An X-Ray Diffraction Study on an Aqueous Solution of CdSO₄ at 9 and 62 °C

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The X-Ray scattering of a 2 M aqueous solution CdSO₄ has been measured at 9 and 62 °C in a "Θ-Θ" transmission arrangement with a plane-parallel liquid sample. The experimental distribution curves show main peaks at about 1.5, 2.3, 2.8, 3.5, and 4.35 Å. The 3.5 Å peak reveals the formation of inner sphere cadmium-sulphate complexes $Cd(H_2O)_{6-z}(OSO_3)_z^{+2-2z}$, in which oxygens from sulphate groups substitute z water molecules of the hydrated $Cd(H_2O)_6^{2+}$ ions. Least squares refinements of the $i(s)$ curves are consistent with a structural unit in which the sulphate tetrahedron shares a corner with one cadmium octahedron with Cd-O-S angle of 133 deg. The average number (z) of coordinated sulphate ions increases with increasing temperature.

I. Introduction

Remarkable contributions to the knowledge of the coordination of metal ions in aqueous solutions have been provided by X-ray diffraction studies during the last several years [1]. These studies have usually been carried out at different solute concentrations and always at room temperature. In the present work we have therefore investigated a solution at different temperatures. In a previous work [2] we have studied a series of solutions, of different chemical compositions, of CdSO₄ at room temperature. The aim was to study the cation-anion interactions by X-ray diffraction. Previous studies on the cadmium (II) ion have been done on solutions containing halogen ions [3—5]. Our study [2] showed the existence of inner-sphere cadmium-sulphate complexes (anion bonded to cation). In order to determine the preferential position of the sulphate ion bonded to the cation, a CdSO₄ solution has been studied at two temperatures different from the ambient one. Moreover, another object of this study was to investigate the influence of temperature on the distances and standard deviations, as well as the degree of complex formation.

II. Experimental and Data Processing

The solution studied, which was 2M in cadmium, was obtained by dissolving a weighed amount of CdSO₄(H₂O)₈/₃ (Hopkin and Williams Ltd. reagent grade) in water.

Intensity data were collected with the use of a standard X-ray generator and diffractometer equipment. Transmission geometry was used for the measurements. Mok α ($\lambda = 0.7107$ Å) radiation, monochromated by a flat LiF crystal in the primary beam, was used in the s range ($s = 4\pi/\lambda \sin\theta$) from 0.2 to 12 Å⁻¹, with fixed slit system. At least 80 000 counts were collected at each measuring point.

Measurements were performed at discrete points, using a step-scanning facility, with equal intervals $\Delta s = 0.05$ Å⁻¹ in the region $0 \leq s \leq 5$ Å⁻¹ and $\Delta s = 0.1$ Å⁻¹ in the region $5 \leq s \leq 12$ Å⁻¹. The observed intensity values were corrected for background, polarization, absorption and Compton scattering with a procedure described elsewhere [6—8]. For other details of this technique cf. [7—8]. Smoothing of data by fourth differences was applied [9].

Two independent methods are used for finding the factor transforming the numerical values of the experimental intensity from arbitrary units into electron units. The first method consists of simply dividing a theoretical intensity value of the uppermost angle range by the corresponding experimental one. The quotient is used as normalizing factor.

The second method, proposed by Krogh-Moe [10] and Norman [11], compares the integrals of the intensity function taken in the whole accesible reciprocal space.

