X-Ray Diffraction Study on Hydration and Ion-Pairing in Aqueous $ZnSO_4$ Solution

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An X-ray diffraction experiment on a 2.98 molar $ZnSO_4$ aqueous solution has been interpreted in terms of coordination models. The best agreement between model and experimental structure functions was reached when the Zn^{2+} ion is hydrated in octahedral form, with twelve water molecules in a second hydration shell, bonded by shortened H-bonds to the first hydration shell. The sulfate group is loosely coordinated by 8.2 water molecules. Besides the dominating $Zn(H_2O)_6^{2+}$ complexes, about 40% $[Zn(H_2O)_5SO_4]$ inner complexes were found to be consistent with the X-ray data. Alternative models of cationic hydration are critically examined and for the sulfate group the independent atom approximation is compared with a spherical molecular description.

Introduction

In the last decade many X-ray studies have been carried out on aqueous solutions of monovalent, bivalent and trivalent cations, while the more often studied anions were Cl^-, I^- and oxyanions such as SO_4^{2-}, ClO_4^- and NO_3^-. The information about the hydration or coordination of the anions is generally more ambigous than that of the cations. The structure of the water not involved in the hydration spheres of the ions, referred to here as "rest solvent", was also tentatively described. Formation of complexes or ion pairs has been a topic of some recent diffractometric studies for concentrated solutions of oxyanions and bi- or trivalent cations.

It is convenient to distinguish between the two possible forms of ion-pairing. Here we refer to inner-sphere complexes or contact ion-pairing when a counterion is one of the neighbouring particles of a given ion. On the contrary, when the first hydration shell is left pure and there are one or more bridging water molecules between the ions of opposite sign, we speak of outer-sphere complexes. Alternative definitions are also found in the literature.

Various physico-chemical methods have also been applied. Thus for solutes of MSO_4, where M is mostly a transition metal, possible reaction mechanisms with complex formation have often been deduced, starting from some measurements and resulting in a set of equilibrium constants. The Eigen-Tamm three step mechanism [1] assumes that contact ion-pairs may be formed from totally dissociated M^{2+} and SO_4^{2-} ions via outer-sphere complexes. The ability of the cations to form outer or inner-sphere complexes is characterized by corresponding equilibrium constants. A survey of the related literature reveals significant disagreements in the results. Moreover the terminology, used in these works, is sometimes very different from that applied in the diffraction studies. This discrepancy can lead to a misinterpretation of the structure.

A remarkable proposal towards a unification of the terminologies has been made by Libuś et al. [2]. They consider the cations to be present in various coordination states and conclude that some physical properties are in a unique correlation with the coordination states. Comparison of complete coordination models with X-ray data is of main importance in this respect.

In the present work results of X-ray scattering experiment on a 2.98 molar aqueous $ZnSO_4$ solution are reported and analysed in terms of coordination models. The work has three tasks: (i) to give a quantitative analysis of the X-ray data in respect to ion-pair formation, (ii) to investigate the hydrogen bond shortening, and (iii) to decide whether the oxygen sites of the sulfate ions can be distinguished by X-ray scattering or not. The first two tasks are of general chemical interest, the third one has importance for the specialists.

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Table 1. Characteristics of the cationic hydration shells and the rest solvent in models A—E: numbers of water molecules in the hydration shells for the cation (N_1, N_2); number of tetrahedral aggregates for the rest solvent (N_T); number of water molecules treated as pure water (N_p); percentage of ion-pairs (x) and the quality of the fit (σ^2). The sulfate ion is described by independent atom- (model A) or molecular approximation (models B—E).

Model	N_1	N_2	N_T	N_p	x	$\sigma^2 \cdot 10^3$
A	6	12	—	—	0.	2.519
B	6	12	—	—	0.	2.476
C	6	—	7.157	—	0.	2.794
D	6	—	—	35.784	0.	6.645
E	$(1-x)\cdot 6 + x\cdot 5$	$(1-x)\cdot 12 + x\cdot 10$	—	—	40.(10)	2.268

In a recent work of Licheri et al. [3] a series of aqueous $ZnSO_4$ solutions has been investigated. The authors' attention was focused on cation hydration and its concentration dependence. Since no concentration effect was observed, a model with exclusion of ion-pair formation was applied for all solutions. While in this paper the absence of complex formation in $ZnSO_4$ solutions is strongly suggested by qualitative arguments, complex formation could not be ruled out. Although anomalies were observed in parameters for shortened H-bond interactions and sulfate hydration, the authors did see no reason to investigate improved models quantitatively.

