

Neutron Diffraction Study of Aqueous Ionic Solutions. II. Aqueous Solutions of Sodium Chloride and Potassium Chloride

Norio OHTOMO† and Kiyoshi ARAKAWA*

Research Institute of Applied Electricity, Hokkaido University, Sapporo 060

† Faculty of Engineering, Hokkaido University, Sapporo 060

(Received September 20, 1979)

The structure factors $S_m(Q)$ for aqueous solutions of NaCl and KCl at room temperature have been determined by means of the LINAC-TOF-neutron diffraction method. A revised subtraction method was applied to diffraction data of the solutions. Results obtained for the structure of the nearest hydration shell around ions are as follows. (a) The coordination numbers are 8 for Na^+ and 6 for Cl^- in the NaCl solution and 8 for K^+ and 6 for Cl^- in the KCl solution; (b) the average ion-oxygen distances are $2.50 \pm 0.10 \text{ \AA}$ for Na^+ , $2.70 \pm 0.10 \text{ \AA}$ for K^+ , and $3.10 \pm 0.05 \text{ \AA}$ for Cl^- ; (c) around chloride ions water molecules take the configuration to orient the vector which bisects the D-O-D angle on a straight line joining an oxygen atom and the anion. Analysis was performed on the data of LiCl and CsCl solutions.

Neutron diffraction studies have recently been carried out on aqueous ionic solutions.¹⁻³⁾ It was found that the method is useful for the determination of the structures of ionic solutions, in particular the structure parameters of the hydration shell around ions such as coordination numbers, ion-oxygen distances, and orientational arrangements of water molecules within the first hydration shell.

The recent development of the TOF-neutron diffraction method, associated with the proposition of improved correction procedures for inelastic scattering, has made it possible to provide more accurate data.^{1,4-6)} On neutron diffraction data of aqueous ionic solutions, there is no general method of analysis. Three procedures have been proposed so far: the near-neighbor model method by Narten *et al.*,²⁾ the first-order-difference spectroscopy by Soper *et al.*,³⁾ and the subtraction method by the authors.¹⁾ However, the method of Narten *et al.* has been questioned especially concerning the nature of the near-neighbor model itself,^{4,7,8)} while the method of Soper *et al.* using isotopes of nuclear species in the sample is clearly restricted in applicability.

In our study of aqueous solutions of LiCl and CsCl by the subtraction method (Paper I)¹⁾ we obtained information on the structure of the first hydration shell around ions. In order to elucidate the structure of the shell about univalent ions, we have carried out a neutron diffraction study on aqueous solutions of NaCl and KCl, a revised subtraction method being used to confirm the accuracy of the results.

Experimental

The experiment was performed by means of the TOF-neutron diffraction method by LINAC. Details of the apparatus and procedures were reported.^{1,4,9)}

Two 1.0 M alkali halide solutions (1 M = 1 mol dm⁻³) were prepared by the addition of extra pure anhydrous sodium chloride and potassium chloride to heavy water. Samples composed of naturally occurring elements were used, the values of coherent scattering amplitudes of the elements being $0.36 \times 10^{-12} \text{ cm}$ for Na, $0.37 \times 10^{-12} \text{ cm}$ for K, and $0.96 \times 10^{-12} \text{ cm}$ for Cl.¹⁰⁾

Measurements were carried out at room temperature (20.5 °C) at the scattering angle, $2\theta = 45^\circ$. We obtained the $S_m(Q)$ data for a range of low Q , $0.9\text{--}10.0 \text{ \AA}^{-1}$ ($Q =$

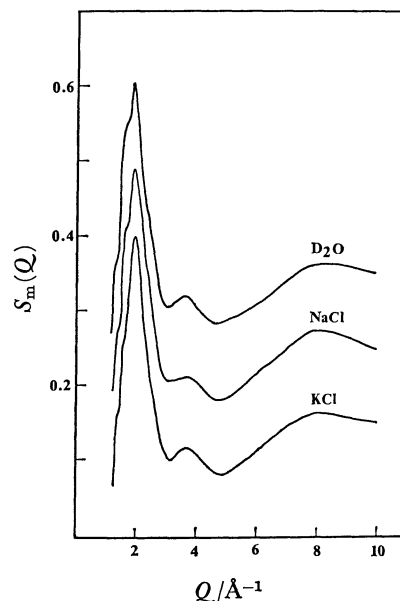


Fig. 1. Observed structure factors for NaCl and KCl solutions at 1 M, compared with the factor for D₂O.