The experimental structure function $i(s)$, is obtained according to the equation

$$i(s) = \left[\alpha I_{cor}(s) - \sum_{i=1}^{m} x_i f_i^2(s) - \sum_{i=1}^{m} x_i I_{inc,i}(s) \right] \bigg/ \left[\sum_{i=1}^{m} x_i f_i(s) \right]^2,$$

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where I_{cor} is the corrected intensity, α the normalizing factor, x_i are the stoichiometric coefficients in a structural unit containing m kinds of atoms, $f_i(s)$ is the scattering amplitude of component i and $I_{inc,i}$ the corresponding Compton intensity. The coherent scattering amplitudes were computed using the formulas of Hajdù [12] for the O, S and H$_2$O and from the International Tables for cadmium [13]. Similarly Compton intensities were calculated with the aid of the analytical formulas of Pàlinkàs [14] for cadmium and of Hajdù [12] for the other species. The Compton intensities were modified by relativistics corrections. The experimental si(s) M(s) structure functions for the solution at two temperatures are shown as dotted lines in Figure 2. M(s) is a modification function of the form $M(s) = \exp(-ks^2)$, which is a damping factor that minimizes the spurious peaks in the $G(r)$ due to a truncation of the integral at s_{max}; the value of k used was 0.01.

The correlation functions $G(r)$ were obtained from $i(s)$ by Fourier transforming according to

$$G(r) = 1 + (2\pi^2 \varrho_0 r)^{-1}$$
$$\cdot \int_{s_{min}}^{s_{max}} \text{si}(s) M(s) \sin(sr)\, ds, \qquad (2)$$

where r is the interatomic distance, s_{min} and s_{max} are the lower and the upper limits of the experimental data, and ϱ_0 is the bulk density of stoichiometric units. Before calculating the final correlation function, the structure function si(s) was corrected for residual systematic errors by means of a procedure described by Levy et al. [15], based on the removal of the peaks in the $G(r)$ at small values of r.

III. Analysis of the Results

A) Correlation Functions

The correlation functions $G(r)$ obtained from the experimental data are plotted in Fig. 3 (points). Three main peaks are centered at about 1.5, 2.3 and 4.35 Å, and two small peaks at about 2.8 and 3.5 Å. The 1.5 Å peak is due to S-O interactions within the sulphate group; the corresponding O-O interactions, occurring at about 2.4 Å, are partially hidden by the close dominant peak at 2.3 Å due to Cd-H$_2$O interactions. The 2.3 Å distance is almost equal to the sum of the radii of the crystalline Cd^{2+} ion (0.97 Å) and of the water molecule or oxygen

atom (1.40 Å) and can be ascribed to Cd-H$_2$O or Cd-O nearest neighbor interactions (in the following Cd-H$_2$O will be used to indicate both Cd-H$_2$O and Cd-O). The 4.35 Å peak is a composite one and can be mainly attributed, as previously suggested [2], to interactions between Cd^{2+} ions and water molecules in a second coordination shell, whereas (H$_2$O)$_I$-(H$_2$O)$_I$ trans distances inside the cation hydration complex should give only small contributions. The peak at 2.8—2.9 Å is close to the usual O-O intermolecular distance and can arise from H$_2$O-H$_2$O interactions or from interactions between the oxygens of SO$_4^=$ and H$_2$O molecules. The 3.5 Å distance is due to Cd-S interactions within the predicted [16] and previously suggested [2] Cd(H$_2$O)$_{6-z}$(OSO$_3$)$_z^{(2+)+(z2-)}$ complexes.

A qualitative comparison between the experimental correlation functions $G(r)$ (see Fig. 3) shows:

a) All interatomic distances are the same for the two temperatures.

b) Only the peak at 3.5 Å (Cd-S distance) increases with the temperature, which is consistent with the results of the studies of equilibrium constants that show generally an increase of the association constants and therefore of the percentage of complex-formation with increasing temperatures.

B) Model

For a quantitative analysis we tested against the experimental data a synthetic function which was refined by least squares. The characteristics of the approach used and the computation procedure are the same as those employed in previous papers [17—19]. For calculating the $i(s)$ theoretical function we used the well-known formula used by Narten and Levy [20] and proposed already by Debye a long time ago. Least squares refinements of the model parameters were performed by the PUTLSR program [21] connected with the generalized least squares LETAGROP program [22] searching the minimum for the function

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

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

In building up the model we took into account the results obtained for solutions [2, 18, 19] and crystals [23] and focused our attention on Cd-S and on second order interactions around Cd^{2+} and SO$_4^=$.

