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X-Ray Diffraction Studies of Aqueous Solutions of Cadmium Perchlorate and Sodium Tetraiodocadmate

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X-Ray diffraction measurements were carried out for aqueous solutions of cadmium perchlorate and sodium tetraiodocadmate. X-Ray scattering data showed that the hydrated Cd^{2+} ion is coordinated to six water molecules, the distance between Cd^{2+} and H_2O being 2.31 ± 0.02 Å, and that the CdI_4^{2-} complex has a tetrahedral configuration with a Cd–I distance of 2.79 ± 0.01 Å. The tetrahedral structure of the CdI_4^{2-} complex was confirmed by Raman spectroscopy.

X-Ray diffraction for investigation of crystal structures was extended to the analysis of the structures of fused salts and pure liquids.[1-4] Its application to electrolytic solutions of relatively high concentration has since been undertaken to determine the structures of ionic species such as hydrated metal ions,[5-9] metal halide complexes[10-16] and polymerized hydrolysis species of metal ions.[17-22]

The structures of hydrated alkali metal,[5] alkaline-earth metal,[6] and transition-metal ions from Mn^{2+} to Zn^{2+} ions[7-9] were investigated in aqueous solutions of chloride, nitrate and sulphate ions.

Few studies, however, seem to have been made on the hydrated cadmium ion. The study by Bol *et al.*[9] of an aqueous cadmium nitrate solution, in which they showed that a cadmium ion is bound to six water molecules with the Cd–OH_2 distance 2.289 Å, appears to be the only case.

A number of equilibrium studies have been made on the cadmium iodide complexes in aqueous solution with various experimental techniques,[26] the results of which are consistent with the formation of only mononuclear complexes of CdI^+, CdI_2, CdI_3^-, and CdI_4^{2-}. From Raman spectroscopic measurements[27-29] it was found that CdI_4^{2-} has a tetrahedral configuration (T_d symmetry) in aqueous solution and organic solvents.

As far as we know, no X-ray diffraction measurement has been carried out for a study of the structures of the cadmium iodide complexes in aqueous solution.

In the present work we deal with aqueous cadmium perchlorate and sodium tetraiodocadmate solutions, the latter being also examined by Raman spectroscopy.

Experimental

Preparation and Analysis of Sample Solutions. Cadmium perchlorate was prepared by dissolving cadmium oxide in dilute perchloric acid and recrystallizing the cadmium perchlorate twice from water. The crystals thus prepared were dissolved in water containing a small amount of perchloric acid in order to prevent the hydrolysis of the Cd^{2+} ions.

The concentration of cadmium ion in the solution was determined both by gravimetry as $CdSO_4$ and by titration with EDTA. The results obtained by the two methods agreed within 0.2%. The perchlorate content of the solution was determined by using a column of cation exchange resin (Dowex 50 W-X12) of the hydrogen form. The hydrogen-ion concentration was calculated from the relation, $[H]^+ = [ClO^-_4] - 2[Cd^{2+}]$.

The cadmium iodide solution in which the tetraiodocadmate ion was predominant was prepared by the addition of NaI to a CdI_2 solution. The amount of NaI to be added was estimated from the distribution of cadmium iodide complexes calculated from the stability constants given by Leden.[30]

The total amount of cadmium in the cadmium iodide test solution was determined by EDTA titration, that of iodide being determined gravimetrically as AgI. The concentration of sodium ion was estimated from the material balance of ions in the solution. The density of the solutions was measured with a pycnometer. The composition of the solutions investigated is given in Table 1.

Table 1. Compositions of the solutions (in g atoms/l)

	Cadmium perchlorate soln.	Cadmium iodide soln.
Cd	2.920	2.246
I	—	11.39
Cl	6.303	—
Na	—	6.899
O	66.02	30.60
H	81.15	61.21

X-Ray Scattering Measurements. The X-ray diffractometer (JEOL Co., Tokyo) used is so designed that diffraction patterns are obtained from the free surface of the solution and that the X-ray tube and detector move symmetrically in a direction opposite the horizontal axis at the surface of the solution, *i.e.*, the Bragg–Brentano geometry is applied. The sample solution is contained in a flat glass tray, diameter 40 mm and depth 10 mm, covered tightly with a Teflon-coated stainless steel cover with a beryllium window for X-rays to protect the solution from evaporation and contamination. A LiF focusing monochromator is placed between a receiving slit and scintillation counter. A pulse-height analyzer is used for further monochromatization.

