X-Ray Diffraction Studies on the Structures of Diammine- and Aquasilver(I) Complexes in Aqueous Solution

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X-Ray diffraction studies were carried out for aqueous diamminesilver(I) nitrate, silver(I) perchlorate and nitrate solutions. The radial distribution curve of the diamminesilver(I) nitrate solution showed that the length of the Ag–NH_3 bond is (2.22±0.02) Å. In the aqueous silver(I) perchlorate solution, a silver(I) ion is combined with two water molecules at a distance of (2.41±0.02) Å, the result being in good agreement with that obtained for the nitrate solution.

It is well known that silver(I) ion forms the stable diammine complex and the diamminesilver(I) ion is believed to have a linear structure. X-Ray structure analysis[1] showed that in crystals of diamminesilver dinitritoargentate, $[Ag(NH_3)_2]Ag(ONO)_2$, the diamminesilver(I) cation has a linear structure, the Ag–NH_3 bond length being 2.11 Å. However, no X-ray diffraction study of the diamminesilver(I) complex in aqueous solution has been carried out. Miles *et al.*[2] and Geddes and Bottger[3] measured infrared and Raman spectra of various diammine silver salts in crystals and solutions, suggesting a linear structure of the complex.

Most authors reported 2 for the hydration number of silver ion in aqueous solution with various methods.[4—7] On the other hand, an NMR method[8] gave a smaller value (0.7) and conductivity[9] and compressibility[10] measurements gave values of 3—4. The X-ray diffraction study on the aquasilver(I) ion has been carried out neither in the crystalline state nor in aqueous solution, because no crystal containing aquated silver(I) ion has been found and aqua silver(I) ion is readily reduced by X-ray irradiation.

In the present work, we aimed at determining the structures of the diammine- and aquasilver(I) complexes in aqueous nitrate and perchlorate solutions by the X-ray diffraction method with a special precaution for reduction of silver by X-rays.

Experimental

Preparation and Analysis of Sample Solutions. A diamminesilver(I) nitrate solution was prepared by dissolving the required amount of recrystallized silver(I) nitrate in a concentrated ammonia solution. The mole ratio of NH_3/Ag in the solution was adjusted to about 2.5 in which each silver(I) ion should be coordinated with two ammonia molecules according to the stability constant of the complex[11,12] The concentration of the silver(I) ion was determined both by gravimetry as AgCl and by electrogravimetry as Ag. The results obtained by the two independent methods were consistent with each other within 0.2%. The ammonia content of the sample solution was determined by the Kjeldahl method. The concentration of the nitrate ion was determined by the stoichiometry of the silver(I) nitrate.

A silver(I) perchlorate solution was prepared by adding silver(I) carbonate crystals to a boiling $HClO_4$ solution, the crystals having been precipitated by adding a sodium carbonate solution to a solution of silver(I) nitrate and then decanted repeatedly with water until no sodium ion was detected by the flame test.

A silver(I) nitrate solution was prepared by dissolving recrystallized silver(I) nitrate in distilled water.

The concentration of the anion in each solution was determined as previously mentioned.[13] The density of the solutions was measured with pycnometers. The compositions of the sample solutions are given in Table 1.

TABLE 1. COMPOSITIONS (g-atoms/dm^3) AND THE STOICHIOMETRIC VOLUMES V PER Ag ATOM OF THE SAMPLE SOLUTIONS

	(A) $Ag(NH_3)_2NO_3$	(B) $AgClO_4$	(C) $AgNO_3$
Ag	3.967	4.235	3.453
Cl	—	4.336	—
N	14.08	—	3.453
O	45.58	61.50	59.44
H	97.69	88.42	98.16
V/Å^3	418.6	392.1	480.9
ρ/g cm^{-3}	1.453	1.684	1.471