The study at room temperature has shown the existence in solution of a complex (see Fig. 1) with a configuration similar to that found in the solid state [23]. Thus this model was a natural starting point for the study at 9 °C. As the interatomic distance Cd-S (3.5 Å) did not change with temperature we assumed the same model to be valid for the experimental data at 62 °C. As for the interactions between the Cd^{2+} ion and its second shell of H_2O molecules, the existence of a peak at 4.35 Å in the solution at the high temperature shows the strong stability of this contribution, not only at room temperature [2] but also at higher mobilities of particles. Although the hydration of the sulphate ion does not give a distinct peak in the $G(r)$ function (the S-H_2O interaction falls within the large peak at 4.35 Å), the corresponding contribution was introduced on the basis of previous results [2, 18, 19]. Taking into account the stability constants for the Cd-SO₄ complex formation the average number of sulphate groups bonded to the cadmium ion will be less than 1, so that the free hexaquo cadmium and sulphate ions will be in equilibrium with the inner cadmium-sulphate complexes. Therefore we can propose the average form for these inner complexes $Cd(H_2O)_{6-z}(OSO_3)_z^{+2-2z}$, in which oxygens from the sulphate groups substitute z water molecules of the hydrated $Cd(H_2O)_6^{2+}$ ions.

On these basic assumptions the model used was composed of:

1) The interactions involved in the complex, namely, Cd-S, Cd-O_7, Cd-O_8, Cd-O_9 and $(H_2O)_{i=6-z}$-$(SO_3)_z$ (see Figure 1). All these distances are correlated to the Cd-O_6-S angle once the orientation between octahedron and tetrahedron is fixed. Only four independent parameters were found to be suf-

ficient to describe the complex: the average number (z) of bonded sulphate groups and the mean-square deviations for the discrete interactions (Cd-S and Cd-O_7), (Cd-O_8 and Cd-O_9) and (($H_2O_{i=6-z}$-$(SO_3)_z$).

2) The CdO_6 octahedron, $Cd(H_2O)_{6-z}(O)_z$, and the sulphate tetrahedron, $SO_4^=$, were each described by three independent parameters: the distances r_{S-O}, r_{Cd-H_2O} with the mean-square deviations σ_{S-O}, σ_{O-O}, and σ_{Cd-H_2O}, $\sigma_{H_2O-H_2O}$, respectively.

3) H_2O-H_2O interactions at about 2.8 Å were introduced for the "free" water. We think in this case it is not possible to distinguish between $(H_2O)_I$-$(H_2O)_{II}$ around cadmium, O-H_2O interactions, and residual water not involved in hydration. Three independent parameters did describe these contributions: $r_{H_2O-H_2O}$, $\sigma_{H_2O-H_2O}$, and $n_{H_2O-H_2O}$.

4) Second order interactions around cadmium and sulphur atoms (Cd-$(H_2O)_{II}$, S-H_2O) were taken into account. They were each described with three independent parameters, the distances $r_{Cd-(H_2O)_{II}}$, r_{S-H_2O}, the mean-squares deviations $\sigma_{Cd-(H_2O)_{II}}$, σ_{S-H_2O}, and $n_{Cd-(H_2O)_{II}}$, n_{S-H_2O}.

