X-Ray Diffraction Studies on the Structures of Hydrated Oxonium Ion, and the Chlorocobalt(II) and Tetrachlorocobaltate(II) Complexes in Aqueous Solutions

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The structure of hydrated oxonium ion has been determined in a concentrated hydrochloric acid solution by the X-ray diffraction method. The oxonium ion H_3O^+ combines with four water molecules to form a trigonal pyramid structure in which three water molecules have an H_3O^+–H_2O distance of 2.44 Å, while the water molecule at the apex of the pyramid is separated by 2.90 Å from the central oxygen atom of the oxonium ion. The structure of the $CoCl^+$ determined in a relatively dilute lithium chloride solution (the Cl/Co mole ratio is 3.38) shows that the cobalt(II) ion is coordinated with five water molecules, the Co–OH_2 distance being 2.14 Å. The Co–Cl distance within the complex is 2.35 Å. The $CoCl_4{}^{2-}$ complex has a regular tetrahedral structure both in a concentrated lithium chloride (Cl/Co=22.1) and a hydrochloric acid (Cl/Co=21.1) solutions with the Co–Cl bond length of 2.29 Å.

Proton is present as H_3O^+ in water. The H_3O^+ ion is further hydrated with some water molecules through hydrogen bonds to form hydrated oxonium ion $H_3O(H_2O)_n{}^+$. The hydration number of oxonium ion has been determined by various methods, but the results are not well consistent with each other. For instance, the hydration number n is estimated to be 3—4 from X-ray and neutron diffraction measurements,[1–3] but the number is zero (*i.e.* H_3O^+) or one according to compressibility studies.[4] Most thermodynamic investigations give the hydration number of 3, *i.e.*, $H_9O_4{}^+$.[5,6]

Oxonium ion H_3O^+ can probably combine with four water molecules through hydrogen bonds. In crystal, however, an oxonium ion has three hydrogen bonds to combine with other oxonium ions or anions.[7–9] A theoretical calculation by a molecular orbital method[10] suggests that an oxonium ion has an almost planar structure in which each hydrogen atom binds to a water molecule through the hydrogen bond, the bond energy being about 190 kJ mol^{-1}. One water molecule situates above the oxonium ion, but the interaction between the oxonium ion and the water molecule is so weak that the bond energy is about 0 kJ mol^{-1}.[10]

The structure of oxonium ion so far estimated by diffraction methods[1–3] was regular tetrahedral, which was not in a satisfactory agreement with the structure expected from the crystallographic analysis[7–9] and the quantum mechanical calculation.[10] Moreover, the hydration number of an oxonium ion determined by the diffraction methods does not coincide with the numbers obtained by other methods. One of the aim of the present study is to establish the structure of hydrated oxonium ion in solution.

Cobalt(II) chloride complexes are formed in an alkali chloride or in a hydrochloric acid solution. It is a well known fact that cobalt(II) chloride solutions show dichromism with temperature and concentrations of chloride ions originating from a change of the octahedral structure to the tetrahedral one with varying numbers of chloride ions and water molecules coordinated.

A number of equilibrium studies have been carried out for cobalt(II) chloride complexes in aqueous solutions with various techniques. According to stability constants determined by Bjerrum *et al.*[11,12] and Smithson and Williams,[13] the mono- and tetrachloro complexes are present as dominant species in solutions of relatively low and high concentrations, respectively, of chloride ions, while the dichloro and trichloro complexes have a narrow concentration range of the existence.

X-Ray diffraction measurements of aqueous and alcoholic solutions of cobalt(II) chloride have been made by Wertz *et al.*,[14] and they have determined the structures of the $Co(OH_2)_6{}^{2+}$ and $CoCl_4{}^{2-}$ complexes in the solutions. The structure of hexahydrated cobalt(II) ion has also been determined by Ohtaki *et al.*[15] who obtained the Co–OH_2 bond length of 2.08 Å.

In the present investigation the structures of hydrated oxonium ion, and the $CoCl^+$ and $CoCl_4{}^{2-}$ complexes have been determined in aqueous solutions of lithium chloride and hydrochloric acid by the X-ray diffraction method.

