorrelated orientation model"[14] and the "revised watery model" (free rotation) by the authors.[12] The main features of the three curves are in good agreement with each other except for the bump at about 4 $Å^{-1}$.

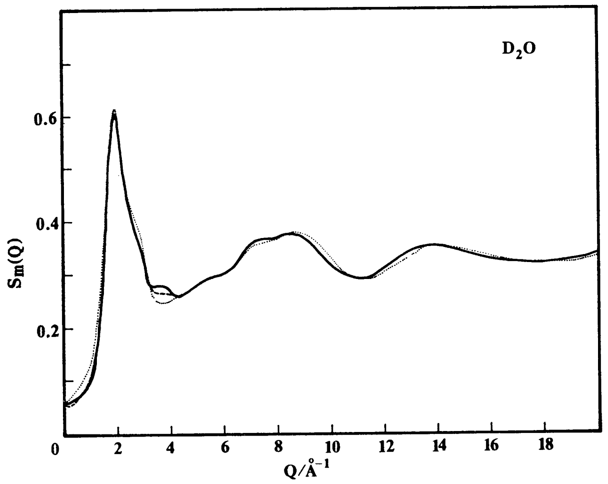

Fig. 2. Comparison between the calculated curves of $S_m(Q)$ for various structure models of liquid water.
——: $S_m(Q)$ for the "revised watery model" ($\xi=60°$),
----: $S_m(Q)$ for the "revised watery model" (free rotation), ······: $S_m(Q)$ for the "uncorrelated orientation model".

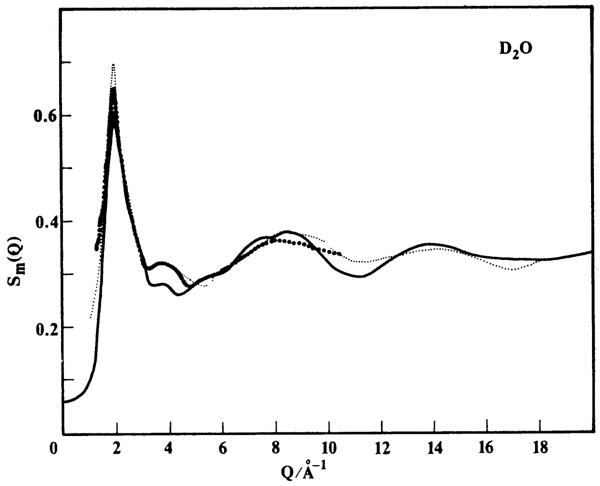

Fig. 3. Comparison between the calculated $S_m(Q)$ values for the present "revised watery model" and the observed ones by the authors.
——: Calculated $S_m(Q)$ for the "revised watery model",
• : observed $S_m(Q)$ in the present study (14 °C),
······: observed $S_m(Q)$ previously.[12]

In Fig. 3, the calculated curve of $S_m(Q)$ for the present "revised watery model" is compared with the observed $S_m(Q)$ curve. From Figs. 2 and 3, we see that the behavior of the curves near 4 $Å^{-1}$ is essential for judging the adequacy of the model proposed.[14] The curves (Fig. 2) show a gradual approach to the observed curve, indicating that the "revised watery model" is the best of all the models for liquid water presented so far in neutron diffraction studies.

Results and Analysis of Aqueous Solutions of LiCl and CsCl

Diffraction Data. Two 1.0 M alkali halide solutions (M: mol dm^{-3}) were prepared by the addition

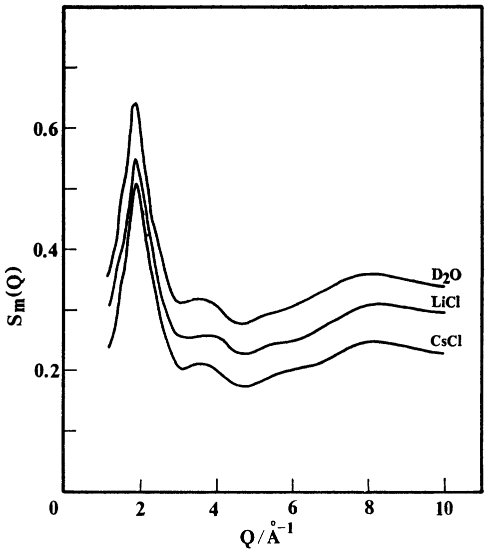

Fig. 4. Observed structure factors for LiCl and CsCl solutions at 1 M, compared with the factor for D_2O (14 °C).

of extra pure anhydrous lithium chloride and caesium chloride to heavy water.[20]

The structure factors are shown in Fig. 4 for LiCl and CsCl solutions including those for pure heavy water.[21] The change of the bump at *ca.* 4 Å^{-1} as well as that of the main peak with a shoulder at 2.8 Å^{-1} indicates the effects of ions on the structure of the first hydration sphere.