5) A uniform distribution of distances (continuum) was assumed.
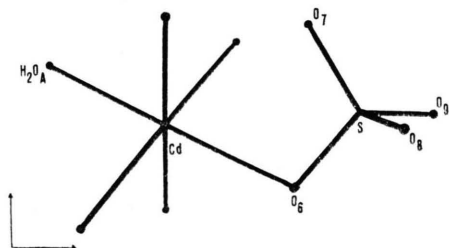

Fig. 1. The model assumed for the bonding of the sulphate group to the hydrated cadmium (II) ion. The model has a mirror plane containing the Cd-atom, the H_2O_A, the bridging oxygen (O_6), the S atom and the O_7 atom. The Cd-O_6-S angle is 133 degr.
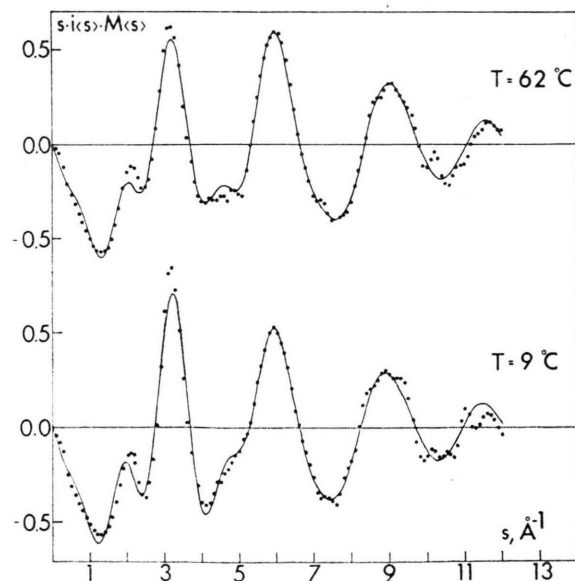

Fig. 2. Structure functions obtained from the experimental data, in the si(s)M(s) form (······), and structure function calculated with the model parameters, obtained from least squares refinements reported in Table 1 (———).
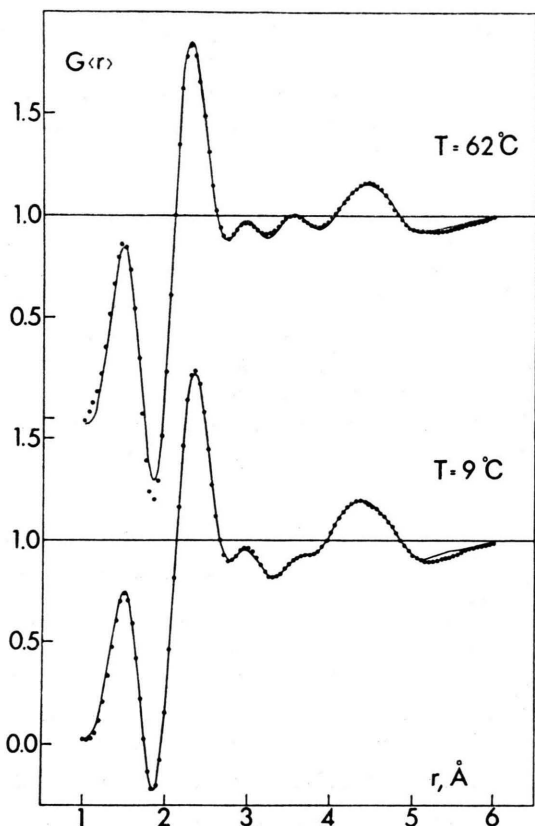
Fig. 3. Correlation functions G(r) obtained from the experimental data (·······) and from the model structure (———). s_{max} used 11 Å^{-1}.

Table 1. Parameter values [r = distance (Å); σ = mean-squares deviation; n = frequency factor and standard deviations (in parentheses)] obtained from least squares fitting; z = the average number of sulphates bonded to Cd^{2+}. When one molecular species is indicated in Column 1 [Cd(H$_2$O)$_{6-z}$·(O)$_z$, Complex, SO$_4^=$] all the interactions arising from that species are taken into account.