X-Ray Scatterings. X-Ray measurements were carried out at (25±1) °C with a JEOL θ-θ diffractometer using a Philips Mo X-ray tube (λ=0.7107 Å) over the s range from 0.6 to 16 Å^{-1} ($s=4\pi\sin\theta/\lambda$), where 2θ is the scattering angle. The details of the diffractometer, measurements and data treatments are reported elsewhere.[13—15] Preliminary X-ray measurements revealed that precipitates of silver metal reduced by X-rays appeared on the surface of a solution within a few days. Therefore, prior to measurements, the change of scattered intensities was examined with the elapse of time at two fixed scattering angles of 12° and 60°. In the case of the diamminesilver(I) nitrate solution, the change of scattered intensities was found to be less than 1.5% within two days of X-ray irradiation. The silver(I) perchlorate and nitrate solutions showed a change of less than 2% within one day. Thus, an irradiated sample was replaced by a new one during the experiments every two days for the diamminesilver(I) nitrate solution and every day for the silver(I) perchlorate and nitrate solutions.

Intensities of X-rays scattered were corrected for background, absorption in the sample,[16] polarization[16] and incoherent scatterings,[13] and then scaled to electron units by the conventional methods.[13,17,18] The values of coherent, incoherent and anomalous scatterings of all atoms were quoted from the literature.[19] In the case of the silver(I)

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perchlorate and nitrate solutions the molecular form factor for H_2O[20] was used when we calculated the interaction among water molecules in the systems. Reduced intensities $i(s)$ obtained by subtraction of independent scatterings of each atom and water molecules from the scaled intensities were Fourier transformed into the radial distribution function $D(r)$ after smoothing correction.[21] The modification function used was $\{(f_{Ag}(0)+\Delta f'_{Ag})^2+(\Delta f''_{Ag})^2\}/\{(f_{Ag}(s)+\Delta f'_{Ag})^2+(\Delta f''_{Ag})^2\}\exp(-0.01s^2)$ where f_{Ag}, $\Delta f'_{Ag}$, and $\Delta f''_{Ag}$ are the scattering factor, the real and the imaginary parts of anomalous dispersion of Ag atom, respectively. Spurious ripples found in the hard-core region of the $D(r)$ curves were removed by the previous manner.[13] Experimental scaled intensities, reduced intensities multiplied by s, the $D(r)$ and $D(r)-4\pi r^2\rho_0$ curves for the solutions investigated are shown in Figs. 1—4. Theoretical reduced intensities $i(s)_{\text{calcd}}$ of given atom pairs were calculated by Eq. 1 and they were transformed into the theoretical radial distribution curves by Fourier inversion.

$$i(s)_{\text{calcd}} = \sum_{\substack{i \\ i\neq j}}\sum_{j} n_{ij}\{(f_i+\Delta f'_i)(f_j+\Delta f'_j)+(\Delta f''_i)(\Delta f''_j)\} \times \frac{\sin(sr_{ij})}{sr_{ij}}\exp(-b_{ij}s^2) \qquad (1)$$

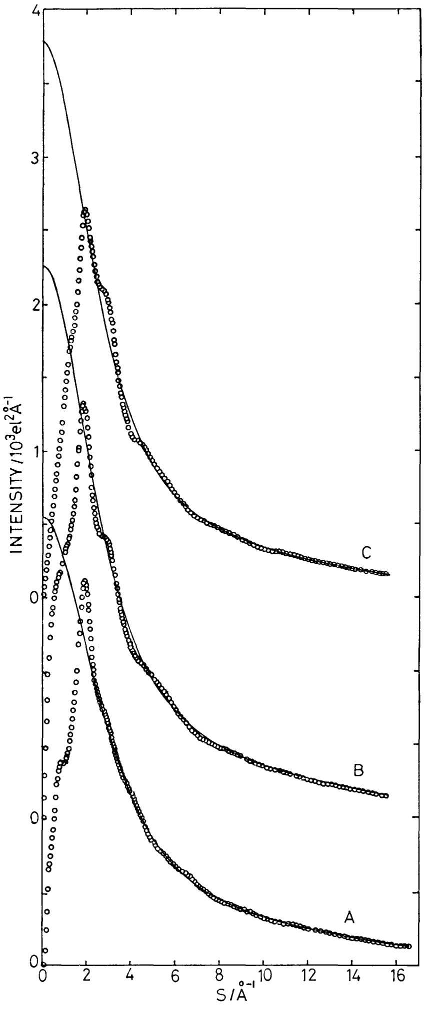

Fig. 1. Experimental scaled-intensities (circles) and calculated intensities (solid lines) of independent scatterings for solutions: A. $Ag(NH_3)_2NO_3$; B. $AgClO_4$; C. $AgNO_3$.

