

On the Structures of Cadmium Sulfate Complexes in Aqueous Solutions

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X-Ray diffraction data on concentrated aqueous solutions of cadmium(II) sulfate and perchlorate show the hydrated cadmium(II) ion to have a regular octahedral structure not significantly different from the one found in crystals of $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$ and $\text{Cd}(\text{ClO}_4)_2(\text{H}_2\text{O})_6$. The Cd–O bond length in solution is found to be 2.28(1) Å. In the sulfate solutions, the scattering data give evidence for complex formation between Cd^{2+} and SO_4^{2-} with the sulfate group bonded as a monodentate ligand. The Cd–O–S angle is $134(2)^\circ$, which is similar to corresponding values found in crystals of $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$. No corresponding complex formation between Cd^{2+} and ClO_4^- occurs in the perchlorate solution. A method is described for the quantitative evaluation of the complex formation in the sulfate solutions by using the perchlorate solution as a reference.

In the present work an attempt has been made to analyze, from X-ray scattering data, the complex formation between a moderately heavy metal ion, Cd^{2+} , and sulfate ions. In order to eliminate, as far as possible, the influence from the unknown intermolecular interactions the data for the sulfate solutions were analyzed by comparison with a reference solution of cadmium perchlorate in which no complex formation with the anions takes place.

Previous X-ray diffraction measurements on cadmium(II) solutions include aqueous nitrate¹ and perchlorate² solutions and perchlorate and halide solutions in dimethyl sulfoxide (DMSO).^{3,4} In all of these the solvated cadmium(II) ion has been found to have a regular octahedral structure, while, for example, the CdI_4^{2-} complex is tetrahedral.⁴ Several values have been reported for stability con-

stants of the cadmium(II) sulfate complexes.⁵ The first complex, CdSO_4 , seems to be well established and the occurrence of the higher complexes, $\text{Cd}(\text{SO}_4)_2^{2-}$ and $\text{Cd}(\text{SO}_4)_3^{4-}$ has been claimed by some investigators. Formation constants for polynuclear complexes have not been given.

Crystals of cadmium(II) perchlorate hexahydrate contain octahedral $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ ions with Cd–O bond lengths of 2.292(3) Å.⁶ The same complex occurs in crystals of cadmium ammonium sulfate hexahydrate,⁷ where the average Cd–H₂O distance has been found to be 2.28 Å. In $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$, however, both water molecules and sulfate groups, acting as monodentate ligands, are coordinated to the cadmium ion.⁸ The coordination sphere is still, however, an almost regular octahedron (Fig. 1). No significant differences occur between distances from Cd^{2+} to oxygens of water molecules and to oxygens belonging to sulfate groups.^{8b}

The compositions of the solutions investigated, which were all 3 M in sulfate, are given in Table 1. The perchlorate solution, which was 3 M in perchlorate, was used as a reference, since no complex formation between Cd^{2+} and ClO_4^- is expected and the perchlorate ion has the same tetrahedral structure and contains the same number of electrons as the sulfate ion. In order to vary the extent of complex formation in the sulfate solutions, the Cd^{2+} ions in some of the solutions were partly replaced by NH_4^+ or H^+ .

EXPERIMENTAL

Preparation and analysis of the solutions

The solutions were prepared by weighing appropriate amounts of reagent grade $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$,

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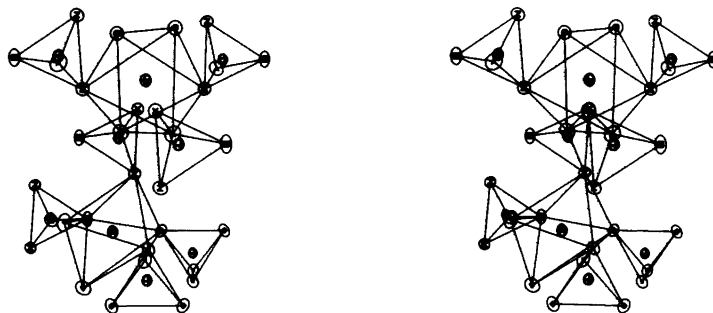


Fig. 1. Stereoscopic drawing of part of the crystal structure of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, showing the surroundings of the two non-equivalent cadmium ions in the structure.

$(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 , or $\text{Cd}(\text{ClO}_4)_2(\text{H}_2\text{O})_6$, dissolving in water and diluting to a known volume. The solutions were analyzed for Cd^{2+} by colorimetric titration with standard EDTA.¹¹ The sulfate and perchlorate concentrations were determined by passing a portion of a solution through a column with a cation exchanger (Dowex 50W-X8) and titrating the eluate with standardized NaOH solution.