$4\pi/\lambda \sin\theta$). $S_m(Q)$ curves of NaCl and KCl solutions including that of D₂O are given in Fig. 1. The change in the bump at *ca.* 4 \AA^{-1} as well as that in the main peak accompanied by a shoulder at 2.8 \AA^{-1} indicate the main effects of ions on the structure of the first hydration shell.

The statistical errors are the same as those reported:¹⁾ 0.5–0.6% in the Q range $2\text{--}5 \text{ \AA}^{-1}$ and 0.9% at *ca.* 8 \AA^{-1} .

Analysis of Aqueous Solutions of Alkali Chlorides

Subtraction Method of Analysis. In order to analyze the data of comparatively dilute aqueous solutions for determination of the structure of the first hydration shell, we have used a subtraction method in which the structure factor $S_m(Q)_{\text{D}_2\text{O}}$ of D₂O multiplied by an appropriate fraction is subtracted from the total structure factor $S_m(Q)_{\text{total}}$ of solutions.¹⁾ The remaining factor $\Delta S_m(Q)$ thus obtained has been compared with the $\Delta S_m(Q)_{\text{calcd}}$ calculated for a structure model of the hydration shell, the structure model which gives the best fit curve being determined. In applying the subtraction method we modify Eq. 2, Paper I,

in an attempt to make the method more available. By introducing a term multiplied by a coefficient a which indicates a contribution of the interactions between water molecules within the first hydration shell and environmental molecules outside of the shell in addition to Eq. 2, Paper I, the remaining factor $\Delta S_m(Q)$ for the first hydration shell becomes

$$\Delta S_m(Q) = S_m(Q)_{\text{total}} - \left(\frac{N_w'}{N_w} - x \right) S_m(Q)_{D_2O} - ax S_m(Q)_{D_2O}, \quad (1)$$

$$x = \frac{c(n_+ + n_-)}{55.3}, \quad (2)$$

where N_w and N_w' are the mole numbers of water in 1 dm³ of pure water and those of water in 1 dm³ of the solutions, respectively, x is the mole fraction of D₂O molecules coordinated in the first hydration shell around ions, n_+ and n_- are the coordination numbers around the cation and the anion, respectively, and c is concentration in M. The second term in Eq. 1 shows the contribution from bulk water outside of the hydration shells, and the third one that from the pairs between molecules within hydration shells and bulk water molecules. In aqueous solutions as dilute as 1 M, we can assume $N_w'/N_w \simeq 1$,¹¹⁾ and we get

$$\Delta S_m(Q) = S_m(Q)_{\text{total}} - (1-x) S_m(Q)_{D_2O} - ax S_m(Q)_{D_2O}. \quad (3)$$

In order to study the contribution of the interactions between water molecules in the first hydration shell ($c(n_+ + n_-)$ mol) and those outside, the magnitude of a is estimated as follows. The contribution of the interactions to $S_m(Q)$ is supposed to be equal to that of $c(n_+ + n_-)/2$ mol of bulk water molecules on the average, since $c(n_+ + n_-)$ mol of the water molecules in the nearest hydration shell are in contact with ions on the one side, the contribution to the total water-water interactions then becoming approximately half as much as that of the same mol of bulk water. Thus, the magnitude of a is 1/2 in this case. In the analysis used in Paper I, the contribution was neglected, and Eq. 2 in the paper is identical with the case of $a=0$ in Eq. 3 above. We will now compare the two cases, $a=1/2$ and $a=0$.

Calculation of $\Delta S_m(Q)$. In order to determine the structure of the nearest hydration shell in the NaCl and KCl solutions, the observed values of $\Delta S_m(Q)$ are compared with those calculated for various structure models assumed.

The structure of the hydration shell is characterized by several parameters, coordination numbers, ion-oxygen distances, and orientational arrangements of water molecules around ions. The coordination numbers and ion-oxygen distances reported so far are located given in Tables 1 and 2 together with the tables in Paper I. As regards the configuration of water molecules around ions, two forms, linear and bifurcated, are assumed for cations where lone-pair electrons are located in the vicinity of the ions (Paper I, Figs. 5 (a) and (b)) and also for anions where deuterium atoms are located in the vicinity of the ions (Paper I, Figs. 5(c) and (d)).