The values of the averaged distance r_{ij} between atoms i and j, the temperature factor $b_{ij}=1/2\langle\Delta r^2\rangle$ ($\langle\Delta r^2\rangle$ is the mean square amplitude of the molecular vibration) and the frequency factor n_{ij} were refined by the least squares method where the following function U was minimized.

$$U = \sum_{s_{\min}}^{s_{\max}} s^2(i(s)_{\text{obsd}}-i(s)_{\text{calcd}})^2 \qquad (2)$$

Here $s_{\max}$ and $s_{\min}$ are the upper and lower limits of selected s regions. All calculations were performed with the aid of the M 180 computer by the KURVLR[22] and NLPLSQ[14] programs.

Results

Diamminesilver(I) Nitrate Solution. In the $D(r)$ and $D(r)-4\pi r^2\rho_0$ curves of solution A, three peaks appeared at 1.2, 2.2, and 3—5 Å. The first peak around 1.2 Å corresponds to the N–O bond within NO_3^- ion.[23,24] The O–H and N–H bonds within H_2O and NH_3 molecules also contribute in part to this peak. The second and rather distinct peak appeared at 2.2 Å, which can be ascribed to the distance between Ag and NH_3 molecules. The O–O interaction within the planar NO_3^- ion partly contributes to the peak ($1.26\ \text{Å}\times\sqrt{3}=2.18\ \text{Å}$). The structure of the diamminesilver(I) complex ion was determined by analyzing

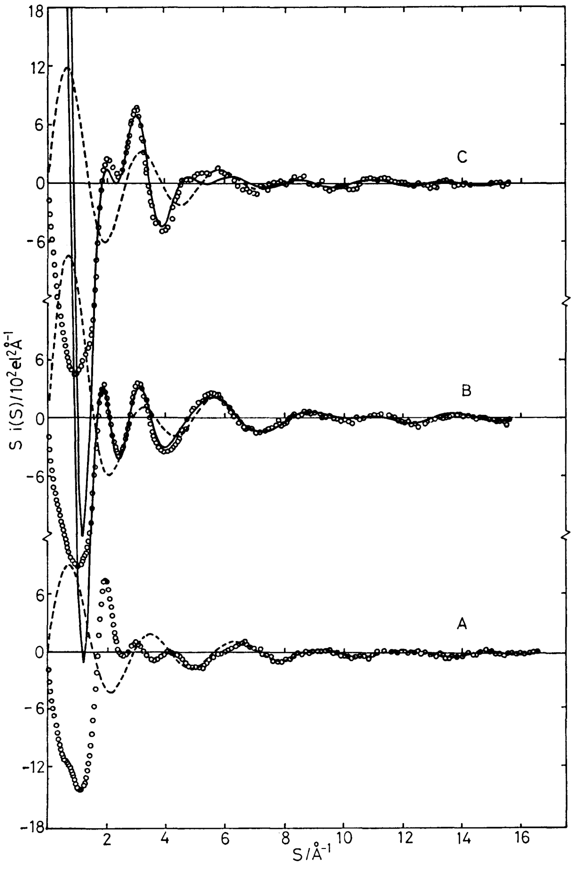

Fig. 2. Observed $s\cdot i(s)$ values (circles) for solutions A, B and C. Dashed and solid lines show the calculated $s\cdot i(s)$ values for the short- and (short+long)-range interactions, respectively, with parameter values listed in Table 3.