Densities were determined with a digital precision densimeter (Anton Paar K. G.).

X-Ray scattering measurements

Data for the solution S3 were collected with a $\theta-\theta$ X-ray diffractometer for liquids, manufactured by Rich. Seifert and Co., which has been previously

described.⁹ The X-ray scattering from the solutions SN3, SA3, and CIA3 was measured in a similar $\theta-\theta$ diffractometer built in Stockholm.¹⁰

$\text{MoK}\alpha$ -radiation ($\lambda = 0.7107 \text{ \AA}$) was used and the range in θ , which could be covered, varied from $\sim 2^\circ$ to $\sim 68^\circ$ corresponding to an s range ($s = 4\pi \sin \theta / \lambda$) between ~ 0.6 and $\sim 16.4 \text{ \AA}^{-1}$. Measurements were performed at discrete points at intervals of 0.25° up to $\theta = 40^\circ$, and of 0.5° to $\theta = 68^\circ$ for the S3 solution. A constant angular interval of 0.25° in the whole range from $\theta = 2^\circ$ up to $\theta = 68^\circ$ was used for the SN3, SA3, and CIA3 solutions. Two combinations of opening, receiving and scattering slits, were used to cover the complete θ -range. For each slit opening the measured intensities after corrections for background radiation (about 0.8 counts per second) and absorption¹² were recalculated to a

Table 1. Compositions of solutions. The concentrations are given as mol l^{-1} (upper figures) and as number of atoms in the stoichiometric unit of volume, $V/\text{\AA}^3$ (lower figure). Column 8 gives the stoichiometric volume, containing one S or Cl atom, used for data normalization. The last column gives the absorption coefficient of the solutions.

Solution	Ratio	Concentrations						$\frac{V}{\text{\AA}^3}$	$\frac{\mu}{(\text{cm}^{-1})}$	
		Cd	S	O	H	N	Cl			
		SO ₄ :Cd								
S3	1.0	3.09	3.09	66.78	108.9	—	—	538.17	11.92	3 M CdSO ₄
		1	1	21.64	35.3	—	—			
SN3	3.09	1.0	3.09	59.04	109.8	4.17	—	538.26	5.37	1 M CdSO ₄ + 2 M (NH ₄) ₂ SO ₄
		0.32	1.0	19.14	35.6	1.35	—			
SA3	3.09	1.0	3.09	62.61	104.7	—	—	538.26	5.39	1 M CdSO ₄ + 2 M H ₂ SO ₄
		0.32	1.0	20.30	33.9	—	—			
		ClO ₄ :Cd								
CIA3	3.08	1.0	—	60.78	98.0	—	3.08	539.13	5.65	1 M Cd(ClO ₄) ₂ + 1 M HClO ₄
		0.33	—	19.73	31.8	—	1			

common slit width with the use of measurements in overlapping regions. The time interval required to accumulate 100000 counts at each measured point was recorded. The whole angular range was scanned twice. Differences between the two data sets were usually less than 1 % of the measured intensities and average values were used for the final set of data.

The amount of incoherent radiation passing through the monochromator was estimated from the spectrum of the X-ray tube and the resolving power of the monochromator. It was also estimated by comparing measurements obtained with a zirconium filter placed between the X-ray tube and the sample with those obtained with the filter between the sample and the detector.¹³ All measurements were carried out in a room thermostated at $25 \pm 2^\circ\text{C}$.

Symbols

$I(s)$	Scaled intensity values after correction for background, polarization, and absorption
$i(s)$	reduced intensity values
s_{\max}	the maximum value of $s = 4\pi/\lambda \sin \theta$ accessible in the measurements
$D(r)$	the radial distribution function
ρ_0	the average scattering power of the stoichiometric unit of volume
$Mod(s)$	the modification function in the Fourier transform
n_i	number of atoms in a stoichiometric unit of volume
$f_i(s)$	the scattering factor for atom "i"
$\Delta f'_i(s)$	the real part of the anomalous dispersion correction for atom "i"
$\Delta f''_i(s)$	the imaginary part of the anomalous dispersion correction for atom "i"
$del(s)$	fraction of the total incoherent scattering reaching the counter
$I_{i,\text{incoh}}(s)$	incoherent scattering of atom "i"
K	the damping factor in the exponential part of the modification function $Mod(s)$
r_{ij}	the distance between the atoms "i" and "j"
b_{ij}	the temperature coefficient for the distance between the atoms "i" and "j"
R_i	the radius of the sphere around a complex "i" defining the emergence of the continuum
B_i	the temperature coefficient in the expression for the interaction between the complex and the sphere defining the surrounding continuum
V	the stoichiometric unit of volume