MoKα radiation ($\lambda = 0.7107$ Å) was used, a Philips PW210500 X-ray tube being employed. The scattered intensity was measured at discrete points (about 200 points in all) between $\theta = 1°$ and $70°$, where 2θ is the scattering angle. The time required to accumulate 40000 counts was measured at angular intervals; 0.125° to $\theta = 6°$, 0.25° to 20° and 0.5° to 70°. Three slit combinations, with 1/12°, 1/4° and 1° divergent slits, were employed. The whole angle range was scanned twice in order to detect the variation of measured intensities during the course of continuous operation. The variation was usually less than 2% of the measured intensities and the intensities measured at each angle were averaged. The intensities for each slit combination were corrected for background radiation, determined by placing a lead plate just behind the receiving slit, and were normalized to the intensities measured with the 1° divergent slit from the data of overlapping regions.

The amount of incoherent radiation passing through the monochromator was estimated from the spectrum of the X-ray and the resolving power of the monochromator. It was also measured with a zirconium filter at large scattering angles. The Zr filter was first placed between the X-ray tube and the solution and the scattered intensity was measured. It was then placed between the solution and the detector and another measurement was carried out at the same scattering angle.

Raman Spectroscopic Measurements. Raman spectra for the tetraiodocadmate solution were measured with a JEOL Laser Raman Spectrophotometer JRS-S1 and a Shimadzu Laser Raman Spectrophotometer R-2D with use of the 4880 Å excitation line of Ar.

The composition of the sample solution was the same as that of the solution used for the X-ray measurements except that it contained ClO_4^- ion as an internal standard (A_1 line of ClO_4^-).

Treatment of X-Ray Intensity Data

The measured intensities were corrected for polarization in both the sample solution and monochromator and for absorption of the sample, and were scaled to absolute intensities (electron units) by comparing the asymptote with the sum of the calculated coherent and incoherent radiations at large scattering angles ($\theta \gtrsim 50°$). The scale factors thus calculated agreed within 1% with those calculated by the method of Norman[31] and Krogh-Moe.[32]

The scattering factors for Cd, I, Cl, Na, and O were taken from Cromer and Waber,[33] and those for H from the International Tables.[34] The values used for the incoherent scattering were those given by Cromer and Mann[35] for Cd and Na, by Cromer[36] for I, Cl, and O, and by Compton and Allison[37] for H. The incoherent scattering values were corrected by the Breit-Dirac factors. The values used for anomalous dispersion were taken from Cromer and Liberman.[38]

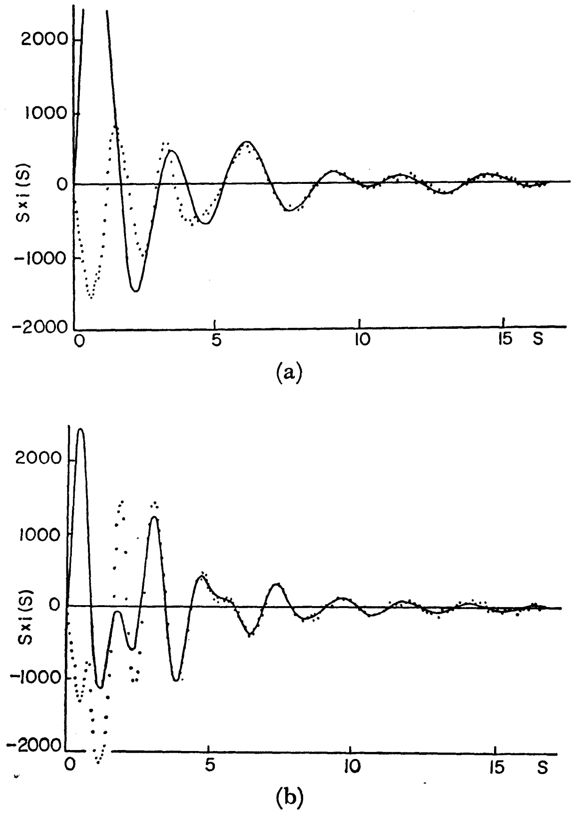
The reduced intensities $i(s)$ due to interatomic interactions in the system were evaluated from the measured intensities $I(s)$ which had been corrected for polarization and absorption, and also for scaling to electron unit, by subtracting intensities due to component atoms. The calculations were made by the equation