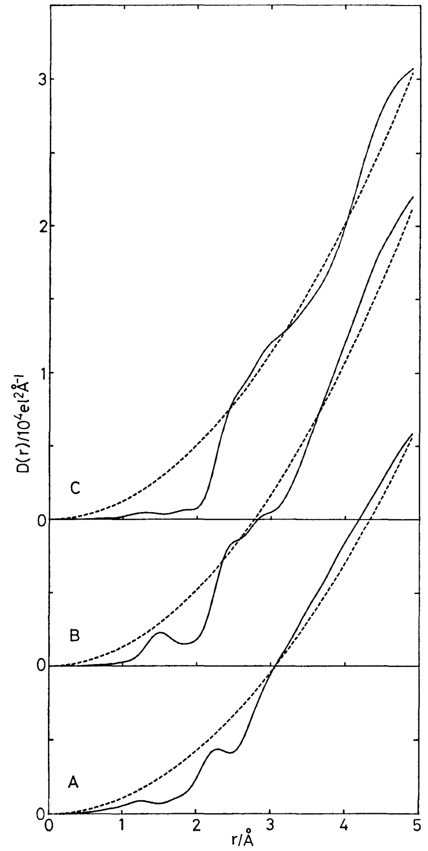

Fig. 3. Radial distribution functions $D(r)$ (solid lines) and $4\pi r^2\rho_0$ (dashed lines) for solutions A, B, and C.

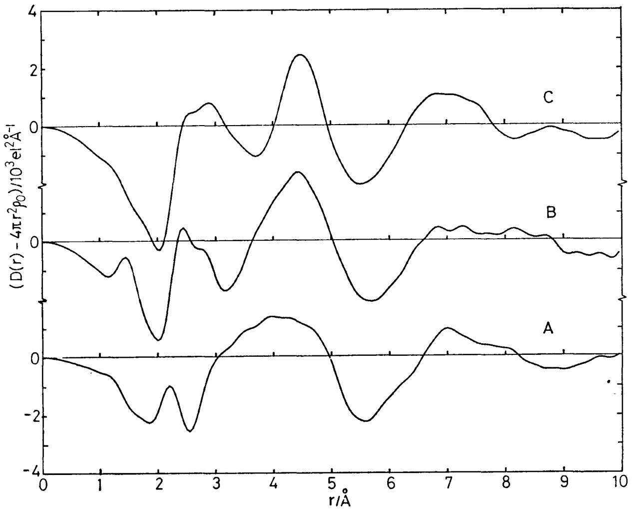

Fig. 4. The $D(r)-4\pi r^2\rho_0$ curves for solutions A, B, and C.

the second peak after subtraction of the peaks due to the N–O and O–O pairs within NO_3^- ion from the $D(r)$ curves. The average distances of the atom pairs used in the calculation were those given in the literature[24] and the temperature factors were calculated from spectroscopic data[25] by the Cyvin method,[26] the values being listed in Table 3.

The chain lines in Fig. 5 (a and b) show the residual curves obtained by subtraction of the theoretical curves of the O–H bond within H_2O, the N–H bond within NH_3, the N–O, and O–O contacts within NO_3^- ion from the original curves (solid lines). The length of the Ag–NH_3 bond and the coordination number of the silver ion were determined from the residual curve by the trial-and-error method. The Ag–NH_3 bond length finally determined was (2.22±0.02) Å. The number of ammonia molecules coordinated to a silver(I) ion was estimated to be about 2 from the peak area. The temperature factor for the Ag–NH_3 bond was determined to be 0.002—0.003 Å^2, which was in good agreement with the value of 0.0018 Å^2 calculated by using spectroscopic data.[27] Further subtraction of the theoretical peak due to two Ag–NH_3 bonds from the residual curve gave a smooth background curve (dashed line), which shows no more appreciable intramolecular interaction left within 3 Å, except for a broad peak around 2.8 Å due to the bulk structure.[28]