Experimental

Preparation and Analysis of Sample Solutions. Cobalt(II) chloride and lithium chloride (Wako Pure Chemical Co., reagent grade) were recrystallized twice from water. Three sample solutions (A, B, and C) were prepared for the X-ray diffraction measurements. Solutions A and B contained lithium chloride and solution C was a concentrated hydrochloric acid solution, in all the solutions cobalt chloride was dissolved. The former two solutions were prepared by mixing a cobalt(II) chloride solution with a lithium chloride solution. Suitable Cl/Co mole ratios of the solutions for the present study were estimated from the stability constants given by Bjerrum *et al.*[11,12] In solution A the $CoCl^+$ complex existed as the main species, besides the hydrated cobalt(II) ion. On the other hand, the $CoCl_4{}^{2-}$ complex was formed in solutions B and C. A small amounts of hydrochloric acid was added to solutions A and B in order to prevent the hydrolysis of Co(II) ion.

The concentration of cobalt(II) ions was determined both by EDTA titration using a Cu–PAN indicator and electrogravimetry. The results obtained by the two methods agreed each other within the error of ±0.2%. The concentration of chloride ions was determined gravimetrically as AgCl. Con-

TABLE 1. THE COMPOSITION (g-atoms $\mathrm{dm^{-3}}$) AND STOICHIOMETRIC VOLUME V PER COBALT ATOM IN THE SOLUTIONS

	A	B	C
Co	2.133	0.6129	0.5235
Cl	7.200	13.57	11.02
Li	2.902	12.28	—
O	49.38	39.35	42.92
H	98.79	78.76	95.81
$V/\mathrm{Å^3}$	778.4	2709	3172
Cl/Co	3.38	22.1	21.1

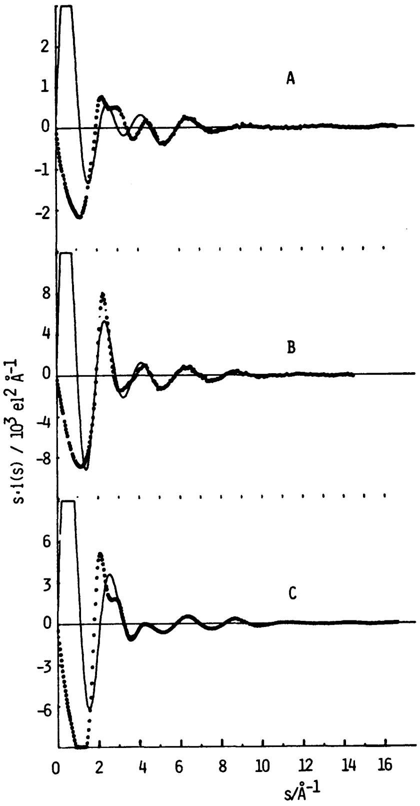

Fig. 1. The reduced intensities multiplied by s for solutions A, B, and C. The observed $s\cdot i(s)$ curves are shown by circles and the calculated ones by solid lines.

centrations of hydrogen ions in the lithium chloride–cobalt chloride systems were determined coulometrically. The concentration of lithium ions was estimated from the material balance of ions in the solutions. The density of the solutions was measured with a pycnometer. The composition of the solutions is given in Table 1.

X-Ray Scattering Measurements. X-Ray scattering measurements were carried out with a JEOL θ-θ diffractometer in a room thermostated at (25 ± 1) °C. Mo $K\alpha$ radiation (λ= 0.7107 Å) was used as an X-ray source. The scattering intensities were measured at discrete points of θ values from 1° to 70°, where 2θ is the scattering angle. Times required to accumulate 80000 counts were measured at each angle. Details of the measurements and treatments of X-ray scattering data were described in previous papers.[15–17]

All calculations were carried out by using programs KURVLR[18] and NLPLSQ.[15]

Results and Discussion

When several complexes coexist in a solution, it is usually necessary to know the formation constants of the complexes for analyzing X-ray scattering data. Since the formation constants determined in high ionic media are available in the literature for cobalt(II) chloride complexes,[11,12] the distribution of the complexes can be estimated for the sample solutions used in the present study.