The calculated remaining factor, $\Delta S_m(Q)_{\text{calcd}}$, we

TABLE 1. COORDINATION NUMBERS OF Na⁺ AND K⁺ DETERMINED FROM X-RAY (X) DIFFRACTION STUDY AS WELL AS FROM MOLECULAR DYNAMICS (MD) AND MONTE CARLO (MC) CALCULATIONS

Ion	Coordination number	Solute	Concentration M	Method	Ref.
Na ⁺	5—6			MC	iii
	4±1.5	NaI	7	X	v
	5			MD	vi
	6.6±0.1	NaCl	2.2	MD	vii
	7.3		0.55	MD	viii
K ⁺	4.3			MC	ix
	4	KOH	12	X	i
	5.3	KCl	2—4	X	ii
	5—7			MC	iii
	3.2—1.7	KJ	0.5—5	X	iv
	5.1			MC	ix

i) E. W. Brady, *J. Chem. Phys.*, **28**, 464 (1958). ii) D. S. Terekhova, A. I. Ryss, and I. V. Radchenko, *Zh. Strukt. Khim.*, **10**, 923 (1969). iii) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **61**, 799 (1974). iv) M. Ya Fishkis and T. E. Soboleva, *Zh. Strukt. Khim.*, **15**, 186 (1974). v) M. Maeda and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **48**, 3755 (1975). vi) Ref. 9. vii) Ref. 8. viii) Ref. 10. ix) E. Clementi and R. Barsotti, *Chem Phys. Lett.*, **59**, 21 (1978).

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

Ion	Distance Å	Solute	Concentration M	Method	Ref. ^{a)}
Na ⁺	2.3±2.4			MC	iii
	2.40±0.03	NaI	7	X	v
	2.31	NaCl	2.2	MD	vii
	2.59			MC	ix
K ⁺	2.8±2.9			MC	iii
	3.27			MC	ix

a) References are the same as those in Table 1.

have

$$\Delta S_m(Q)_{\text{calcd}} = \sum_{\alpha=\pm} [x'_\alpha \left(\sum_{n=1}^{m_\alpha} b_n \right)^{-2} \sum_{i=1}^{m_\alpha} \sum_{j=1}^{m_\alpha} b_i b_j \times \exp(-\gamma_{\alpha ij} Q^2) j_0(Q r_{\alpha ij})], \quad (4)$$

where

$$j_0(Qr) = \frac{\sin(Qr)}{Qr}, \quad (5)$$

with summation for α over two contributions from the hydrated structure of cation (+) and anion (-). m_α is the number of atoms within the hydrated structure labelled by α , x'_α the mole fraction of D₂O molecules coordinated in the shell around cation and anion, and b_i the coherent scattering length of nucleus i . $r_{\alpha ij}$ is the distance between nuclei i and j within the hydrated structure labelled by α and their mean-square variations $2\gamma_{\alpha ij}$.

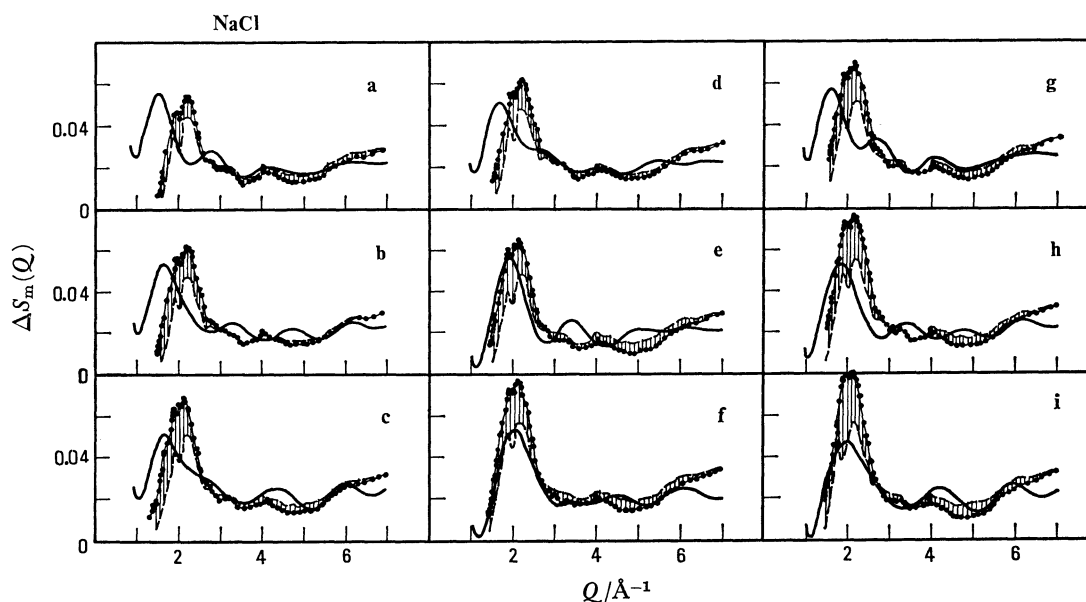


Fig. 2. Changes in the calculated $\Delta S_m(Q)$ with variation of the coordination number for NaCl solution,