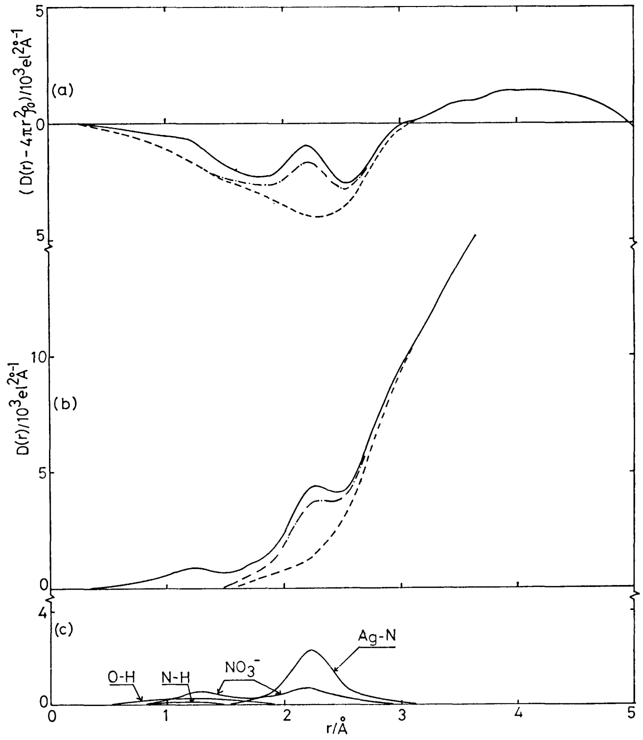

Fig. 5. (a) The $D(r)-4\pi r^2\rho_0$ curve for diamminesilver(I) nitrate solution. The chain line shows the residual curve after subtraction of the theoretical peaks from original curve (solid line), the peaks being those for the O–H and N–H bonds within H_2O and NH_3, respectively, and the N–O and O–O pairs within NO_3^- ion. The dashed line gives the difference between the original curve and the sum of the whole theoretical peaks shown in (c). (b) The corresponding $D(r)$ curve. (c) The theoretical peak shapes of each atom pair.

The theoretical $s \cdot i(s)$ curve of the diamminesilver(I) nitrate solution was calculated on the basis of the proposed models for the complex, nitrate ion, ammonia, and water molecules. The theoretical values (dashed line in Fig. 2, curve A) of $s \cdot i(s)$ thus evaluated were compared with the experimental ones (circles). Over the range of 4 Å^{-1} $<s<$ 15 Å^{-1} satisfactory agreement was found between them. Discrepancy in the calculated and experimental values at $s<4$ Å^{-1} is due to neglect of long-range interactions in the theoretical calculations.

Silver(I) Perchlorate and Nitrate Solutions. In Fig. 3, we see a peak around 1.5 Å in the $D(r)$ curve obtained for the perchlorate solution (curve B), which is due to the Cl–O bond within the perchlorate ion. A peak around 1.2 Å found in the nitrate system (curve C) is ascribed to the N–O bond within the nitrate ion. Peaks around 2.5, 2.8, and 4.3 Å are seen in the $D(r)$ and $D(r)-4\pi r^2\rho_0$ curves for both the solutions (see Figs. 3 and 4). The second peak around 2.5 Å can be attributed to the Ag–OH_2 bond within the hydrated silver(I) ion, which is expected from the sum of the radius of Ag^+ (1.26 Å[29]) and the size of a water molecule (1.40 Å[30]). The O–O contacts within the anions also contribute to the peak ($1.5\text{ Å}\times\sqrt{8/3}=2.4$ Å for tetrahedral ClO_4^- and $1.2\text{ Å}\times\sqrt{3}=2.1$ Å for planar NO_3^-). The peak around 2.8 Å is due to the hydrogen-bonded H_2O–H_2O interaction in the bulk water structure. Since the peaks at about 2.5 Å and 2.8 Å are overlapped, analysis of the structure of the aquasilver(I) ion from the peak shape at 2.5 Å was not possible without taking into account the contribution of the H_2O–H_2O interaction in the bulk. The wing of the peak due to long-range interactions which appeared at 4.3 Å may partly contribute to the peak at 2.5 Å. The 4.3 Å peak also influences the shape of the 2.8 Å peak. Therefore, in order to analyze the peak shape at 2.5 Å, interactions included in the peaks at 2.8 Å and 4.3 Å must be taken into consideration. The long-range interactions may be estimated on the basis of appropriate models of molecular interactions. The peak at 4.3 Å might include the interaction between silver ion and water molecules in the second hydration sphere.[31] Interactions between the central atoms of the perchlorate and nitrate ions and water molecules hydrated with the anions may also contribute to the broad peak. According to X-ray diffraction studies on concentrated HNO_3[23] and NH_4NO_3[24] aqueous solutions, the N(within NO_3^-)–O(within H_2O in the hydration sphere) interaction should appear at about 3.4 Å. For the perchlorate system, on the other hand, the corresponding Cl–O interaction is expected to appear around 3.6 Å, which is seen as a hump in curve B of Fig. 4. Such a hump has been observed in concentrated $Fe(ClO_4)_3$ aqueous solutions.[32]