Solution A contained two kinds of complexes, about 60 mol% of $\mathrm{CoCl^+}$ and 40 mol% of $\mathrm{Co^{2+}}$. In solutions B and C, the only $\mathrm{CoCl_4^{2-}}$ complex should be formed, since the solutions contained a large excess of chloride ions. In solution C, $\mathrm{H_3O^+}$ ions are present in contrast to hydrated lithium ions which are contained in solution B. The observed $s\cdot i(s)$ and $D(r)$ curves are shown in Figs. 1 and 2, respectively.

Solution A. The solution A is magenta. In the $D(r)$ (Fig. 2A) and $D(r)-4\pi r^2\rho_0$ (Fig. 3) curves we see four peaks around 1.0, 2.2, 3.3, and 4.5 Å. The small and broad peak at 1.0 Å is due to the O–H bond distance in water molecules. The second peak is attributed to the interactions between the central Co(II) and ligand atoms of its first neighbor. The Li–O distance of hydrated $\mathrm{Li^+}$ ions also partly contributes to this peak. The third peak can be attributed to the Cl–O contact of hydrated $\mathrm{Cl^-}$ ions. The fourth peak contains contributions from several kinds of atom pairs; for instance, O–O interactions due to the tetrahedral network of bulk water and interactions between the Co(II) atom and solvent molecules in the second coordination shell. In order to estimate the structural parameters of the $\mathrm{CoCl^+}$ complex, the appropriate interactions within hydrated cobalt, lithium and chloride ions should be subtracted from the observed radial distribution curve. The structural parameters used for the subtraction were quoted from the result reported for aqueous solutions of cobalt(II) perchlorate by Ohtaki *et al.*,[15] ($\mathrm{Co(OH_2)_6^{2+}}$, Co–$\mathrm{OH_2}$: 2.08 Å) and lithium chloride by Licheri *et al.*,[20] ($\mathrm{Li(OH_2)_4^+}$, Li–$\mathrm{OH_2}$: 2.10 Å; $\mathrm{Cl(H_2O)_6^-}$, Cl–$\mathrm{H_2O}$: 3.20 Å). The residual curve (chain line) in Fig. 3 shows two peaks which locate around 2.2 Å and 3.0 Å. The peak around 2.2 Å should be due to the Co–Cl and Co–O bonds within the $\mathrm{CoCl^+}$ complex. The structure of the $\mathrm{CoCl^+}$ complex was thus determined from the residual curve by a trial-and-error method. From the analysis, we found that the Co(II) ion within $\mathrm{CoCl^+}$ complex combines with one chloride ion and five water molecules at the distance of 2.35 Å and 2.14 Å, respectively. Subtraction of peaks due to the Co–Cl, Co–O, O–O, and Cl–O interactions within the $\mathrm{CoCl(OH_2)_5^+}$ complex from the residual curve led to a smooth background curve (broken line) having no appreciable peak over the range $r<4$ Å, except for the peak at about 2.9 Å which was ascribed to the O–O bonds within the bulk water. The parameter values thus estimated from the analysis of the radial distribution curve were finally refined by the least-squares method for the $s\cdot i(s)$ curve over the range $s>5$ Å^{-1}. The low-angle scattering data, which were dominated by contributions from long-range intermolecular interactions, were not included in the refinements. The results are summerized in Table 2. In the A-1 calculation, all