In the present work five coordination models have been checked for the interpretation of the X-ray scattering data (models A – E). The models differ in the description of the coordination states of the cation and the treatment of SO_4^{2-} group. The primary hydration shell of the cation is assumed to consist of six water molecules (A – D) or partly of five water molecules and one anion (E). Models A, B, E include, in addition, secondary hydration for the cation. Models C and D treat only the first neighbour hydration, but rest solvent is also taken into account, for the structure of which either a tetrahedral arrangement is assumed (C), or it is substituted by the pure solvent structure (D). For the description of anion hydration no symmetry is assumed, and the only difference appears in the treatment of X-ray scattering of the sulfate ion itself. Thus model A includes the tetrahedral structure of anions, but in models B – E the anion is represented as a structureless spherical scattering unit. As a consequence of the latter difference, in models B – E the number of parameters is decreased because no parameter appears for sulfate O site-solvent interactions. The differences in the five models are summarized in Table 1.

The experimental conditions for the registration of the scattered intensity as well as the correction and normalization process was essentially the same as in [3]. The obtained structure function is denoted here by $kH_d(k)$, k being the scattering variable, while $G_d(r)$ stands for the correlation function. The

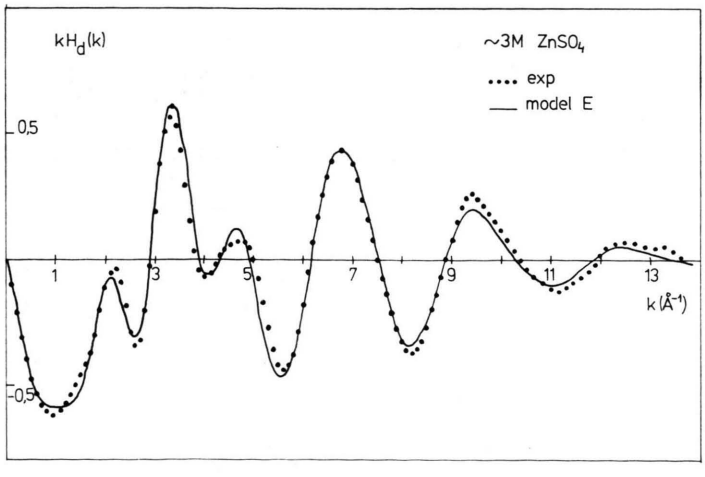

Fig. 1. Experimental structure function (dots) and best fit from model E (full line) for the 2.98 molar $ZnSO_4$ solution.

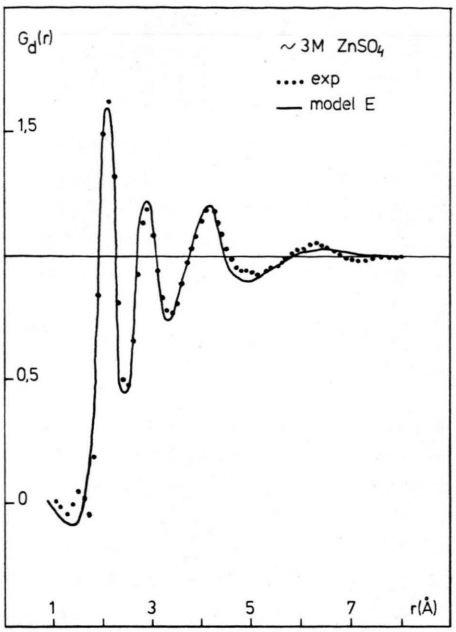

Fig. 2. Experimental (dots) and model E (full line) distance spectra for the 2.98 molar $ZnSO_4$ solution, obtained by Fourier transformation of the corresponding structure functions in Figure 1.

formula for the construction of the "synthetic" structure functions $k H_{ML}(k)$ based on the model assumptions is expressed in Eq. (1) of [3].

The models were tested by fitting the corresponding $k H_{ML}(k)$ functions to the experimental one by adjusting their independent parameters. The quality of the fit was expressed as

$$\sigma = \sqrt{\frac{\sum_k [k H_{ML}(k) - k H_d(k)]^2}{N-1}} . \qquad (1)$$

The σ^2 values for the models are shown in Table 1.

The best fit was obtained for model E. The corresponding $k H(k)$ and $G_d(r)$ functions are shown in Figures 1 and 2, respectively. The parameters of model E are presented in Tables 2 and 3. No significant variations were detected for different models as far as the primary hydration of ions is concerned.

Hydration Shells of Zn^{2+}

In each model Zn^{2+} is hydrated in the $Zn(H_2O)_6^{2+}$ form, with octahedrally arranged water molecules. In model E this is partly changed by inner-sphere complexes of Zn^{2+} and SO_4^{2-}. As concerns the six water molecules in the first hydration shell, this is in good agreement with the literature data, and the $r_{Znw_1} = 2.10$ Å distance is also near to those reported [3 – 5].