••: observed $\Delta S_m(Q)$ ($a=0$), ----: observed $\Delta S_m(Q)$ ($a=1/2$),

(a) $n_+=4$, $n_-=4$, (b) $n_+=6$, $n_-=4$, (c) $n_+=8$, $n_-=4$, (d) $n_+=4$, $n_-=6$, (e) $n_+=6$, $n_-=6$,
(f) $n_+=8$, $n_-=6$, (g) $n_+=4$, $n_-=8$, (h) $n_+=6$, $n_-=8$, (i) $n_+=8$, $n_-=8$.

TABLE 3. RANGE OF PARAMETERS FOR STRUCTURE MODELS

Ion	Coordination number	Ion-oxygen distance/Å	Type of configurations around ions (ϕ /degree)
Na ⁺	4, 6, 8	2.20—2.70	linear (44.75—64.75) bifurcated (0.0 —20.0)
K ⁺	4, 6, 8	2.70—3.40	linear (44.75—64.75) bifurcated (0.0 —20.0)
Cl ⁻	4, 6, 8	3.00—3.20	linear (0.0 —20.0) bifurcated (0.0 —20.0)

The contribution from the hydrated structure for each kind of ion is calculated by a similar procedure to that for the water structure previously described,⁴⁾ constructed for the corresponding structure models. The model consists of several parameters varying in a range of magnitude (Table 3). For example, in the case of $n_{\pm}=4, 6$, and 8, tetrahedral, octahedral, and cubic coordination is assumed, respectively, with the variation of ion-oxygen, ion-deuterium, oxygen-oxygen, and oxygen-deuterium distances and the orientational angles.

We calculated $\Delta S_m(Q)$ for a number of structure models with various magnitudes of parameters (Table 3). For both solutions, 36 different structure models with respect to the coordination number and type of orientational configuration were assumed; for each structure model, ion-oxygen distances and the angle ϕ were varied successively at intervals of 0.05 Å and 10°, respectively. In all, we calculated the $\Delta S_m(Q)$ curves for 1,680 different structure models of the first hydration shell in the NaCl solution and for 1,824 different models in the KCl solution, the best structure model being then determined by a comparison of the $\Delta S_m(Q)_{\text{calcd}}$ curves with those observed for both solutions.

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

Ion	Coordination number	Ion-oxygen distance/Å	Configuration around ions (ϕ /degree)
Na ⁺	8	2.50 ± 0.10	undetermined
K ⁺	8	2.70 ± 0.10	undetermined
Cl ⁻	6	3.10 ± 0.05	bifurcated (0.0)

Results of Analysis. The $\Delta S_m(Q)_{\text{calcd}}$ curves for different sets of coordination numbers for NaCl and KCl solutions are shown in Figs. 2 and 3, respectively, two sets of observed values of $\Delta S_m(Q)$ being plotted for $a=1/2$ and $a=0$ and the interval between those being hatched. The best fit curves with observed $\Delta S_m(Q)$ are obtained in the case of $n_{\text{Na}^+}=8$ and $n_{\text{Cl}^-}=6$ for the NaCl solution (Fig. 2 (f)) and in the case of $n_{\text{K}^+}=8$ and $n_{\text{Cl}^-}=6$ for the KCl solution (Fig. 3 (f)). The curves other than the best fit ones deviate appreciably from both observed $\Delta S_m(Q)$ ($a=1/2$ and $a=0$) (Figs. 2 and 3).

The $\Delta S_m(Q)$ curves with various magnitudes of parameters are shown in Figs. 4 (a)—(d) for $n_{\text{Na}^+}=8$ and $n_{\text{Cl}^-}=6$ for the NaCl solution, and in Figs. 4 (a')—(d') for $n_{\text{K}^+}=8$ and $n_{\text{Cl}^-}=6$ for the KCl solution.