Interactions	Parameters	9 °C	62 °C
Cd(H$_2$O)$_{6-z}$(O)$_z$	r_{Cd-H_2O}	2.32 (1)	2.30 (1)
	σ_{Cd-H_2O}	0.09 (1)	0.08 (1)
	$\sigma_{H_2O-H_2O}$	0.19 (1)	0.19 (2)
Complex	σ_{Cd-S}, σ_{Cd-O_7}	0.12 (1)	0.14 (1)
	σ_{Cd-O_8}, σ_{Cd-O_9}	0.25 (6)	0.34 (5)
	$\sigma_{(H_2O)_{(-6-z)}-(SO_3)_z}$	0.26 (6)	0.35 (5)
	z	0.34 (5)	0.64 (4)
SO$_4^=$	r_{S-O}	1.48 (1)	1.46 (1)
	σ_{S-O}	0.09 (1)	0.05 (3)
	σ_{O-O}	0.10 (4)	0.08 (5)
H$_2$O-H$_2$O	$r_{H_2O-H_2O}$	2.806 (7)	2.800 (6)
	$\sigma_{H_2O-H_2O}$	0.15 (1)	0.13 (1)
	$n_{H_2O-H_2O}$	1.91 (4)	1.88 (4)
S-H$_2$O	r_{S-H_2O}	3.89 (2)	3.83 (1)
	σ_{S-H_2O}	0.15 (3)	0.13 (2)
	n_{S-H_2O}	6.9 (7)	6.0 (4)
Cd-(H$_2$O)$_{2nd}$	r_{Cd-H_2O}	4.36 (1)	4.37 (1)
	σ_{Cd-H_2O}	0.32 (1)	0.31 (1)
	n_{Cd-H_2O}	11.9 (3)	10.3 (3)

C) Results

The fitting procedure showed a good compatibility of the model with the experimental data as can be seen in Figure 3. The structure functions from the best fit are shown in Fig. 2 together with the experimental data. The final values of the most significant parameters are listed in Table 1 for the solution at the two different temperatures.

IV. Discussion

An examination of the parameters in Table 1 shows some different points:

1) The parameters related to the cation hydration are almost temperature independent. The standard deviations of the distances are identical and also the Cd-(H$_2$O)$_I$ distances are very similar. The value of the distance, $r_{Cd-(H_2O)_I}$, within the precision of the method, is the same as found in nitrate [24]

and perchlorate solutions [25] and in solid structures of CdSO$_4$(H$_2$O)$_{8/3}$ [23] and Cd(ClO$_4$)$_2 \cdot$ 6 H$_2$O [26].

2) The values found in this study for the S-O distance are similar to the values previously found in solution [2, 18, 19] and in solid compounds [27].

3) As regards the H$_2$O-H$_2$O contribution, although our approximation considers a single contribution, the obtained values are coherent with the last work about liquid pure water [28].

4) As regards the parameters that specify the complex and the second shell around the cadmium and sulphur atoms we have a change with temperature. It is quite evident that there is an appreciable increase of complex-formation when the temperature increases. This fact will be reflected in a decrease in the sulphate hydration as well as in the second shell around the cadmium ion. As seen, the n_{S-H_2O} and $n_{Cd-(H_2O)_{II}}$ parameters decrease when the temperature increases, i.e. when the percentage of complex-formation increases.

On the other hand an increase in temperature implies a greater mobility of the particles in solution. This fact is reflected in the variation of the standard deviations of the distances for the complex species.

V. Conclusions

The analysis of the correlation functions and the least squares results, in connection with literature information, lead to the following conclusions:

1) The presence of a distinct peak at about 3.5 Å in the $G(r)$ functions is consistent with the formation of an inner sphere cadmium-sulphate complex. The number of coordinated sulphate groups is between 0.34 (9 °C) and 0.64 (62 °C). The model proposed initially explains satisfactorily the experimental data. The cis-position for the $SO_4^=$ group bonded to cadmium seems to be preferred. The same position occurs in the solid state [23].

2) The parameters that specify the first coordination sphere of the cation do not change substantially with temperature. The $SO_4^=$ anion hydration is confirmed as well as the strong stability of the second sphere around cadmium.

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