$$i(s) = I(s) - \sum_i n_i[(f_i(s)+\Delta f_i')^2 + (\Delta f_i'')^2 + \Phi(s)\cdot I_i^{\mathrm{inco}}(s)] \qquad (1)$$

where s represents $4\pi\sin\theta/\lambda$ (λ=0.7107 Å), n_i the number of atom i, $\Delta f_i'$ and $\Delta f_i''$ the real and imaginary parts of the anomalous dispersion, respectively, $\Phi(s)$ the fraction of the incoherent radiation reaching the counter.

All the calculations were referred to a stoichiometric volume of a solution containing one cadmium atom. The reduced intensities $i(s)$ thus calculated are shown in Fig. 1 after being multiplied by s.

The radial distribution curves $D(r)$ were calculated from the intensity curves by the integral formula



(a)

(b)

Fig. 1. Values $s\cdot i(s)$ for the two solutions as a function of s. Full circles are experimental points and full curves are calculated with the parameters given in Tables 2 and 4.
(a) the cadmium perchlorate solution, (b) the sodium tetraiodocadmate solution.

$$D(r) = 4\pi r^2\rho_0 + 2r\pi^{-1}\int_0^{s_{\max}} s\cdot i(s)\cdot M(s)\cdot\sin(rs)\mathrm{d}s \qquad (2)$$

where ρ_0 denotes the average scattering density of the sample in electron unit, the modification function $M(s)$ being chosen to be $(f_{\mathrm{Cd}}^2(0)/f_{\mathrm{Cd}}^2(s))\exp(-0.01s^2)$.

The calculated radial distribution curve showed small spurious peaks in the range less than 1 Å, which can not be related to any interatomic distance. Thus the reduced intensities were corrected for spurious peaks by means of the Fourier inversion of the radial distribution curve below 1 Å by taking into account the contributions from water and the perchlorate ion.

Theoretical intensities due to interatomic interactions were calculated by

$$i(s) = \sum_i\sum_j n_{ij} f_i(s) f_j(s)\frac{\sin(r_{ij}s)}{r_{ij}s}\exp(-b_{ij}s^2) \qquad (3)$$

where $f_i(s)$ and $f_j(s)$ denote the scattering factors of atoms i and j, respectively, and n_{ij}, r_{ij}, and b_{ij} represent the frequency factor, the distance and the temperature factor of the interaction between any atoms i and j, respectively.

The calculations were carried out with the help of the KURVLR program specially compiled for the analysis of X-ray diffraction data by Johansson and Sandström.[39]