The calculated $\Delta S_m(Q)$ curves of the best models thus determined for both solutions are given in Figs. 2 (f) and 3 (f) for NaCl and KCl solutions, respectively. The magnitudes of parameters and orientational configurations for the best models of the first hydration shell are given in Table 4. Concerning the configurations of water molecules within the first hydration shell around Cl⁻, we have confirmed that the bifurcated type is predominant for both solutions (Figs. 4 (d) and (d')).¹²⁾ However, with respect to the configurations around cations, we could not determine which

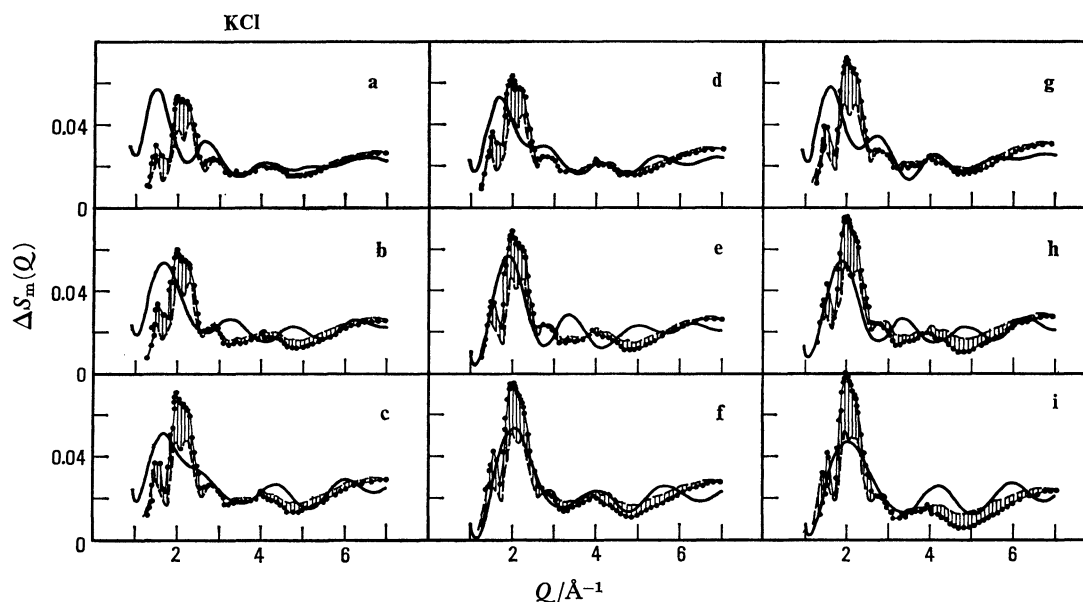


Fig. 3. Changes in the calculated $\Delta S_m(Q)$ with variation of the coordination number for KCl solution, \bullet : observed $\Delta S_m(Q)$ ($a=0$), ----: observed $\Delta S_m(Q)$ ($a=1/2$), (a) $n_+=4$, $n_-=4$, (b) $n_+=6$, $n_-=4$, (c) $n_+=8$, $n_-=4$, (d) $n_+=4$, $n_-=6$, (e) $n_+=6$, $n_-=6$, (f) $n_+=8$, $n_-=6$, (g) $n_+=4$, $n_-=8$, (h) $n_+=6$, $n_-=8$, (i) $n_+=8$, $n_-=8$.