Treatment of the intensity data

All calculations were carried out on an IBM 360/75 computer with the use of the KURVLR and PUTSLR programs.¹⁴

The measured intensities were corrected for background radiation and absorption. After scaling to a common slit width, corrections were made for polarization in the sample and in the monochromator by dividing with $(1 + \cos 2\alpha \cos^2 2\theta)/(1 + \cos 2\alpha)$, where 2α is the scattering angle at the monochromator. Smoothing of the data by fourth differences was applied for all solutions.¹⁵ The corrected intensities were normalized by comparison with the total independent scattering using both integral and high-angle methods.^{16,17} Scattering factors, $f_i(s)$, for the neutral atoms were used,^{18,19} except for H, where those proposed by Stewart *et al.*,²⁰ were employed. Values of anomalous dispersion corrections, $\Delta f'_i(s)$ and $\Delta f''_i(s)$, for all atoms were taken from Cromer.²¹ Values for the incoherent scattering for the heavy atoms were those given by Cromer.²² For hydrogen, Compton and Allison's values²³ and for the H_2O molecule the spherical form factors given by Narten and Levy²⁴ were used. Corrections for the Breit-Dirac factors²⁵⁻²⁷ in the appropriate form for a radiation counter, $(\lambda/\lambda')^2$, were applied. Reduced intensity values were calculated from eqn. (1).

$$i(s) = I(s) - \sum n_i \{ [f_i(s) + \Delta f'_i(s)]^2 + [\Delta f''_i(s)]^2 + del(s) [\lambda/\lambda']^2 I_{i,\text{incoh}}(s) \} \quad (1)$$

The summations were performed over all atoms in the stoichiometric unit of volume, V , which was in most cases chosen to correspond to a volume containing one sulfate or perchlorate group. The function $del(s)$ was determined as described above.

The electronic radial distribution functions, $D(r)$, were calculated by means of the Fourier transform according to eqn. (2), where the modifica-

$$D(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^{s_{\max}} s i(s) Mod(s) \sin(rs) ds \quad (2)$$

tion function, $Mod(s)$, was chosen to be

$$\{ [\sum n_i |f_i(0) + \Delta f'_i|^2 + [\sum n_i \Delta f''_i]^2] / \{ [\sum n_i |f_i(s) + \Delta f'_i|^2 + [\sum n_i \Delta f''_i]^2] \} e^{-Ks^2}$$

A value of 0.01 was used for K . The average scattering power in $\text{e}^2/\text{\AA}^3$, ρ_0 , was calculated from the expression:

$$\rho_0 = \{ [\sum n_i |f_i(0) + \Delta f'_i|^2 + [\sum n_i \Delta f''_i]^2] / V$$

The reduced intensity functions were corrected for low-frequency contributions leading to spurious

peaks below about 1 Å in the $D(r)$ functions. This was done by a Fourier transformation of the relevant part of the $D(r)$ curve, taking into account expected contributions from intramolecular H_2O , NH_4^+ , SO_4^{2-} or ClO_4^- interactions extending into that region.¹³

Intramolecular contributions to the intensities were calculated according to the expression:

$$i_{\text{calc}}(s) = \sum_{i \neq j} \sum_j [(f_i(s) + \Delta f_i'(s))(f_j(s) + \Delta f_j'(s)) + \Delta f_i''(s)\Delta f_j''(s)] \frac{\sin r_{ij}s}{r_{ij}s} \exp(-b_{ij}s^2)$$

Here $b_{ij} = \frac{1}{2} \langle \Delta r^2 \rangle$ is a coefficient, equal to half the mean square variation in r_{ij} . When the variation in r_{ij} is caused only by molecular vibrations, the amplitude of vibration is equal to Δr . Corresponding peak shapes were obtained from the calculated intensities by a Fourier transformation carried out in the same way as for the experimental intensities.¹⁴

Least squares refinements of model parameters were made with the use of the PUTSLR program,¹⁴ connected with the generalized least squares LETAGROP program,²⁸ searching the minimum, in a selected s range, for the function:

$$U = \sum w(s) [i_{\text{obs}}(s) - i_{\text{calc}}(s)]^2$$

where $w(s)$ is the weight given to each experimental point.

Tables of normalized intensities and reduced intensity values for the investigated solutions are available from the authors on request.

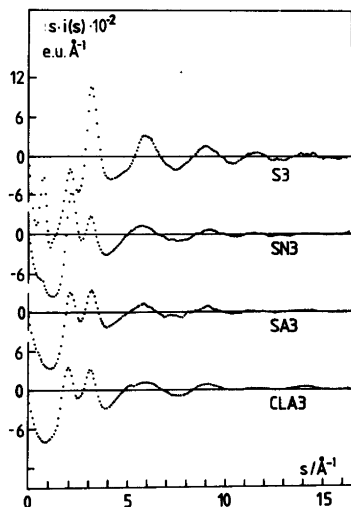


Fig. 2. Observed $s \cdot i(s)$ values (dots) as a function of $s = 4\pi\lambda^{-1} \sin\theta$ for the four solutions investigated.