Analysis of Intensity Data and Results

Cadmium Perchlorate Solution. The radial distribution curve $D(r)$ is shown in Fig. 2(a). Two distinct peaks are seen at around 1.4 and 2.3 Å. The former peak is attributed to the Cl–O bonds within the perchlorate ion, which has been confirmed by several investigators.[17,40,41] The latter might be due to the Cd–O bonds within the hydrated cadmium ion, as expected from X-ray diffraction data for the crystal[42] and cadmium nitrate solution,[9] and contains a contribution from the O–O contact within ClO_4^- ion which has a tetrahedral structure. The distance and frequency factor of the Cd–O bond within the hydrated cadmium ion were estimated from the residual peak after subtraction of the O–O contribution from the second peak according to the following procedures. The theoretical intensities due to the O–O contact within ClO_4^- ion were calculated by means of Eq. (3) assuming that $r_{O-O}=2.33$ Å (which corresponds to $\sqrt{8/3}\times 1.43$ Å), $n_{O-O}=6$ and $b_{O-O}=0.002$. The theoretical peak corresponding to the O–O contact was evaluated by the Fourier inversion of the theoretical intensities according to Eq. (2) and was subtracted from the second peak. The area under the residual peak was estimated by a graphical technique with use of a planimeter and was correlated with the number of oxygen atoms around cadmium n_{Cd-O} by the relation $A_{Cd-O}=2x_{Cd}n_{Cd-O}Z_{Cd}Z_O$.[2] Here A_{Cd-O} denotes the area under the peak of the $D(r)$ curve caused by the Cd–O interaction, x_{Cd} the concentration of the cadmium ion, and Z_{Cd} and Z_O the atomic numbers of Cd and O, respectively. The frequency factor n_{Cd-O} thus evaluated was about six, and the Cd–O distance was found to be 2.31 ± 0.02 Å. The temperature factor for the Cd–O bond was estimated to be 0.002 from the peak shape.

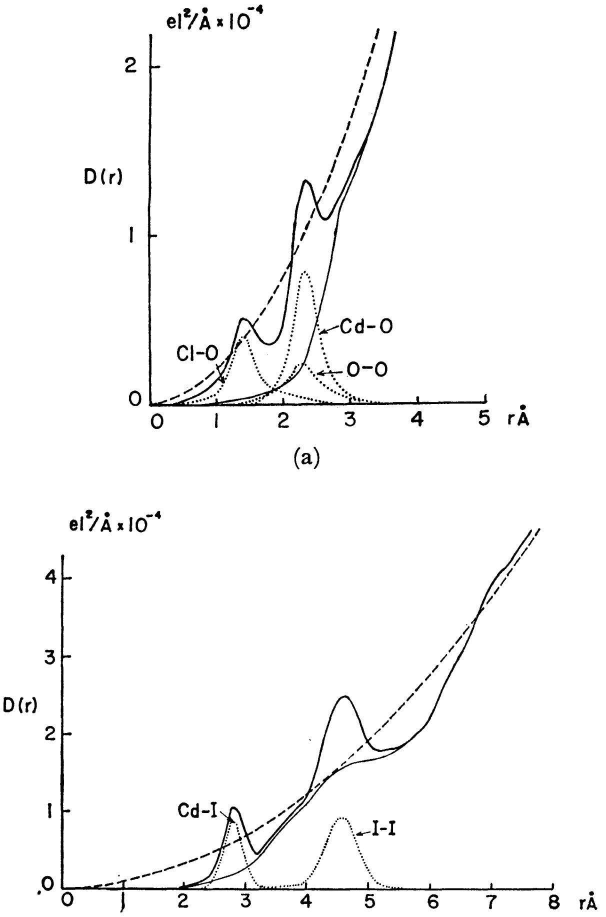


Fig. 2. Radial distribution curves $D(r)$ for the two solutions. The thick curves give $D(r)$ functions, the smooth brocken curves $4\pi r^2\rho_0$ functions, and the thin curves the difference curves obtained by subtraction of the theoretical peaks (dotted curves) from the $D(r)$ functions. The theoretical peaks (dotted curves) are calculated with the parameters listed in Tables 2 and 4.

(a) the cadmium perchlorate solution, (b) the sodium tetraiodocadmate solution.

The values for r, b, and n for the Cd–O bond within the cadmium hydrate and for the Cl–O and the O–O contacts within the tetrahedral perchlorate ion are given in Table 2.