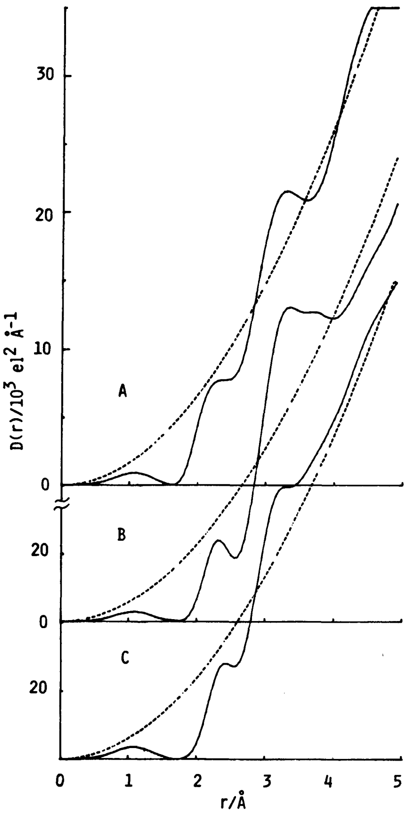

Fig. 2. Radial distribution functions $D(r)$ (solid lines) and $4\pi r^2\rho_0$ curves (broken lines) for solutions A, B, and C.

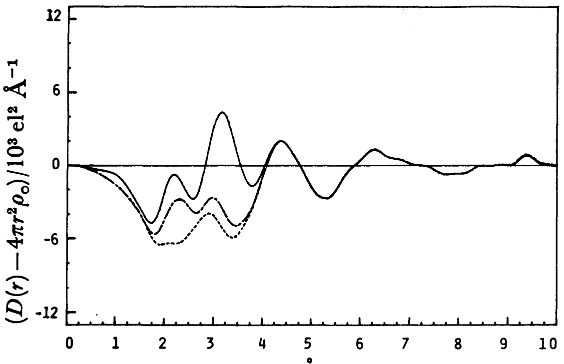

Fig. 3. The $D(r)-4\pi r^2\rho_0$ curve for solution A.
The chain line shows the residual curve obtained by subtracting the contributions of the hexaaquacobalt(II) ion, the hydrated chloride and the hydrated lithium ions from the original curve (solid line). The broken line gives the curve after subtraction of the peak shape due to the monochlorocobalt(II) ions from the chain-curve.

parameters given in the table were floated, the values being first guessed from the analysis of the radial distribution curve of solution A. On the other hand, the frequency factors of the atom-pairs in the table were fixed at the given values in the A-2 treatment. No significant difference was found in the bond lengths in the both calculations. The Co–OH_2 bond within the $CoCl(OH_2)_5^+$ complex is longer by 0.06 Å than that within the $Co(OH_2)_6^{2+}$ complex. This result suggests that a stronger electron-donation from the Cl^- ion compared with that from a water molecule weakens the Co–OH_2 bond within the former complex. The Li–O distance was not definitely determinable by the least-squares method, because of the low concentration and low scattering power of lithium ion.

Table 2. RESULTS OF THE LEAST-SQUARES REFINEMENTS FOR SOLUTION A

Standard deviations are given in parentheses. r: Bond distance, b: temperature factor, n: frequency factor.

Interaction	Parameter	A-1	A-2
$CoCl(OH_2)_5^+$			
Co–Cl	r/Å	2.353(9)	2.348(12)
	b/Å^2	0.0063(6)	0.0057(7)
	n	1.03(3)	1.0[a)]
Co–O	r/Å	2.135(5)	2.138(7)
	b/Å^2	0.0058(3)	0.0056(4)
	n	5.0(1)	5.0[a)]
Cl–O	r/Å	3.09(3)	3.08(4)
	n	4.1(3)	4.0[a)]
O–O	r/Å	2.99(4)	2.99(5)
	n	8.7(8)	8.0[a)]
$Cl(H_2O)_6^-$			
Cl–O	r/Å	3.193(7)	3.190(9)
	n	5.98(8)	6.0[a)]

a) The values were kept constant during the calculations.