The validity of the symmetry assumption for the hydration shells, although commonly accepted, still remains questionable. For an X-ray analysis it is only a working hypothesis and refers to the average arrangement of the first neighbours. In a recent study this hypothesis was analysed by combined X-ray and molecular dynamics investigations of various ions, and it was concluded that the probability of finding six water molecules simultaneously in a slightly distorted octahedron is about 60% for Mg^{2+} [6], which makes the symmetry assumption rather convincing. Since for the Zn^{2+} ion no similar estimation is available, the assumption for symmetry is supported only by the similarity of the Mg^{2+} and Zn^{2+} ions both in size and charge.

No secondary hydration for the Zn^{2+} ion was found in some previous papers [4, 5]. In [3], however, a second hydration shell was incorporated in the model describing the cationic hydration, similarly as it was done recently for various trivalent [7, 8] and bivalent [6, 9, 10] cations, and even for Li^+ [11]. In these models distances of about 2.65 – 2.80 Å have been found, which were always assigned to $w_1 - w_2$ distances between the two hydration

n_{SO_4-w}	r_{SO_4-w}	l_{SO_4-w}	r_{Zn-SO_4}	l_{Zn-SO_4}	$r^0_{SO_4-w}$	$l^0_{SO_4-w}$
8.2 (4)	3.83 (3)	0.27 (2)	3.13 (5)	0.32 (5)	4.7 (1)	0.43 (5)

Table 2. Structural parameters for the hydration shell of the anion and the ion-pair from model E.

α	$r_{αw1}$	$l_{αw1}$	$r_{αw2}$	$l_{αw2}$	$r^0_{αw}$	$l^0_{αw}$
Zn	2.10 (1)	0.16 (3)	4.26 (2)	0.37 (3)	4.9 (1)	0.47 (5)
w_1	(2.97)	0.14 (3)	2.70 (1)	0.11 (1)	2.8 (1)	0.10 (5)
w_2	—	—	4.4 (2)	0.8 (3)		

Table 3. Structural parameters for the hydration shells of the cation from the model E and for the solvent aggregates from the model C (last row). The value for $r_{w_1w_2}$ in parenthesis results from the octahedral geometry of the first shell.

shells, based upon Brown's H-bond analysis [12]. These are obviously shorter than the average 2.85 Å distances usually found for the first neighbour distances in pure water. The models constructed generally resulted in very good fits to the experimental data, therefore alternative explanations for the distance shortening were neglected. Moreover, a tendency for having shortened H-bonds if $s > 0.4$, where $s = Z/CN$ with Z the cationic charge and CN the coordination number in the first shell, was stated.

Some indications show, however, that one has to be careful in the a priori application of these assumptions. Firstly, the last statement is questionable for the bivalent cations ($s = 0.33$) and Li^+ ($s = 0.17$), where second spheres with shortened distances are also reported. Secondly, these distances generally have small, often unacceptable l_{w1w2} rmsd values, pointing to some incoherences in the models (see $\sigma_{w_1-w_2}$ values in Table 2 of [3]). Finally, the assignement to the w_1w_2 interactions is also questionable while alternative possibilities are not critically analyzed; the question may sometimes be connected with the handling of the rest solvent as unperturbed pure water, or with other incoherences in the model, as in [3] where the shortened H-bonds are partly assigned to O_S-W_A interactions, with unphysically small rmsd values. This is in contradiction with the conclusion that the hydration of SO_4 is weak.

In order to study this phenomenon, two different ways may be followed; searching directly for the shortened distances, or isolate them indirectly by the exclusion of unacceptable alternatives. The first way was followed for a 1.1 M $MgCl_2$ solution where a molecular dynamics simulation provided special statistics for the $r_{w_1w_2}$ distances and yielded about 0.1 Å shortening with respect to the average first neighbour oxygen-oxygen distance [6].

In the present study an indirect way was followed. In model B all of the Zn^{2+} had two hydration shells with six and twelve water molecules involved, respectively.

The second sphere was then dropped in model C (Zn-w_2 and $w_1 - w_2$ type contributions excluded) with simultaneous introduction of tetrahedral units for the rest solvent as in [13]. Only a 13% increase in the σ^2 was detected, with the appearence of the same $r_{w-w} = 2.68$ Å and $l_{w-w} = 0.10$ Å values. An additional test, with the substitution of the rest solvent contribution by an experimental structure function of pure water (model D) resulted in a significant increase in σ^2. From these effects it can be concluded that the rest solvent is highly perturbed by the presence of the ions. This perturbation results in a preference for forming shortened H-bonds between the water molecules (Models A, B, C). Assigning them to the $w_1 - w_2$ interactions, based only on X-ray data, however, is not obvious because of the not very convincing improvement of the fit.