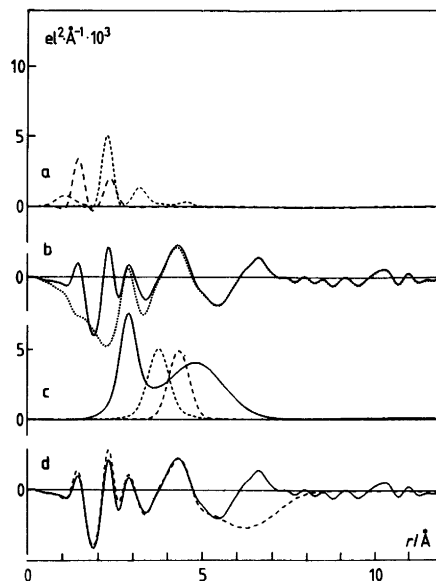


Fig. 3. The radial distribution function and calculated peak shapes for the cadmium perchlorate solution (CLA3). a. Peak shapes calculated for the intramolecular interactions of H_2O , ClO_4^- , and $\text{Cd}(\text{H}_2\text{O})_6^{2+}$. b. The experimental $D(r) - 4\pi r^2 \rho_0$ function (solid line) and the difference curve (dotted line) obtained after subtraction of the peaks in a. c. Calculated contributions to the distribution function from the assumed tetrahedral water structure (solid line) and from interactions between Cd and water molecules in a second coordination sphere (long dashes) and between Cl and water molecules assumed to be packed around ClO_4^- (short dashes). d. Comparison between the observed $D(r) - 4\pi r^2 \rho_0$ function (solid line) and that calculated with the parameter values given in Table 2.

Analysis of the data

The reduced intensity values, $i(s)$, multiplied by s , for the solutions investigated are shown in Fig. 2. The electronic radial distribution functions $D(r)$ and $D(r) - 4\pi r^2 \rho_0$ are shown in Figs. 3 and 4 for the perchlorate solution and in Figs. 6 and 7 for the sulfate solutions.

The perchlorate solution. The radial distribution curve shows expected peaks corresponding to Cl—O interactions at 1.4 Å and Cd— H_2O interactions at 2.3 Å, with peak sizes of a magnitude expected for a tetrahedral ClO_4^- group and an octahedral $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ complex. More accurate parameter values for the distances and temperature coefficients

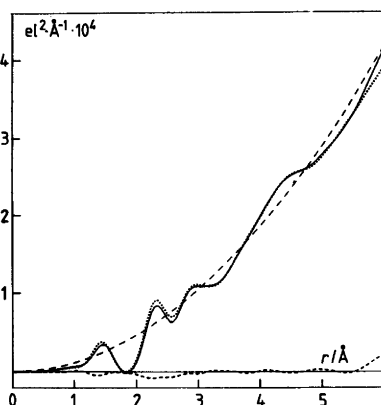


Fig. 4. The observed (solid line) and the calculated (dotted line) $D(r)$ function for the cadmium perchlorate solution. The difference between them is given by the dashed line. Long dashes indicate the $4\pi r^2 \rho_0$ function.

of these interactions were obtained in a least squares refinement using the high-angle part of the intensity curve in which the intramolecular interactions should give dominant contributions. The refinements were done assuming a regular tetrahedral symmetry for ClO_4^- and a regular octahedral symmetry for $\text{Cd}(\text{H}_2\text{O})_6^{2+}$. The results are given in Table 2. The $\text{Cd}-\text{H}_2\text{O}$ bond length of 2.292(5) Å is the same as the value of 2.292(3) Å found for the $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ complex in crystals of $\text{Cd}(\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})_6$.⁶ The $\text{Cl}-\text{O}$ distance within the perchlorate

group does not differ significantly from values previously found in crystals^{6,29,30} and in solutions.^{2,31,32}

The corresponding peak shapes calculated with the parameters determined (Table 2) are shown in Fig. 3a. Subtraction of these peaks from the observed $D(r) - 4\pi r^2 \rho_0$ function gives a difference curve (Fig. 3b) which is consistent with the assumed structures of the complexes. Remaining significant peaks in the distribution curve occur at about 2.9 Å, corresponding to water-water contact distances, at 4.4 and 6.5 Å. The two last peaks obviously contain contributions from many different types of interactions. The 4.4 Å peak probably includes second water-water interactions from the remaining water structure in the solution. Closely packed water molecules around a $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ complex — a second coordination sphere — will give $\text{Cd}-\text{H}_2\text{O}$ interactions in the same region and the same may be true for water molecules around a ClO_4^- ion (Fig. 3c).