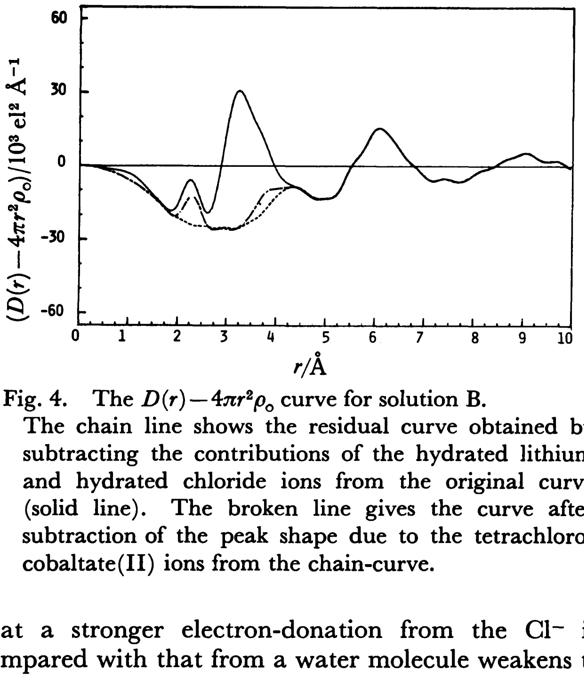

Fig. 4. The $D(r)-4\pi r^2\rho_0$ curve for solution B.
The chain line shows the residual curve obtained by subtracting the contributions of the hydrated lithium and hydrated chloride ions from the original curve (solid line). The broken line gives the curve after subtraction of the peak shape due to the tetrachlorocobaltate(II) ions from the chain-curve.

Solution B. The solution B is blue and the $D(r)$ and $D(r)-4\pi r^2\rho_0$ curves in Figs. 2B and 4 show three peaks and a shoulder at about 1.0, 2.3, 3.2, and 3.7 Å, respectively, in the range of $r<4$ Å. The peaks at 1.0 and 3.2 Å are ascribed to the O–H and Cl–O interactions, respectively, as previously observed in the case of solution A. The second peak centered around 2.3 Å may correspond to the interatomic distance between Co(II) and Cl^- ions, which has been found in the $CoCl_4^{2-}$ complex in alcoholic solutions.[14)] A part of the peak is also due to the Li–O distance within hydrated lithium ions.

In the analysis of the radial distribution curve, the

TABLE 3. RESULTS OF THE LEAST-SQUARES REFINEMENTS FOR SOLUTION B

Standard deviations are given in parentheses. *r*: Bond distance, *b*: temperature factor, *n*: frequency factor.

Interaction	Parameter	B-1	B-2
$CoCl_4^{2-}$			
Co–Cl	*r*/Å	2.29(1)	2.29(1)
	b/Å^2	0.0019(5)	0.0018(5)
	n	4.1(1)	4.0[a]
Cl–Cl	*r*/Å	3.74(7)	3.74(6)
	n	4.9(6)	6.0[a]
$Li(OH_2)_4^+$			
Li–O	*r*/Å	2.18(2)	2.18(2)
	n	4.3(3)	4.4(2)
$Cl(H_2O)_6^-$			
Cl–O	*r*/Å	3.19(1)	3.19(1)
	n	6.1(1)	6.2(1)

a) The values were kept constant during the calculations.

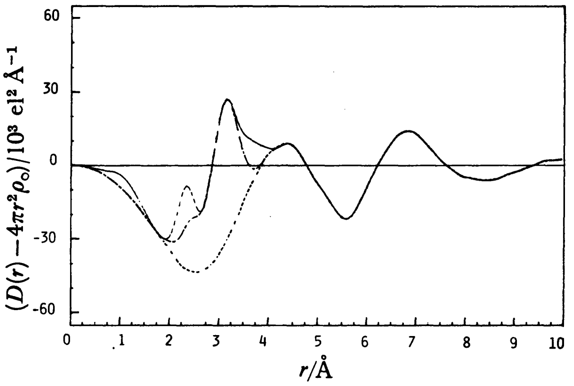

Fig. 5. The $D(r)-4\pi r^2\rho_0$ curve for solution C.
The chain line shows the residual curve obtained by subtracting the contribution of the tetrachlorocobaltate(II) ion from the original curve (solid line). The broken line gives the curve after subtraction of the peak shape calculated from model c of the hydrated oxonium and the hydrated chloride ions.