Short-range intramolecular interactions mainly contribute to the high angle part of the $s\cdot i(s)$ function, whereas long-range intermolecular interactions largely contribute to the low angle part of the function and rapidly diminish with increasing s values. We have seen in the silver nitrate–ammonia system (Fig. 2, curve A) that the short-range interactions for the diamminesilver(I) nitrate solution are responsible for the $s\cdot i(s)$ values at $s>4$ Å^{-1}. Therefore, at a first step of approach in estimating the parameter values of the short-range interactions in the silver(I) perchlorate

TABLE 2. PARAMETER VALUES OF THE INTRAMOLECULAR INTERACTIONS OBTAINED BY THE LEAST SQUARES REFINEMENTS WITH VARIOUS s RANGES FOR THE SILVER(I) PERCHLORATE SOLUTIONS
The values in parentheses are their standard deviations.

Atom pair	5 Å$^{-1}\le s\le$15 Å^{-1}	6 Å$^{-1}\le s\le$15 Å^{-1}	7 Å$^{-1}\le s\le$15 Å^{-1}	8 Å$^{-1}\le s\le$15 Å^{-1}
r_{Ag-OH_2}/Å	2.427(5)	2.410(4)	2.406(4)	2.405(5)
b_{Ag-OH_2}/Å	0.0040(3)	0.0040(2)	0.0040(2)	0.0039(2)
n_{Ag-OH_2}	1.98(3)	1.99(3)	1.99(3)	2.00(4)
r_{Cl-O}/Å	1.474(3)	1.473(2)	1.471(2)	1.472(2)

TABLE 3. FINAL PARAMETER VALUES AND STANDARD DEVIATIONS (IN PARENTHESES) FOR THE SHORT- AND LONG-RANGE INTERACTIONS OBTAINED BY THE LEAST SQUARES REFINEMENTS FOR THE SILVER(I) PERCHLORATE AND NITRATE SOLUTIONS

System	Atom pair	r_{ij}/Å	b_{ij}/Å	n_{ij}
$Ag(NH_3)_2NO_3$	Ag-NH_3 (within $Ag(NH_3)_2^+$)	2.22(2)	0.0018[a]	2.0(5)
	N-O (within NO_3^-)	1.26[b]	0.00086[a]	3.0[c]
$AgClO_4$	Ag-OH_2 (within $Ag(OH_2)_2^+$)	2.410(4)	0.0040(2)	1.99(3)
	Cl-O (within ClO_4^-)	1.473(2)	0.00076[a]	4.0[c]
	H_2O-H_2O (in the bulk)	2.83(3)	0.014[d]	4.4[d]
	Cl (within ClO_4^-)-H_2O	3.57(4)	0.128(7)	25.6(8)
	Ag-$(H_2O)_{II}$	4.44(6)	0.105(5)	9.5(3)
$AgNO_3$	Ag-OH_2 (within $Ag(OH_2)_2^+$)	2.450(8)	0.004(2)	2.45(7)
	N-O (within NO_3^-)	1.24(2)	0.00086[a]	3.0[c]
	H_2O-H_2O (in the bulk)	2.91(7)	0.014[d]	4.4[d]
	N (within NO_3^-)-H_2O	3.17(7)	0.036(8)	43(2)
	Ag-$(H_2O)_{II}$	4.29(6)	0.019(7)	17.3(6)

a) Calculated values from spectroscopic data (Refs. 25, 27, and 33). b) Ref. 24. c) Fixed on the basis of the structure model. d) Ref. 30.

and nitrate solutions, the least squares method was applied to the $s \cdot i(s)$ values of variable subsets covering various s ranges ($5\,\text{Å}^{-1} \leq s \leq 15\,\text{Å}^{-1}$). Then, long-range interactions were taken into consideration for explaining the data of almost whole angle range of the $s \cdot i(s)$ values.