Method for Analysis. All the neutron diffraction studies for aqueous ionic solutions have been made so far for concentrated solutions (>1 M).[4,13] We give here the diffraction data for more dilute solutions (1 M). In order to analyze the data of dilute solutions, we have subtracted the structure factor $S_m(Q)_{D_2O}$ of D_2O multiplied by an appropriate fraction from the total structure factor $S_m(Q)_{total}$ of solutions. The remaining factor, $\Delta S_m(Q)$, becomes

$$\Delta S_m(Q) = S_m(Q)_{total} - (1-x) S_m(Q)_{D_2O}, \qquad (2)$$

$$x = \frac{c(n_+ + n_-)}{55.3}, \qquad (3)$$

where x is the mole fraction of D_2O coordinated in the nearest hydration shell around ions, n_+ and n_- are the coordination number about the cation and the anion, respectively, and c is concentration.

In order to determine the structure of the nearest hydration shell we compare the observed values of $\Delta S_m(Q)$ with those calculated for various structure models assumed.

Procedure for Analysis of LiCl and CsCl Solutions. The structure of the hydration shell is characterized by parameters, coordination number n, ion-oxygen distances, and orientational arrangements of water molecules around ions (Fig. 5).

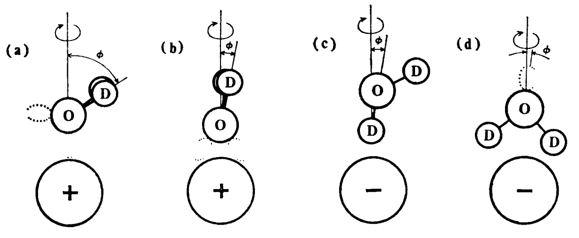

Fig. 5. Orientational arrangements of water molecules around ions.
(a) Linear form for cation, (b) bifurcated form for cation, (c) linear form for anion, (d) bifurcated form for anion.

The coordination number and ion-oxygen distances, so far obtained experimentally, are given in Tables 1 and 2. They are very diversified. As regards configuration of water molecules around ions, two forms, "linear" and "bifurcated," are expected for cations where lone-pair electrons are in the vicinity of the ions (Figs. 5(a) and (b)) and also for anions, where deuterium atoms are located in the vicinity of the ions (Figs. 5(c) and (d)). Very few experimental results have been reported so far concerning the orientation of water molecules around ions.

TABLE 1. COORDINATION NUMBERS OF Li^+, Cs^+, AND Cl^- DETERMINED FROM X-RAY (X) AND NEUTRON (N) DIFFRACTION STUDIES AS WELL AS MOLECULAR DYNAMICS (MD) AND MONTE CALRO (MC) CALCULATIONS

Ion	Coordination number, n	Solute	Concentration/M	Method	Reference
Li^+	4±1	LiCl	<7	X,N	v
	4	LiCl		MC	vii
	4 and 6	LiBr	2.1—5.6	X	ix
	4—6	LiF		MC	x
	5.7±0.2	LiCl	2	MD	xiv
	7.1±0.1	LiI	2.2		
Cs^+	2.0—6.2	CsCl	2.5—10	X	ii
	1.9—6.0	CsBr	2.5, 5		
	2.3—2.7	CsI	2.5		
	7.3±0.7	CsF	2.2	MD	xiv
	8.2±0.8	CsCl			
	7			MD	xv
Cl^-	8—9	LiCl	6	X	i
	5.4—11.0	LiCl	2.5—10	X	ii
	8.2	MgCl		X	iv
	8.9	$MgCl_2$			
	7.9—8.0	$CaCl_2$			
	8.0	$BaCl_2$			
	8.0	$SrCl_2$			
	6±1	LiCl	<7	X,N	v
	7.1—10.2	LiCl	2.15—7.30	X	vi
	5—7			MC	vii
	4	HCl	<7	X	xi
	6	$CaCl_2$	1, 2, 4	X	xii
	6	$[Cr(H_2O)_6]Cl_3$	0.25	X	xiii
	7.4±0.4	LiCl	2	MD	xiv
	6.7±0.3	NaCl	2.2		
	7.9±0.3	CsCl	2.2		
	5.5±0.2	NaCl	5.32	N	xvii
	6	$NiCl_2$	2, 4	X	xviii
	6	$CrCl_2$	1	X	xix