A fairly precise reproduction of the experimental $D(r)$ curve up to and including the 4.4 Å peak can be obtained by introducing these types of interactions (Figs 3d and 4). The calculated curve has been obtained by assuming the solution to contain discrete tetrahedral ClO_4^- , octahedral $\text{Cd}(\text{H}_2\text{O})_6^{2+}$, and tetrahedral $\text{H}_2\text{O}(\text{H}_2\text{O})_4$ complexes, approximating intermolecular interactions with a continuous electron distribution outside a sphere of radius R surrounding each complex.¹⁴ The parameter values used are given in Table 2. The close agreement between calculated and observed $D(r)$ functions (Figs 3d and 4) and between calculated

Table 2. Parameter values used for the calculation of theoretical curves.

Interactions	Parameter values		
CdO_6 octahedron	$r_{\text{Cd}-\text{O}}$: 2.29 Å $R=4.0$ Å (4.5 Å)	$b_{\text{Cd}-\text{O}}$: 0.0046 Å ³	$b_{\text{O}-\text{O}}$: 0.0051 Å ² $B=0.02$ Å ²
ClO_4 tetrahedron	$r_{\text{Cl}-\text{O}}$: 1.439 Å $R=3.3$ Å	$b_{\text{Cl}-\text{O}}$: 0.0032 Å ²	$b_{\text{O}-\text{O}}$: 0.0037 Å ² $B=0.02$ Å ²
SO_4 tetrahedron	$r_{\text{S}-\text{O}}$: 1.48 Å $R=3.3$ Å	$b_{\text{S}-\text{O}}$: 0.003 Å ²	$b_{\text{O}-\text{O}}$: 0.0044 Å ² $B=0.02$ Å ²
$\text{H}_2\text{O}(\text{H}_2\text{O})_4$ tetrahedral structure	$r_{\text{H}_2\text{O}-\text{H}_2\text{O}}$: 2.86 Å $R=4.75$ Å		$b=0.015$ and 0.3 Å ² $B=0.1$ Å ²
$\text{Cd}-\text{OSO}_3$ in complexes	$\text{Cd}-\text{O}-\text{S}$ 133°		$r_{\text{Cd}-\text{S}}$: 3.48 Å $b=0.017$ Å ² $r_{\text{Cd}-\text{O}}$: 3.55, 4.4, 4.4 Å $b_{\text{Cd}-\text{O}}$: 0.03, 0.08, 0.08 Å ²
$\text{Cd}-(\text{H}_2\text{O})$ $\text{S}-(\text{H}_2\text{O})$	$r_{\text{Cd}-\text{H}_2\text{O}}$: 4.33 Å $r_{\text{S}-\text{H}_2\text{O}}$: 3.74 Å	$b_{\text{Cd}-\text{H}_2\text{O}}$: 0.04 Å ² $b_{\text{S}-\text{H}_2\text{O}}$: 0.04 Å ²	$n_{\text{H}_2\text{O}}=12$ $n_{\text{H}_2\text{O}}=12$

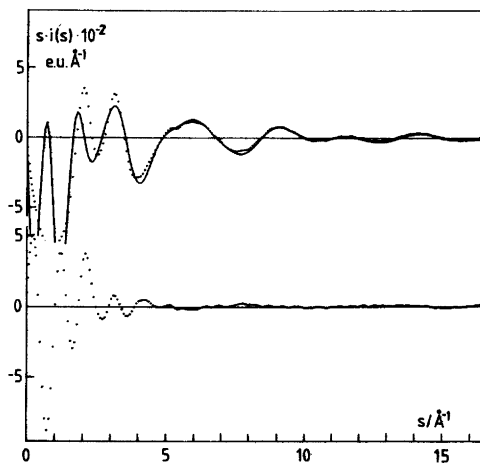


Fig. 5. Observed (dots) and calculated (solid line) $s \cdot i(s)$ values for the cadmium perchlorate solutions. The dotted line in the lower half of the figure gives the difference $(s \cdot i(s))_{\text{obs}} - (s \cdot i(s))_{\text{calc}}$.