essentially same procedure as that used for solution A was employed. After subtraction of theoretical peaks due to the interatomic interactions within $Li(OH_2)_4^+$ and $Cl(H_2O)_6^-$, the chain line was obtained as the residual curve as seen in Fig. 4, from which we estimated the parameter values of interatomic interactions within the $CoCl_4^{2-}$ complex. The Co–Cl and Cl–Cl distances within the $CoCl_4^{2-}$ complex were estimated to be 2.30 Å and 3.75 Å, respectively. The ratio of the distances of Co–Cl to Cl–Cl is close to the value expected from a tetrahedral structure. The results of least-squares refinements are given in Table 3. In the course of the least-squares refinement of the structural parameters of the atom-pairs given in the table, all parameter values were allowed to change to search the best-fit result in the B-1 calculation, while the frequency factors of the Co–Cl and Cl–Cl atom-pairs were fixed at 4.0 and 6.0, respectively, in the B-2 calculation. The essentially same results were obtained in the both treatments. No evidence has been found for the existence of the hexacoordinated tetrachlorocobaltate(II) ion, $CoCl_4(OH_2)_2^{2-}$, in the present system and, therefore, no information has been obtained for the equilibrium between the hexa- and tetracoordinated $CoCl_4^{2-}$ ions.

In the $CoCl^+$ and $CoCl_4^{2-}$ complexes the Co–Cl bond distance of the former is slightly longer than that of the latter. According to Shannon,[21)] the crystal radius of Co^{2+} ion having the coordination number 6 is 0.79 Å, but the radius of the Co^{2+} ion becomes 0.72 Å when the coordination number of the Co^{2+} ion decreases to 4. The change in the Co–Cl distance with changing number of chloride ion within $CoCl_n^{(2-n)+}$ complexes observed in the present investigation is consistent with Shannon's estimation for the ionic radius of cobalt(II) ion.

Solution C. The Cl/Co mole ratios of solutions B and C are almost the same. Therefore, we can reasonably assume that the $CoCl_4^{2-}$ complex in solution C has the same structure with that in solution B, and then, calculated the theoretical $s\cdot i(s)$ curve for the interactions due to Co–Cl and Cl–Cl pairs within the $CoCl_4^{2-}$ complex and the Cl–O contact within hydrated Cl^- ions. However, a comparison between the theoretical and experimental $s\cdot i(s)$ curve gave no satisfactory agreement. This might arise from the structure of hydrated oxonium ions which was not taken into consideration in the calculation in spite of a very high concentration of hydrochloric acid in the solution. Therefore, at the next step of the analysis of the $D(r)$ curve, the structure of $H_3O(H_2O)_n^+$ was taken into account. At first, peak shapes due to the Co–Cl and Cl–Cl interactions within $CoCl_4^{2-}$ were subtracted from the radial distribution curve, as seen in Fig. 5. The residual curve (chain line) shows a peak centered at 2.45 Å. The peak has not been observed in the $D(r)$ curve of the lithium chloride systems. Triolo and Narten[2)] observed that the peak characteristic of the O–O hydrogen bond in hydrochloric acid solutions shifts toward a shorter distance with increasing HCl concentration from 2.85 Å in $HCl-95.7H_2O$ to 2.52 Å in $HCl-3.99H_2O$. The peak found at about 2.45 Å should be ascribed to the O–O bond within hydrated oxonium ion.

In order to determine the structure of the hydrated oxonium ion, a least-squares method was applied to the following three models.

(a) $H_3O^+(OH_2)_4$ (regular tetrahedron)
(b) $H_3O^+(OH_2)_3$ (planar triangle)
(c) $H_3O^+(OH_2)_3\cdots(H_2O)$ (trigonal pyramid)

for searching the optimum distance for the $H_3O^+-H_2O$ interactions.