TABLE 2. FINAL PARAMETER VALUES FOR THE CADMIUM ION COORDINATED TO SIX WATER MOLECULES AND THE PERCHLORATE

	r(Å)	b	n
Cd–O	2.31	0.002	6
Cl–O	1.43	0.001	4
O–O	2.33	0.002	6

The peaks calculated with these values were compared with those of the radial distribution curve (Fig. 2(a)). Subtraction of the calculated peaks from the radial distribution curve gives a smooth curve in the region less than 2.8 Å. This shows that the values of the parameters are reasonable and that other interatomic distances within the hydrated cadmium ion are ruled out. The intensities calculated with the parameters are also compared with the observed intensities (Fig. 1(a)). The agreement is satisfactory except in the low s region where contributions from the intermolecular atom pair interactions to the intensities are significant.

The residual curve obtained by subtraction of the calculated peaks from the residual distribution curve shows a very broad peak over the range 2.7—3.4 Å. If we assume that the hydrated cadmium ion possesses a regular octahedron, the distance between adjacent oxygen atoms should be 3.27 Å, which may be consistent with the present results. However, the configuration of water molecules around a cadmium atom could not be determined from the radial distribution curve, since the broad peak would be due to not only the contribution from the O–O contact within the hydrated cadmium ion, but also to contributions from the O–O distances between a ClO_4^- ion and a water molecule[40] and also from other atom pairs of longer distances.

The Cd–O distance 2.31 Å found in the present work is close to the values found in the crystal of

Table 3. Least squares refinement for the cadmium tetraiodide solution

		$2.5<s<16.5$	$3<s<16.5$	$5<s<16.5$	$7<s<16.5$
A.	r_{Cd-I}	2.784 ± 0.004	2.782 ± 0.003	2.787 ± 0.003	2.788 ± 0.003
	b_{Cd-I}	0.0016 ± 0.0005	0.0036 ± 0.0006	0.0043 ± 0.0006	0.0043 ± 0.0007
	n_{Cd-I}	3.18 ± 0.08	3.8 ± 0.1	4.2 ± 0.2	4.2 ± 0.4
	r_{I-I}	4.556 ± 0.005	4.568 ± 0.005	4.551 ± 0.007	4.544 ± 0.013
	b_{I-I}	0.054 ± 0.004	0.031 ± 0.003	0.029 ± 0.004	0.041 ± 0.007
	n_{I-I}	11.6 ± 0.5	7.4 ± 0.4	8 ± 2	17 ± 6
		$3<s<16.5$	$4.5<s<16.5$	$6<s<16.5$	$8<s<16.5$
B.	r_{Cd-I}	2.790 ± 0.002	2.787 ± 0.003	2.786 ± 0.003	2.790 ± 0.004
	b_{Cd-I}	0.0050 ± 0.0014	0.0037 ± 0.0010	0.0045 ± 0.0017	0.0007 ± 0.0041
	b_{I-I}	0.023 ± 0.002	0.021 ± 0.001	0.024 ± 0.002	0.030 ± 0.004

$Cd(NH_4)_2(SO_4)_2\cdot 6H_2O$43) and in the cadmium nitrate solution,9) which are 2.28 Å on the average and 2.289 Å, respectively.

Sodium Tetraiodocadmate Solution. The radial distribution curve $D(r)$ is shown in Fig. 2(b). It shows two prominent peaks in the region less than 6 Å. The peak at around 2.8 Å can be ascribed to the Cd–I bonds, and that at about 4.6 Å to the distance between iodide ions within the tetraiodocadmate complex. The ratio between these two distances is in good agreement with that expected for a tetrahedral structure. The number of iodide ions coordinated to a cadmium ion was estimated to be about four from the area under the peak at around 2.8 Å according to graphical procedure. It was not possible to determine the number of pairs of the adjacent iodide ions within the cadmium iodide complex, since other long-range interactions largely contribute to the peak at around 4.6 Å.