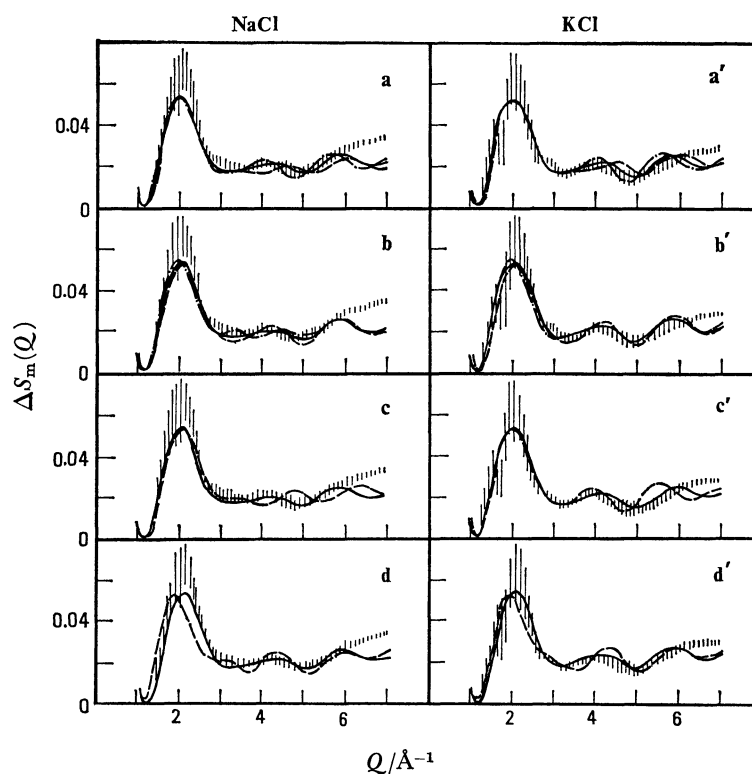


Fig. 4. Changes in the calculated $\Delta S_m(Q)$ with variation of physical parameters for NaCl (a—d) and KCl (a'—d') solutions. The vertical lines indicate the intervals between two sets of observed values of $\Delta S_m(Q)$ ($a=0$ and $a=1/2$).

(a) r_{Na^+-O} (all other parameters are identical with those given in Table 4), ----: 2.40 Å, —: 2.50 Å, —·—: 2.60 Å, (b) r_{Cl^--O} (all other parameters are identical with those given in Table 4), ----: 3.00 Å, —: 3.10 Å, —·—: 3.20 Å, (c) configurations around Na^+ (all other parameters are identical with those given in Table 4), —: bifurcated, ----: linear, (d) configurations around Cl^- (all other parameters are identical with those given in Table 4), —: bifurcated, ----: linear, (a') r_{K^+-O} (all other parameters are identical with those given in Table 4), ----: 2.60 Å, —: 2.70 Å, —·—: 2.80 Å, (b') r_{Cl^--O} (all other parameters are identical with those given in Table 4), ----: 3.00 Å, —: 3.10 Å, —·—: 3.20 Å, (c') configurations around K^+ (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), —: bifurcated, ----: linear.

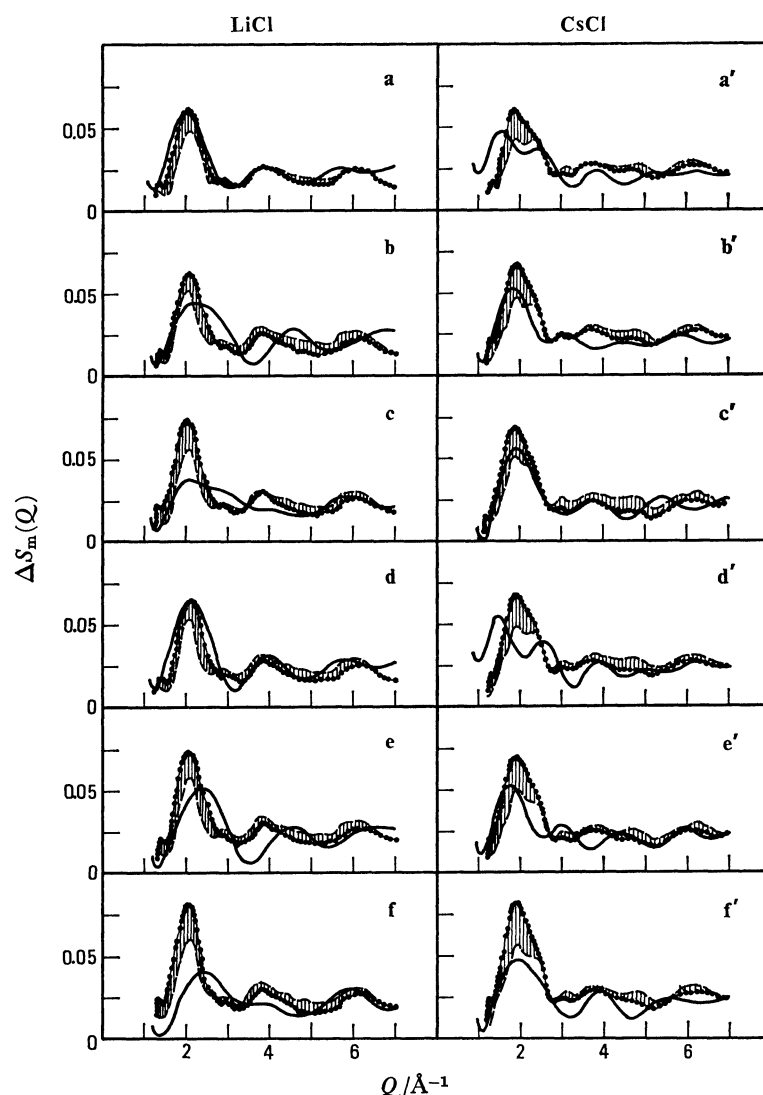


Fig. 5. Changes in the calculated $\Delta S_m(Q)$ with variation of the coordination number for LiCl (a—f) and CsCl (a'—f') solutions.