Defining an *R*-factor as a measure of propriety of models

$$R=\frac{\Sigma\{s\cdot i(s)_{\rm calcd}-s\cdot i(s)_{\rm obsd}\}^2}{\Sigma\{s\cdot i(s)_{\rm obsd}\}^2},$$

we calculated the *R*-values for the three models over the ranges $5\ \text{Å}^{-1}<s<16\ \text{Å}^{-1}$ and found the *R*-factor to be 0.110, 0.100, and 0.065 at the best values of the $H_3O^+-H_2O$ bond distances for models a, b, and c, respectively. The results are summarized in Table 4. The $s\cdot i(s)$ curves of model c gave the best fit result

Table 4. Results of the least-squares refinements for models a, b, and c (solution C)

Standard deviations are given in parentheses. *r*: Bond distance, *b*: temperature factor, *n*: frequency factor.

Interaction	Parameter	a	b	c
$CoCl_4^{2-}$				
Co–Cl	r/Å	2.28(1)	2.292(2)	2.290(2)
	b/Å^2	0.0035(2)	0.0031(1)	0.0030(1)
	n	4.0[a]	4.0[a]	4.0[a]
Cl–Cl	r/Å	3.70(3)	3.72(3)	3.69(3)
	n	6.0[a]	6.0[a]	6.0[a]
$H_3O(H_2O)_n^+$				
O–O	r/Å	2.46(2)	2.45(2)	2.44(1), 2.90(2)
	n	4.0[a]	3.0[a]	3.0[a], 1.0[a]
$Cl(H_2O)_n^-$				
Cl–O	r/Å	3.110(2)	3.121(2)	3.130(2)
	n	5.17(2)	5.03(2)	4.98(1)

a) The values were kept constant during the calculations.

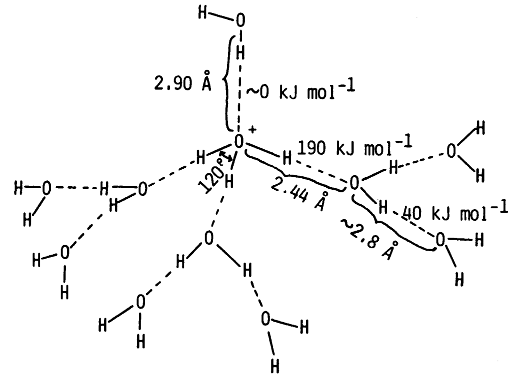

Fig. 6. The structure of the hydrated oxonium ion.

to the experimental data. The structure of model c well explains the picture of hydrated oxonium ion proposed by Grahn[10] from a molecular orbital calculation. The calculations of the total energy of the hydrated H_3O^+ ion by Grahn as a function of the H–O–H bond angle led to the minimum value when the bond angle to be 120°, *i.e.*, a planar configuration for the $H_3O^+(H_2O)_3$ moiety. The H–O–H bond angle of the hydrated H_3O^+ ion has been estimated to be 115—119° from NMR measurements for crystalline hydrates of strong acids.[22,23] From these results the structure of the $H_3O^+(OH_2)_3$ unit of the hydrated oxonium ion is anticipated to be an almost planar triangle, and one water molecule combines with the central oxygen atom of the $H_3O^+(H_2O)_3$ moiety of the hydrated oxonium ion through a weak interaction. The structure of the hydrated oxonium ion is depicted in Fig. 6, together with the bond energies calculated by Grahn.[10]

The picture shown in Fig. 6 well explains structural models of oxonium ion so far proposed by various authors by using different methods. Thus, a method which can detect water molecules most strongly combined with a proton (H^+) (*e.g.*, the compressibility method) reveals the structure of the H_3O^+ ion. When we use a method by which water molecules having relatively strong interactions compared with those between water molecules in the bulk, we might determine the hydration number of the oxonium ion to be 3. Most thermodynamic methods may be included in this category. On the other hand, diffraction methods detect water molecules at the nearest neighbor of the central oxonium ion independent of the strength of the interactions, and therefore, the methods give the hydration number four for each oxonium ion, if the oxonium ion has the structure shown in Fig. 6. The result obtained by the neutron diffraction method[3] perhaps gave an average value of the two different H_3O^+–H_2O distances, which were observed in the present investigation. The water molecule at the apex of the pyramidal structure of the hydrated oxonium ion, which interacts very weakly with the central oxygen atom of the oxonium ion, may be removed by crystallization.