i) E. W. Brady, *J. Chem. Phys.*, **28**, 464 (1958). ii) Ref. 2. iii) G. Licheri, G. Piccaluga, and G. Pinna, *Chem. Phys. Lett.*, **12**, 425 (1971). iv) J. N. Albright, *J. Chem. Phys.*, **56**, 3783 (1972). v) Ref. 4. vi) G. Licheri, G. Piccaluga, and G. Pinna, *J. Appl. Cryst.*, **6**, 392 (1973). vii) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **61**, 799 (1974). viii) H. Bertagnolli, J. U. Weidner, and H. W. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **78**, 2 (1974). ix) Ref. 5. x) J. Fromm and E. Clementi, *J. Chem. Phys.*, **62**, 1388 (1975). xi) R. Triolo and A. H. Narten, *J. Chem. Phys.*, **63**, 3624 (1975). xii) Ref. 7. xiii) Ref. 8. xiv) K. Heinzinger and P. C. Vogel, *Z. Naturforsch.*, **31a**, 463 (1976). xv) Ref. 22. xvi) P. Bopp, K. Heinzinger, and G. Jancso, *Z. Naturforsch.*, **32a**, 620 (1977). xvii) Ref. 13. xviii) Ref. 9. xix) Ref. 11.

We have calculated $\Delta S_m(Q)$ for a number of structure models in which the magnitudes of parameters have been varied (Table 3). For each of the LiCl and CsCl solutions, the 24 different structures with respect to the coordination number and the type of orientational configurations are assumed, ion-oxygen distances and the angle ϕ being varied successively at intervals of 0.05 Å and 10°, respectively, for each of the 24 structure models. As a whole, we calculated the $\Delta S_m(Q)$ curves for 264 different models of the structure of the

TABLE 2. AVERAGE ION-OXYGEN DISTANCES OF THE FIRST HYDRATION SHELL DETERMINED FROM X-RAY (X) AND NEUTRON (N) DIFFRACTION STUDIES AS WELL AS MOLECULAR DYNAMICS (MD) AND MONTE CALRO (MC) CALCULATIONS

Ion	Distance r/Å	Solute	Concentration/M	Method	Reference
Li^+-O	1.95—2.25	LiCl	<7	X,N	v
	2.1	LiCl	2.15—7.30	X	vi
	2.1	LiBr			
	1.9—2.0			MC	vii
	2.139—2.250	LiBr	2.1—5.6	X	xiv
	2.06	LiCl		MD	xiv
	2.10	LiI			
Cs^+-O	3.15	CsCl	2.5—10	X	ii
	3.15—3.22	CsBr	2.5, 5		
	3.02—3.15	CsI	2.5		
	3.14			X	viii
	3.10±0.06	CsCl		MD	xiv
	3.10±0.04	CsF			
	3.32			MD	xv
Cl^--O	3.15—3.2	LiCl	2.5—10	X	ii
	3.20	HCl	1, 4.3	X	iii
	3.2	$MgCl_2$		X	iv
	3.10—3.193	LiCl	<7	X,N	v
	2.9—3.25	LiCl	2.15—7.30	X	vi
	3.4—3.5			MC	vii
	3.137—3.149	$CaCl_2$	1, 2, 4	X	xii
	3.135	$[Cr(H_2O)_6]Cl_3$	0.25	X	xiii
	2.68	LiCl		MD	xiv
	2.66	CsCl			
	2.66	NaCl			
	3.2	$NiCl_2$	5.32	N	xvii
	3.134—3.145	$NiCl_2$	2, 4	X	xviii
	3.08	$CrCl_3$	1	X	xix

References are the same as those in Table 1.