•: Observed $\Delta S_m(Q)$ ($a=0$), ----: observed $\Delta S_m(Q)$ ($a=1/2$),
 (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') $n_+=8$, $n_-=8$.

type, linear or bifurcated, is predominant (Figs. 4 (c) and (c')).

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

The same analysis was performed for the LiCl and CsCl solutions according to the present procedure in order to re-examine the results given in Paper I. The $\Delta S_m(Q)$ curves calculated for different sets of coordination numbers are shown in Fig. 5 and the best fit curves with observed $\Delta S_m(Q)$ are obtained in the case of $n_{Li^+}=4$ and $n_{Cl^-}=6$ for the LiCl solution (Fig. 5 (a)) and in the case of $n_{Cs^+}=8$ and $n_{Cl^-}=6$ for the CsCl solution (Fig. 5 (c')). For the LiCl solution, in the case of a set of coordination numbers which gives the best fit curve ($n_{Li^+}=4$ and $n_{Cl^-}=6$), the $\Delta S_m(Q)$ curves with various magnitudes of parameters are

shown in Fig. 6. The adequacy shown in Figs. 5 (a) and (c') is the same as that given in Table 4, Paper I.

We have calculated the difference $\Delta S_m(Q)_{\text{obsd}} - \Delta S_m(Q)_{\text{calcd}}$ for two cases: $a=1/2$ and $a=0$, where $\Delta S_m(Q)_{\text{obsd}}$ is the observed value of the remaining factor (Eq. 3), $\Delta S_m(Q)_{\text{calcd}}$ being the calculated value for various models. It was found that the difference is practically independent of over Q all the range. The magnitude of $\Delta S_m(Q)_{\text{obsd}} - \Delta S_m(Q)_{\text{calcd}}$ is primarily determined by the factor $(n_+ + n_-)$. $\Delta S_m(Q)_{\text{obsd}} - \Delta S_m(Q)_{\text{calcd}}$ becomes nearly identical for both cases: $(n_+=4, n_-=8)$ and $(n_+=6, n_-=6)$, for example. In Fig. 7, the differences are plotted against $(n_+ + n_-)$ which is an important factor characterizing various models. For the assignment of $a=1/2$, the differences are essentially zero (Fig. 7). This supports adequacy of the assignment superior to the case of $a=0$.

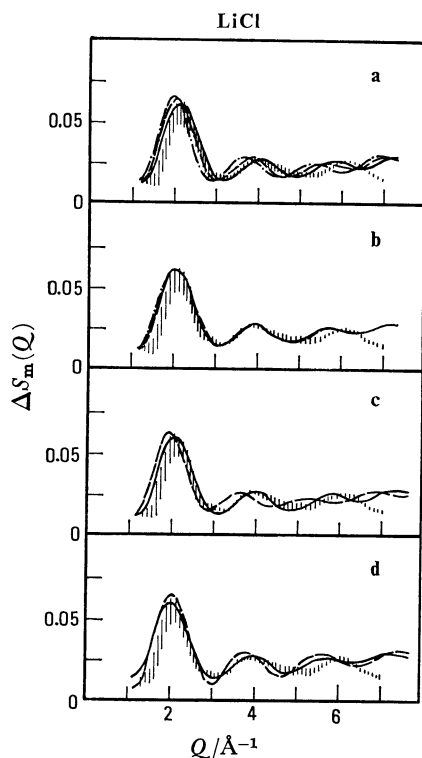


Fig. 6. Changes in the calculated $\Delta S_m(Q)$ with variation of physical parameters for the LiCl solution. The vertical lines indicate the intervals between two sets of observed values of $\Delta S_m(Q)$ ($a=0$ and $a=1/2$). (a) $r_{\text{Li-O}}$ (all other parameters are identical with those given in Table 4), —: 1.90 Å, ----: 2.00 Å, —·—: 2.10 Å, (b) $r_{\text{Cl-O}}$ (all other parameters are identical with those given in Table 4), ----: 3.05 Å, —: 3.10 Å, —·—: 3.15 Å, (c) configurations around Li^+ (all other parameters are identical with those in Table 4), —: linear, ----: bifurcated. (d) configurations around Cl^- (all other parameters are identical with those in Table 4), —: linear, ----: bifurcated.