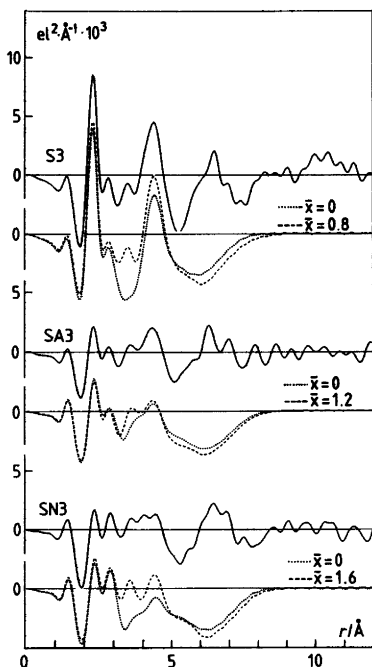


Fig. 6. The experimental $D(r) - 4\pi r^2 \rho_0$ functions (solid lines) for the sulfate solutions compared with functions calculated with (dashed line) and without (dotted line) an assumed complex formation.

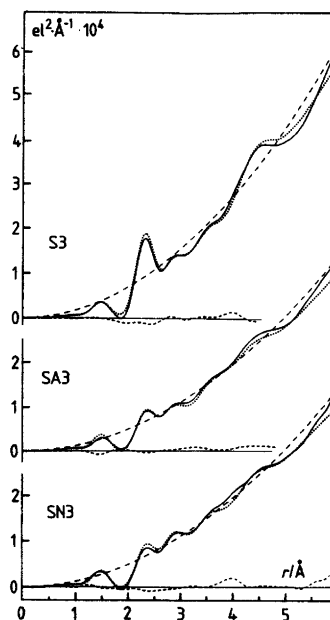


Fig. 7. The experimental distribution functions for the sulfate solutions (solid lines) compared with calculated functions (dotted lines). The parameters given in Table 2 have been used. The difference between experimental and calculated functions are given by dashed lines. Long dashes indicate the $4\pi r^2 \rho_0$ functions.

and observed $s \cdot i(s)$ values (Fig. 5) is consistent with the assumption of the occurrence in the solution of regular octahedral $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ complexes and free ClO_4^- ions not coordinated to the Cd^{2+} ion.

The sulfate solutions. The distribution curves for the sulfate solutions (Figs. 6 and 7) show essentially the same features as that of the perchlorate solution, with the exception of an additional peak at about 3.5 Å. This can be identified as a Cd-S interaction involving a cadmium ion and the sulfur atom of a coordinated SO_4^{2-} ion. In crystals of $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$ corresponding Cd-S distances involving sulfate groups bonded as monodentate ligands (Fig. 1) vary between 3.35 and 3.48 Å (average value 3.44 Å), which corresponds to Cd-O-S bonding angles of 124.5 to 135.7° (average value 131°).^{9b}

A quantitative evaluation of the number of sulfate groups coordinated to each cadmium ion requires a separation of the corresponding interactions in the intensity curves or in the distribution curves. In order to achieve this, the following approximate procedure, based on a comparison with the perchlorate solution, was used.

As shown above, the major peaks in the radial distribution curve for the perchlorate solution can be explained by a model consisting of discrete complexes ClO_4^- , $\text{Cd}(\text{H}_2\text{O})_6^{2+}$, and $\text{H}_2\text{O}(\text{H}_2\text{O})_4$ assumed to occupy spherical holes in an evenly distributed electron density. If the calculated contribution to the distribution function from each complex, including both intramolecular interactions and intermolecular interactions, estimated according to the assumed approximation, is denoted by P , we can write for the experimentally determined distribution function:

$$\{D(r) - 4\pi r^2 \rho_o\}_{\text{perchlorate}} = P_{\text{ClO}_4^-} + P_{\text{Cd}(\text{H}_2\text{O})_6^{2+}} + P_{\text{H}_2\text{O}(\text{H}_2\text{O})_4} + P_{\text{corr}}$$

The last term includes the differences between the experimental distribution curve and that calculated from the simplified model assumed. For the sulfate solutions, we can write correspondingly:

$$\{D(r) - 4\pi r^2 \rho_o\}_{\text{sulfate}} = P_{\text{SO}_4^{2-}} + P_X + P_{\text{H}_2\text{O}(\text{H}_2\text{O})_4} + P_{\text{corr}}$$

where P_X represents the contributions from the unknown $\text{Cd}(\text{SO}_4)_x(\text{H}_2\text{O})_y$ complex. If we make the assumption that $P'_{\text{corr}} \approx P_{\text{corr}}$, the shape function for the unknown complex can be derived:

$$P_X + P_{\text{SO}_4^{2-}} = \{D(r) - 4\pi r^2 \rho_o - P_{\text{H}_2\text{O}(\text{H}_2\text{O})_4}\}_{\text{sulfate}} - \{D(r) - 4\pi r^2 \rho_o - P_{\text{ClO}_4^-} - P_{\text{Cd}(\text{H}_2\text{O})_6^{2+}} - P_{\text{H}_2\text{O}(\text{H}_2\text{O})_4}\}_{\text{perchlorate}}$$

The validity of the approximation $P'_{\text{corr}} \approx P_{\text{corr}}$ will depend on the two solutions compared and on the model used to calculate the intermolecular interactions. It seems reasonable to assume, however, that differences between P'_{corr} and P_{corr} will be rather diffuse and will not, therefore, interfere seriously with sharp peaks characteristic of intramolecular interactions.