Short-range Interactions: The structures of hydrated $Ag(OH_2)_n^+$ and the anion (ClO_4^- or NO_3^-) were taken into consideration in calculation of $s \cdot i(s)$ values over the range of $5\,\text{Å}^{-1} \leq s \leq 15\,\text{Å}^{-1}$ with variable $s_{\min}$, the minimum value of the s range. In the calculation, the Ag–OH_2 distance, the temperature factor, and the number of the bond (n) were independently varied. For the tetrahedral ClO_4^- or planar NO_3^- ion, the only Cl–O or N–O distance was independently refined. The temperature factors of the perchlorate and nitrate ions were kept constant at the values calculated from spectroscopic data: 0.00076 Å^2 (Cl–O) and 0.0012 Å^2 (O–O) for ClO_4^-;[33] 0.00086 Å^2 (N–O) and 0.0010 Å^2 (O–O) for NO_3^-.[25]

Table 2 gives the parameter values thus obtained for the short-range intramolecular interactions of the siver(I) perchlorate solution with varying s ranges. As is seen from Table 2, the results were practically independent of selection of the $s_{\min}$ values. The values of the parameters determined in the range of $6\,\text{Å}^{-1} \leq s \leq 15\,\text{Å}^{-1}$ are taken as the best ones for both the perchlorate and the nitrate solutions. Calculated $s \cdot i(s)$ curves by using the parameter values thus obtained are shown by dashed lines in Fig. 2 (curves B and C).

Long-range Interactions: Interactions between silver(I) ion and water molecules in the second hydration sphere (abbreviated as Ag–$(H_2O)_{II}$) and the Cl–H_2O or N–H_2O interaction due to the hydration of perchlorate or nitrate ion were taken into account in calculation of $s \cdot i(s)$ values over much wider s ranges. The H_2O–H_2O interaction in the bulk phase was so approximated that "free" water molecules formed tetrahedral frameworks, the parameter values of the tetrahedral pentamer moiety of water, $(H_2O)_5$, being quoted from the work by Narten.[30]