In order to confirm the structure of the CdI_4^{2-} complex deduced from the radial distribution curve and to refine the distances, analysis of the reduced intensity curve was carried out by means of a least squares method. For each pair of the Cd–I and I–I interactions three parameters were introduced, distance r, temperature factor b, and frequency factor n. These parameters were allowed to change so that the error square sum $U=\sum s^2(i(s)-i_{calc}(s))^2$ becomes a minimum, where $i(s_{calc})$ denotes the intensity theoretically calculated by means of Eq. (3). Different subsets of the intensity data were used for the refinement in order to detect errors in the refined parameters caused by a contribution to the intensity by the intermolecular interactions and experimental errors contained in the data. The least squares calculations were carried out by means of PUTSLR,39) the generalized least squares program for X-ray diffraction of solution.

Two types of refinement (A and B) were carried out. The calculated results are summarized in Table 3.

In type A, all the six parameters for the Cd–I and the I–I interactions were allowed to change simultaneously. The frequency factor of the Cd–I bond is close to four, which is the value expected from the CdI_4^{2-} complex in any sets of data over the various s regions except the set of data in the region $2.5<s<16.5$ in which large contributions are included.

The ratio between the I–I and the Cd–I distances is about 1.63, which corresponds to $\sqrt{8/3}$ for the complex of the tetrahedral configuration.

The frequency factor n_{I-I} of the I–I pair was not definitely determined by the least squares method; n_{I-I} fell in the range $6<n_{I-I}<23$ when the standard deviations were taken into account (see Table 3).

In type B a tetrahedral structure was assumed, and the Cd–I distance and the two temperature factors for the Cd–I and I–I contacts were refined. The refined parameters are almost the same as those in type A.

Table 4. Final parameter values for the tetrahedral cadmium tetraiodide complex

	r(Å)	b	n
Cd–I	2.79	0.004	4
I–I	4.56	0.025	6

The distances and temperature factors for the Cd–I and I–I contacts for the CdI_4^{2-} complex are listed in Table 4, a tetrahedral structure of the complex being assumed. The assumption was supported by Raman spectroscopic measurements.

The observed intensities are compared with the calculated ones in Fig. 1(b) with use of the parameters in Table 4. It is seen that the agreement is satisfactory except at the low-angle part of the curve where the intermolecular interactions significantly contribute to the $s\cdot i(s)$ curve.

The calculated Cd–I and I–I peaks with use of the parameters given in Table 4 are compared with the radial distribution curve in Fig. 2(b). The residual curve obtained by subtraction of the calculated peaks from the radial distribution curve shows a broad peak in the range 4—5.5 Å. The peak is so broad that it can not be due to the interaction of any one kind of pairs of atoms, but to various kinds of interactions; one of them might be H_2O–H_2O interactions in bulk water.

A Raman spectrum of the CdI_4^{2-} solution is reproduced in Fig. 3, along with the resolved bands on a horizontal background. It shows four bands at around 36, 47, 110, and 145 cm^{-1}. The polarization measurements indicate that the strong band at 110 cm^{-1} is polarized and the other three bands are depolarized. This suggests that the CdI_4^{2-} complex has T_d symmetry. These results are in good agreement with those obtained by means of the Raman effect in which a tetrahedral structure was proposed for the CdI_4^{2-} complex.27–29)

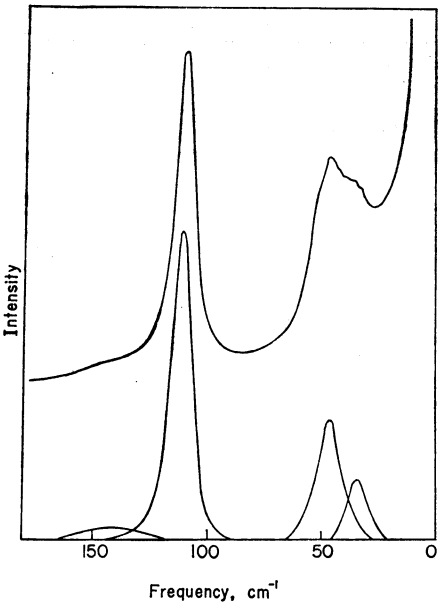


Fig. 3. A Raman spectrum of the CdI_4^{2-} solution, with resolved bands based on the horizontal background.

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