The shape functions derived in this way from the scattering data for the three solutions, which all have the same sulfate concentration = 3 M, that is the same as the concentration of ClO_4^- in the reference solution, are compared in Fig. 8 with functions calculated for different numbers of sulfate groups coordinated to the cadmium ion. The parameter values used are given in Table 2. In the cadmium sulfate complexes, a CdO_6 octahedron and a SO_4 tetrahedron were assumed to be joined by a common corner with the $\text{Cd}-\text{O}-\text{S}$ angle = 133° , which corresponds to a $\text{Cd}-\text{S}$ distance of 3.48 Å. With this being the only constraint on the arrangement, different relative orientations of the CdO_6 octahedron and the SO_4 tetrahedron are possible. Variations in the contributions to the distribution curves vary little with the relative orientations, and

the experimental curves show no characteristic features, which can be used to select a specific orientation. A model, which has a mirror plane containing the Cd, the bridging oxygen, and the S atoms, and leads to a value of 3.16 Å for the shortest distance between oxygen atoms of the sulfate group and water molecules of the hydrated Cd^{2+} ion, was adopted for the following calculations. This model is close to the orientations found in the crystal structure of $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$ (Fig. 1).⁸ Large movements of the oxygens of the sulfate group relative to the CdO_6 octahedron – or slightly different orientations of the coordinated sulfate groups – probably smooth out contributions from interactions between the Cd atom and the oxygens of the sulfate groups. This was simulated in the calculations by the introduction of large temperature coefficients for the corresponding interactions.

The contribution from the tetrahedral water structure $\text{H}_2\text{O}(\text{H}_2\text{O})_4$ was assumed to be proportional to the number of non-coordinated water molecules in the solution.

The derived shape functions in Fig. 8 were based

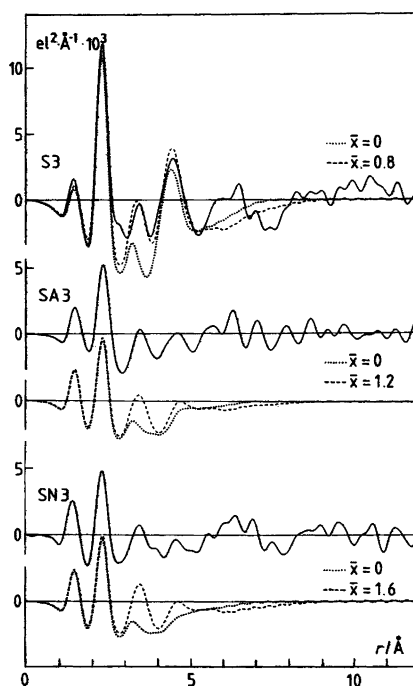


Fig. 8. The shape functions (solid lines) derived for the hydrated cadmium sulfate complexes are compared with functions calculated with and without complex formation. The value of \bar{x} represents the average number of sulfate groups bonded to each Cd^{2+} .

on a stoichiometric unit of volume containing one sulfate or perchlorate ion. The comparison with calculated shape functions shows that the inner coordination sphere of the cadmium ion in the sulfate solution forms a regular octahedron, which does not differ from that in the perchlorate solution. The comparison with the calculated shape functions also shows that the average number of sulfate groups coordinated to each Cd^{2+} varies from about 0.8 in the S3 solution to about 1.6 in the SN3 solution. For the 3 M S3 solution, the second coordination sphere around the cadmium ion appears as a pronounced peak at about 4.3 Å in the derived shape function, since the cadmium concentration in this solution is larger than in the 1 M reference solution and the corresponding $\text{Cd}-\text{H}_2\text{O}$ interactions are not, therefore, fully compensated for.

If differences in the water structure occur between the sulfate and the perchlorate solutions, it would affect primarily the region around 2.9 Å. Such differences may be present to some extent for the 3 M CdSO_4 solution, as judged from the deviation between derived and calculated shape functions. A slight increase in the number of $\text{H}_2\text{O}-\text{H}_2\text{O}$ contact distances in the S3 solution can account for the difference, but does not affect the CdSO_4 peak. For the perchlorate solution, the region around 3.7 Å was assumed to contain contributions from a packing of water molecules around the ClO_4 group (Fig. 3). If corresponding interactions in the sulfate solutions are markedly different, they may to some extent affect the $\text{Cd}-\text{SO}_4$ peak in the derived shape functions. In the ammonium sulfate solution, SN3, in which the complex formation is more extensive than in the other solutions, a small peak at about 4 Å is not accounted for by the models used.