TABLE 3. RANGE OF PARAMETERS FOR STRUCTURE MODELS

Ion	Coordination number, n	Ion-oxygen distance, r/Å	Type of configuration around ions (Angle, ϕ/°)
Li^+	4, 6, 8	1.90—2.25	linear (44.75—64.75) bifurcated (0.0—20.0)
Cs^+	4, 6, 8	2.85—3.35	linear (44.75—64.75) bifurcated (0.0—20.0)
Cl^-	6, 8	3.05—3.20	linear (0.0—20.0) bifurcated (0.0—20.0)

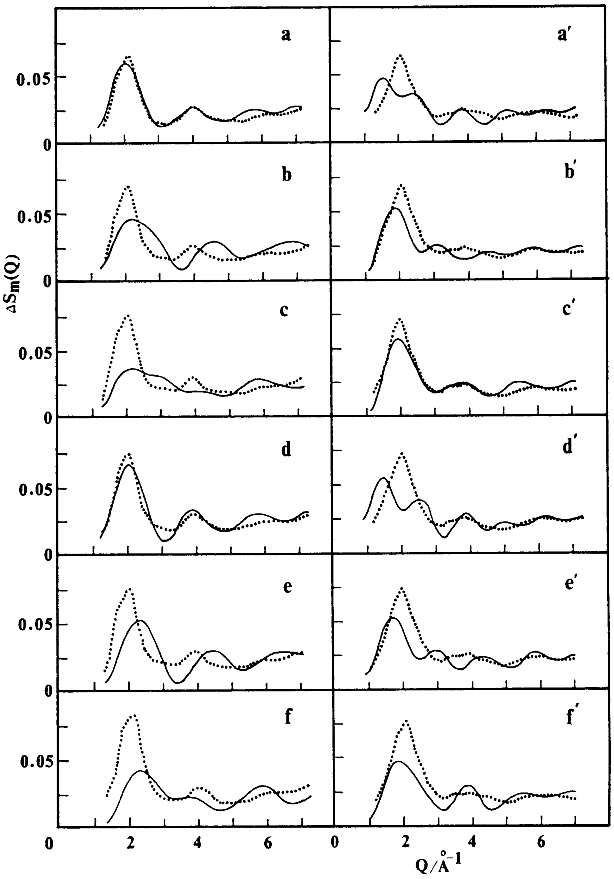

Fig. 6. Changes in the calculated $\Delta S_m(Q)$ with variation of the coordination number for LiCl (a—f) and CsCl (a'—f') solutions.

• : Observed $\Delta S_m(Q)$ (14 °C), (a), (a') $n_+=4$, $n_-=6$, (b), (b') $n_+=6$, $n_-=6$, (c), (c') $n_+=8$, $n_-=6$, (d), (d') $n_+=4$, $n_-=8$, (e), (e') $n_+=6$, $n_-=8$, (f), (f') $n_+=8$, $n_-=8$.

TABLE 4. COORDINATION NUMBERS, ION-OXYGEN DISTANCES AND CONFIGURATIONS AROUND IONS DETERMINED IN THE PRESENT STUDY

Ion	Coordination number, n	Ion-oxygen distance, r/Å	Configuration around ions (Angle, ϕ/°)
Li^+	4	1.90±0.05	linear (54.75)
Cs^+	8	2.95±0.10	linear (54.75)
Cl^-	6	3.10±0.05	undetermined

first hydration shell in the LiCl solution, comparing the calculated curves with those observed, and those for 744 different models in the CsCl solution.

Results of Analysis. We determined the best structure model of the first hydration shell for both solutions. However, it is not possible to show all the curves calculated for the assumed models for comparison (264 and 744 models for LiCl and CsCl solutions, respectively); only typical features of the curves are given.

The calculated $\Delta S_m(Q)$ curves for different sets of coordination numbers are shown for both solutions in Fig. 6; for the LiCl solution, those with various magnitudes of parameter ($r_{Li^+\text{-}O}$, $r_{Cl^-\text{-}O}$, and orientational configurations *etc.*) are shown in Figs. 7(a)—(d) in the case of $n_{Li^+}=4$ and $n_{Cl^-}=6$.

The calculated $\Delta S_m(Q)$ curves of the best mode's thus determined for both solutions are given in Fig. 8 (each curve in Figs. 6(a) and (c') is identical with the best fit curve, respectively). The magnitudes of parameter and orientational configurations for the best structure model of the first hydration shell are given in Table 4.