Discussions and Concluding Remarks

Concerning the structure within the first hydration shell in aqueous solutions of alkali halides, we have determined coordination numbers and average ion-oxygen distances as well as orientational arrangements of water molecules around ions by analyzing the neutron diffraction data. A summary is given herewith on the results of this study and those given in Paper I.

Coordination Number and Ion-oxygen Distances.

For Cl^- the coordination numbers are six in all solutions at 1 M, while the number is four for Li^+ and eight for other cations (Na^+ , K^+ , and Cs^+). The value for Li^+ determined is in line with those reported so far.¹⁾ The values for Na^+ , K^+ , and Cs^+ reported so far are found to be very diversified. However, according to recent results obtained by molecular dynamics studies for these cations,¹³⁻¹⁵⁾ the coordination numbers around the univalent cations are 7–8 except that around Li^+ , which is essentially in agreement with ours. From the results of our two studies, the unique behavior of Li^+ in water as compared with that of other alkaline cations has been clarified.

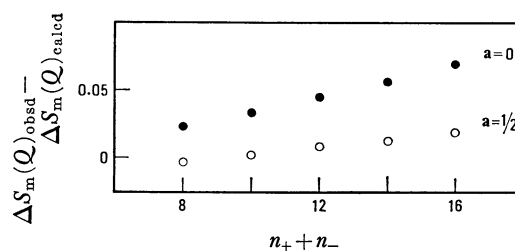


Fig. 7. $\Delta S_m(Q)_{\text{obsd}} - \Delta S_m(Q)_{\text{calcd}}$ plotted against $(n_+ + n_-)$.

The average ion-oxygen distances for Li^+ , Na^+ , K^+ , Cs^+ , and Cl^- within the first hydration shell have been found to be 1.90 ± 0.05 Å, 2.50 ± 0.10 Å, 2.70 ± 0.10 Å, 2.95 ± 0.10 Å, and 3.10 ± 0.05 Å, respectively.

Oriental Configurations around Ions. As regards the orientational configuration of water molecules around ions, it is widely believed that the molecules take either of the two forms, linear or bifurcated, on the average within the hydration shell. we have little experimental knowledge concerning the question.

Our results show that water molecules within the nearest hydration shell take a linear configuration for Li^+ and Cs^+ in LiCl and CsCl solutions and a bifurcated one for Cl^- in NaCl and KCl solutions. Complete determination of the orientational configuration around all ions in solutions has not been achieved.

References

- 1) N. Ohtomo and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **52**, 2755 (1979).
- 2) A. H. Narten, F. Vaslow, and H. A. Levy, *J. Chem. Phys.*, **58**, 5017 (1973).
- 3) A. K. Soper, G. W. Neilson, J. E. Enderby, and R. A. Howe, *J. Phys. C, Solid State Phys.*, **10**, 1793 (1977).
- 4) N. Ohtomo and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **51**, 1649 (1978).
- 5) N. Ohtomo and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **53**, 1510 (1980).
- 6) J. H. Clarke, J. R. Granada, and J. C. Dore, *Mol. Phys.*, **37**, 1263 (1979); G. Walford, J. H. Clarke, and J. C. Dore, *ibid.*, **36**, 1581 (1978).
- 7) G. Licheri, G. Piccaluga, and G. Pinna, *J. Chem. Phys.*, **64**, 2437 (1976).
- 8) J. G. Powles, *Adv. Phys.*, **22**, 1 (1973).
- 9) T. Matsumoto, N. Ohtomo, and M. Senda, *J. Nucl. Sci. Technol.*, **15**, 863 (1978).
- 10) B. Dorner and R. Comès, "Dynamics of Solids and Liquids by Neutron Scattering," ed by S. W. Lovesey and T. Springer, Springer-Verlag, Berlin (1977), Chap. 3, pp. 113–141.
- 11) At 1 M solutions, for instance, the magnitude of error due to an approximation of $N_w/N_w \approx 1$ is smaller than that of the experimental error.
- 12) The bifurcated configuration of water molecules around Cl^- is significant, since the linear type has been reported so far only for more concentrated solutions.^{2,3)}
- 13) K. Heinzinger and P. C. Vogel, *Z. Naturforsch.*, **31a**, 463 (1976).
- 14) C. L. Briant and J. J. Burton, *J. Chem. Phys.*, **64**, 2888 (1976).
- 15) P. Bopp, K. Heinzinger, and G. Jancso, *Z. Naturforsch.*, **32a**, 620 (1977).