By using one of the sulfate solutions, rather than the perchlorate solution, as the reference solution, a check on the consistency of the results was obtained which confirmed that the derived shape functions are not seriously affected by the deviations discussed.

A comparison between observed and calculated radial distribution functions for the sulfate solutions are given in Figs 6 and 7. The parameters used for the calculations are given in Table 2. For the S3 solution observed and calculated $si(s)$ values are shown in Fig. 9.

DISCUSSION

The scattering data are consistent with a regular octahedral coordination of the cadmium(II) ion in aqueous solutions. The data give no evidence for complex formation with perchlorate. In sulfate

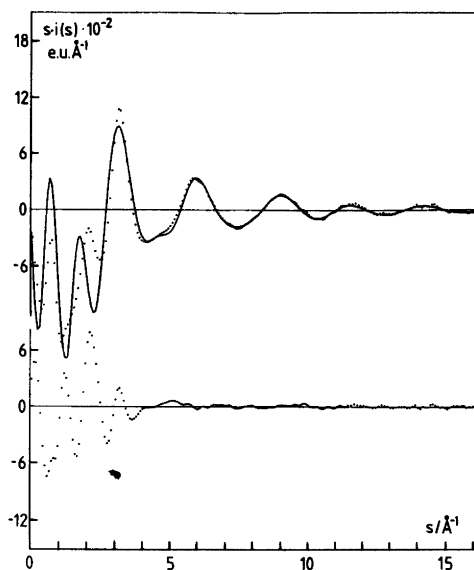


Fig. 9. Comparison between $(si(s))_{\text{obs}}$ (dots) and $(si(s))_{\text{calc}}$ (solid line) for the 3 M cadmium sulfate solution (S3). The dotted line in the lower half of the figure gives the difference between observed and calculated values.

solutions, however, sulfate groups are found to be bonded to the cadmium ion as monodentate ligands with a $\text{Cd}-\text{S}$ distance of 3.48 Å, corresponding to a $\text{Cd}-\text{O}-\text{S}$ bonding angle of 133°.

The $\text{Cd}-\text{S}$ peak is well defined in the radial distribution curves and the distance is probably correctly determined within about 0.05 Å which corresponds to an uncertainty in the $\text{Cd}-\text{O}-\text{S}$ angle of about 4°. This does not differ significantly from corresponding distances in $\text{CdSO}_4(\text{H}_2\text{O})_{8/3}$ (Fig. 1) and the bonding angle, $\text{Cd}-\text{O}-\text{S}$, is, therefore, approximately the same in solution and in the crystals.

The analysis of the $\text{Cd}-\text{S}$ interaction in the different solutions gives an estimate of the average number of SO_4^{2-} bonded to each Cd^{2+} . An accurate estimate of the uncertainty in these values is difficult to make because of the possible influence of various systematic errors. A rough estimate can be made by comparing the theoretical and the experimental functions in Figs. 6 and 8. For the 3 M CdSO_4 solution, the average number, \bar{x} , of sulfate groups bonded to each Cd^{2+} is found to be slightly less than one. This is in approximate agreement with values that can be calculated from stability con-

stants given,⁵ if they are assumed to be valid in the concentrated solutions used here. For the 1 M CdSO₄ solution containing a large excess of SO₄²⁻ (SN3) the value of \bar{x} is larger than one, which would indicate that anionic complexes are also formed. Such complexes have been claimed to occur by Leden³³ and by Hellwege and Schweitzer,³⁴ who have given stability constants for the formation of Cd(SO₄)₂²⁻ and Cd(SO₄)₃⁴⁻ in a 3 M NaClO₄ ionic medium. The value of \bar{x} calculated from these constants is larger, ~2.8, than the value of ~1.6 found here. Moreover, our value may be slightly overestimated because of the presence of the spurious unexplained peak at ~4.0 Å in the SN3 solution.

For the SA3 solution, in which NH₄⁺ is replaced by H⁺, a lower value of \bar{x} , ≈1.2, is found, which is to be expected because of the formation of HSO₄⁻ ions.⁵

In the crystal structure of CdSO₄(H₂O)_{8/3}, the cadmium ions are joined by bridging sulfate groups (Fig. 1) leading to Cd–Cd distances around 5.0 Å. Although some spurious peaks distort the distribution curves at the larger *r* values, there are no indications of peaks in this region, and formation of polynuclear complexes in the solution cannot, therefore, be very extensive.

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