Concerning the configuration of water molecules within the first hydration shell around cations, the results agree with the conclusion obtained by the

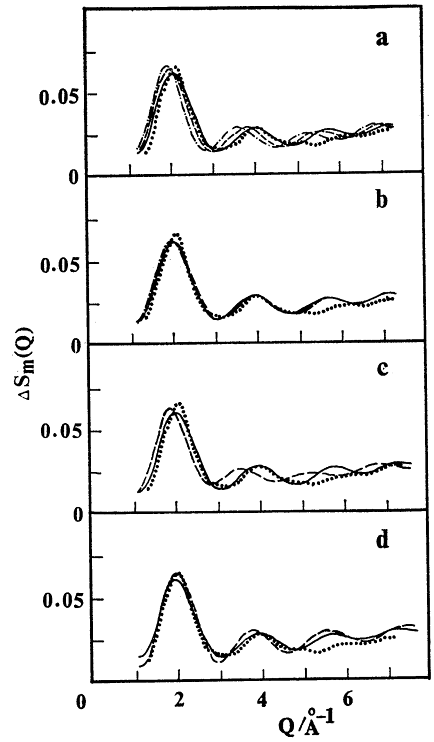

Fig. 7. Changes in the calculated $\Delta S_m(Q)$ with variation of physical parameters for the LiCl solution.

• : Observed $\Delta S_m(Q)$ (14 °C), (a) r_{Li^+-O} (all other parameters are identical with those given in Table 4), ——: 1.90 Å, – – –: 2.00 Å, —•—: 2.10 Å,

(b) r_{Cl^--O} (all other parameters are identical with those given in Table 4), ——: 3.10 Å, – – –: 3.05 Å, —•—: 3.15 Å,

(c) configurations around Li^+ (all other parameters are identical with those given in Table 4), ——: linear, – – –: bifurcated,

(d) configurations around Cl^- (all other parameters are identical with those given in Table 4), ——: linear, ——: bifurcated.

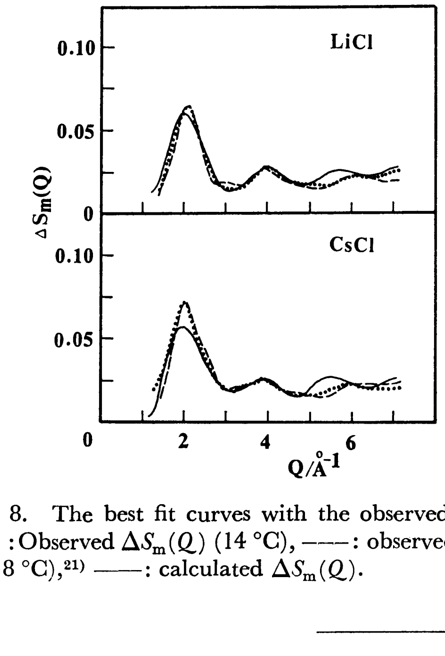

Fig. 8. The best fit curves with the observed $\Delta S_m(Q)$. • : Observed $\Delta S_m(Q)$ (14 °C), ——: observed $\Delta S_m(Q)$ (18 °C),[21] ——: calculated $\Delta S_m(Q)$.

molecular dynamics study of Briant and Burton.[22] However, with respect to the configuration around Cl^-, we can not determine which type of configuration, linear or bifurcated, is predominant (Fig. 7(d)).

From the structure analysis where the parameters have been varied systematically (Table 3), we conclude that the structure models shown in Table 4 give the best fit curves with those observed for the LiCl and CsCl solutions at 1 M.

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17) For the average rotational angle ξ, related to the average of the intermolecular distance r_{DD}, see Fig. 6 in Ref. 14 and Fig. 5 in Ref. 12.

18) Concerning the factor $[S_C(Q)-1]$, in the preceding paper we used the values of X-ray data of Table II in the paper of Narten and Levy (*J. Chem. Phys.*, **55**, 2263 (1971)).

19) In the former report three forms of hydrogen bonded D_2O molecules (Fig. 5) were taken into consideration in the calculation of $f_{2c}(Q)$. However, in the calculation of $f_1(Q)$, the intramolecular separation and the bond angle of the central molecule (r_{OD}: 1.01 Å, T: 109.5°) were used. In the present analysis the effect of the presence of three forms has fully been taken into consideration in $f_1(Q)$ as well as $f_{2C}(Q)$.

20) Samples composed of naturally occurring elements were used. Values of coherent scattering amplitudes of the elements are as follows: -0.18×10^{-12} cm for Li, 0.49×10^{-12} cm for Cs and 0.99×10^{-12} cm for Cl. (B. Dorner and R. Comes, "Dynamics of Solids and Liquids by Neutron Scattering," ed by S. W. Lovessey and T. Springer, Springer-Verlag, Berlin (1977), Chap. 3, pp. 136—141).

21) For the confirmation of the reproducibility of the observed data we give another $\Delta S_m(Q)$ curve observed at 18 °C The two curves agree well.

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