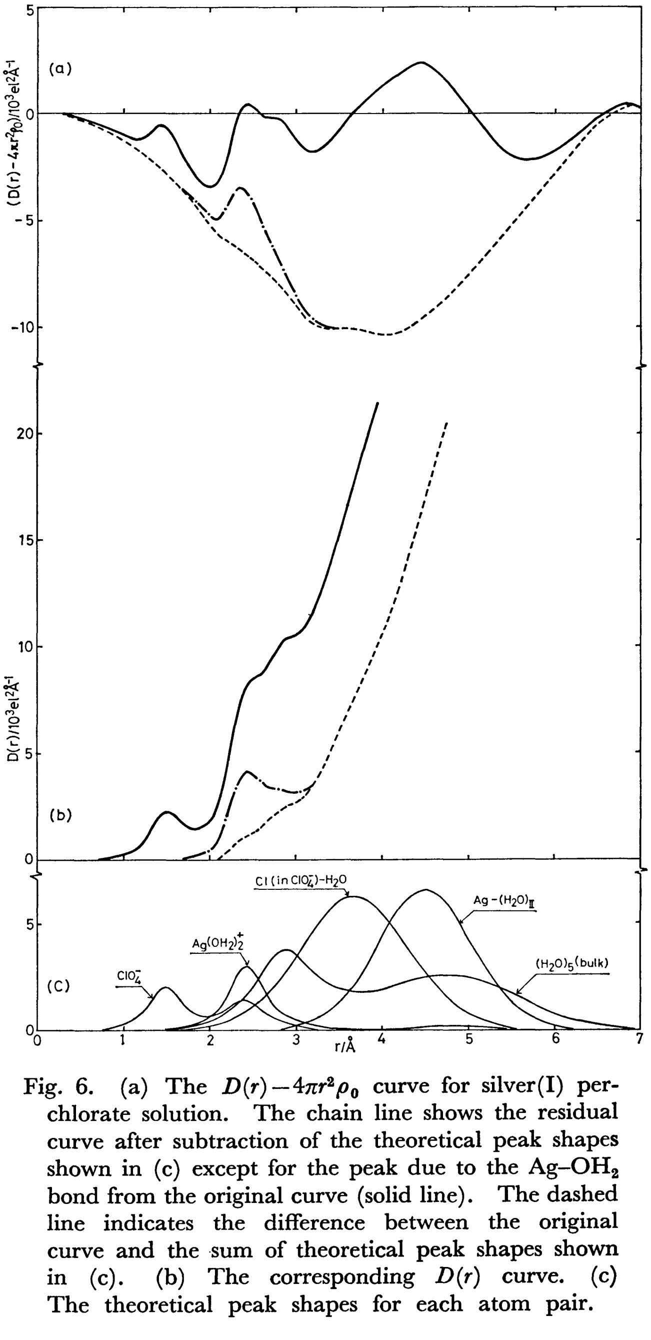

Fig. 6. (a) The $D(r)-4\pi r^2 \rho_0$ curve for silver(I) perchlorate solution. The chain line shows the residual curve after subtraction of the theoretical peak shapes shown in (c) except for the peak due to the Ag–OH_2 bond from the original curve (solid line). The dashed line indicates the difference between the original curve and the sum of theoretical peak shapes shown in (c). (b) The corresponding $D(r)$ curve. (c) The theoretical peak shapes for each atom pair.

When we took into account the long-range interactions in addition to the short-range intramolecular interactions previously discussed, satisfactory agreements were obtained between the experimental and theoretical $s \cdot i(s)$ values in both the perchlorate and nitrate systems over the whole range of s except $s < 1.5\,\text{Å}^{-1}$, where much longer-range intermolecular interactions and the scattering from the "holes" in an uniform medium[22] contribute to the $s \cdot i(s)$ values. The distance between silver(I) ion and water molecules in the second coordination sphere was estimated to be 4.3—4.4 Å. The Cl(within ClO_4^-)–H_2O and N(within NO_3^-)–H_2O distances were converged to 3.57 Å and 3.17 Å, respectively. The final results are summarized in Table 3, together with the values for the diamminesilver(I) nitrate solution given in the previous section. A small deviation of the theoretical $s \cdot i(s)$ curve from the experimental one was observed in the range of $5\,\text{Å}^{-1} < s < 6\,\text{Å}^{-1}$ in the silver(I) nitrate system. However, no further refinement was possible with any other models of the system. Figure 6(c) shows the radial distribution curve of each interaction in the silver perchlorate system estimated from the analysis of the $s \cdot i(s)$ curve described above. The peaks due to the Ag–OH_2 bond are clearly seen at 2.4 Å, shown by chain lines in Fig. 6 (a and b), when the theoretical peaks due to the intra- and intermolecular interactions except for the Ag–OH_2 bond were subtracted from the original curves shown by solid lines in Fig. 6 (a and b). Further subtraction of the peak due to the Ag–OH_2 bond from the residual curves gave smooth background curves, which indicated no other intra- and intermolecular interactions shorter than 6 Å.

Discussion

X-Ray diffraction data revealed that an Ag(I) ion is coordinated with two ammonia molecules at a distance of 2.22 Å in aqueous solution and no water molecule combines with the diamminesilver(I) complex. The Ag–NH_3 bond in the $Ag(NH_3)_2^+$ complex in solution is longer than that in crystal.[1] In the present X-ray analysis we could not draw a definite conclusion that the complex has a linear structure because non-bonded NH_3–NH_3 distance was not determined. According to the preceeding work,[1] $Ag(NH_3)_2^+$ complex in $[Ag(NH_3)_2]Ag(NO_2)_2$ crystals has a linear structure. Therefore, we would like to say that the diamminesilver (I) ion has a linear structure in solution as well as in crystals. The aquasilver(I) ion may also have a linear structure. The values of the distance between a silver(I) ion and a water molecule r_{Ag-OH_2} and the coordination number of the silver(I) ion n_{Ag-OH_2} in the nitrate system are slighly different from those of the perchlorate system (Table 3). However, the difference is not significant.

It should be noted that the Ag–NH_3 distance is much smaller than the Ag–OH_2 distance observed in the present work, the fact suggesting the formation of strong coordination bonds between silver ion and ammonia molecules compared with that between silver ion and water molecules.

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