Thus, the structure of oxonium ion determined in the present study gives a satisfactory interpretation for different models previously proposed by various methods, and moreover, it agrees well with the result of the theoretical calculation.[10]

The hydration number of 5.0 was obtained for a chloride ion in the hydrochloric acid system (solution C). The value is significantly smaller than that found in the lithium chloride systems, *i.e.*, $n=6$ (solutions A and B). The decrease in the hydration number of the chloride ion in the concentrated hydrochloric acid solution may be explained by assuming the formation of a contact ion pair between H_3O^+ and Cl^- ions. In the concentrated hydrochloric acid solution the distance between an oxonium ion and a chloride ion may simply be estimated to be about 3.1 Å, and there is practically no free water molecule in the solution. Therefore, some oxonium ions may exist in the first solvation shell of chloride ions, and the ion-dipole repulsion between the oxonium ion and water molecules in the nearest neighbor of the chloride ion becomes so large that some water molecules may be expelled from the solvation shell of the chloride ion. If a part of the total chloride ions pairing with oxonium ions has a much lower coordination number ($n \ll 6$) compared with the free chloride ion ($n=6$), the average coordination number of the total chloride ions in the concentrated hydrochloric acid solution may become small even if the concentration of the $H_3O^+ \cdot Cl^-$ pair is relatively low.

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References

1) D. S. Terekhova, *Zh. Strukt. Khim.*, **11**, 530 (1970).

2) R. Triolo and A. H. Narten, *J. Chem. Phys.*, **63**, 3624 (1975).

3) N. Ohtomo, K. Arakawa, M. Takeuchi, T. Yamaguchi, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **54**, 1314 (1981).

4) A. Passynskii, *Acta Physicochim. URSS*, **8**, 835 (1938).

5) R. P. Bell and K. N. Bascombe, *Discuss. Faraday Soc.*, **24**, 158 (1957).

6) E. Wicke, M. Eigen, and T. Ackermann, *Z. Phys. Chem. (Frankfurt)*, **1**, 342 (1954).

7) J. O. Lundgren and I. Olovsson, "The Hydrated

Proton in Solids," in "The Hydrogen Bond," ed by P. Schuster, G. Zundel, and C. Scandorfy, North-Holland Publ., Amsterdam (1976), Vol. II, Chap. 10.

8) I. Olovsson, *J. Chem. Phys.*, **49**, 1063 (1968).

9) R. Attig and J. M. Williams, *Angew. Chem.*, **88**, 507 (1976).

10) R. Grahn, *Arkiv Fysik*, **1**, 13 (1962).

11) J. Bjerrum, A. S. Holonin, and L. H. Skibsted, *Acta Chem. Scand., Ser. A*, **29**, 326 (1975).

12) L. H. Skibsted and J. Bjerrum, *Acta Chem. Scand., Ser. A*, **32**, 429 (1978).

13) J. M. Smithson and R. J. P. Williams, *J. Chem. Soc.*, **1958**, 457.

14) D. L. Wertz and R. F. Kruh, *J. Chem. Phys.*, **50**, 4313 (1969).

15) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976). "Analytical Chemistry—Essays in Memory of Anders Ringbom" ed by E. Wänninen, Pergamon, Oxford (1977), pp. 163—168.

16) H. Ohtaki and M. Maeda, *Bull. Chem. Soc. Jpn.*, **47**, 2194 (1974).

17) H. Ohtaki, M. Maeda, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974).

18) G. Johansson and M. Sandström, *Chem. Scripta*, **4**, 195 (1973).

19) T. Yamaguchi, Doctoral Thesis, Tokyo Institute of Technology, March (1978).

20) G. Licheri, G. Piccaluga, and G. Pinna, *J. Appl. Crystallogr.*, **6**, 392 (1973).

21) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).

22) R. E. Richards and J. A. S. Smith, *Trans. Faraday Soc.*, **47**, 1261 (1951).

23) D. E. O' Reilly, E. M. Peterson, and J. M. Williams, *J. Chem. Phys.*, **54**, 96 (1971).