The Sulfate Ion

In [3] the description of the anion structure resulted in some anomalies. According to the authors this is probably due to the relatively small contribution of the sulfate-water interactions to the structure function and the weakly bounded hydration shell of the anion. Based on these arguments, a further attempt is made here for studying the behaviour of the sulfate ion. Thus models A and B agree in the description of the cationic hydration, but differ in that of the anion. In model A the independent atom approximation is used for the sulfate group. Fitted parameters for the intramolecular contributions yielded values of $r_{SO} = 1.49$ Å, $l_{SO} = 0.05$ Å, $l_{OO} = 0.08$ Å, with $r_{OO} = 2.43$ Å, calculated from the fixed geometry. In model B a molecular approximation was applied, where the scattered intensity for the sulfate ion was computed according to the Debye-Ehrenfest formula

$$I_{SO4} = \sum_i \sum_j \sum_\alpha f_i f_j \frac{\sin k r_{ij\alpha}}{k r_{ij\alpha}} \exp\left\{-\tfrac{1}{2} l_{ij\alpha}^2 k^2\right\}. \qquad (2)$$

The sum is over the distances (α) and types (i, j) within the unit. The scattering factor f_{SO4} was approximated by the spherical part a_0^0 of the molecular scattering amplitude.

In both models, as well as in the remaining three, the hydration or, more precisely, the coordination state of the sulfate group was characterized by a free coordination number n_{SO4-w}, neclecting any symmetry in the shell. Going from model A to B, the number of fitted parameters was reduced by 4, with the exclusion of O-w type interactions from the sulfate oxygens. In spite of this, a slight decrease in σ^2 could be observed (Table 1). This indicates that there is no reason for a separate description of sites in the sulfate group. Treating the SO_4 group as spherically symmetric unit, although this approxima-

tion is not obviously valid in general for tetrahedral molecules, leads to a more reasonable explanation for the parameters of anionic hydration. The coordination number n_{SO_4-w} and the large l_{SO_4-w} rmsd parameters support also the idea of weak interaction between sulfate and water.

Ion-pairing

The results of the recent studies on complex formation for MSO_4 salt solutions vary greatly. The conclusion that "most metal sulfates are very highly associated even in dilute solutions" [14] is generally accepted, but the estimated ratios of outer- to inner-sphere complexes are very different. The predominance of outer-sphere complexes is often emphasized [2, 15, 16]. The degree of inner-sphere complexation varies from 10%, determined by infrared spectrophotometry [17], to 50% from association constants [18]. The stability constants for the transition metal sulfates show the decreasing order $Cd^{2+} > Co^{2+} > Zn^{2+} > Ca^{2+}$ from conductivity data [19] and $Cu^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$ from combined methods [20]. The partial molal volume changes give a stability order of $Ni^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mn^{2+} > Cd^{2+}$ [16], while from absorption spectra it is concluded that $CoSO_4$, $NiSO_4$, $CuSO_4$ and $ZnSO_4$ are associated to the same extent at any given concentration [2]. As emphasised by Yokoyama et al. [15], differences can arise from the uncertainties in the definitions of the inner-sphere and outer-sphere complexes. Defining an inner-sphere complex when the cation and the anion are closer to each other than the sum of their ionic radii and the diameter of a water molecule, they derived the ratio of inner-sphere complexes related to the total complexes for the $ZnSO_4$ as 0.36 from spectrophotometry and 0.48 from conductivity data. An estimation from ultrasonic relaxation data gives 0.30, but from volume and compressibility data only 0.20 [16], while for $CdSO_4$ it is even smaller (0.12). In spite of the disagreement in the quantitative estimates, inner-sphere complex formation does not seem to be negligible for $ZnSO_4$ and $CdSO_4$.

In earlier X-ray diffraction studies this phenomenon was not considered for the $ZnSO_4$ solution. The way to do it is construction of a coordination model, where, at least partly, the water molecules in the first hydration shell are substituted by anions.

For the description of ion-pairing, in model E, the ions were assumed to be in the following coordination states:

$$(1-x)\,[Zn(w_1)_6(w_2)_{12}],$$
$$x[Zn(w_1)_5(SO_4)\,(w_2)_{10}],$$

and

$$(1-x)\,[(SO_4)\,w_{n_{SO_4-w}}].$$

The x parameter was varied in 0.1 increments from 0 to 1, and in each case the whole parameter set was refined. According to this choice, $x=0$ corresponds to the cations being hydrated completely by two hydration shells, while $x=1$ gives the situation when each cation is in contact with one sulfate group, with partly destroyed second hydration shells.

Figure 3 shows σ^2 as the function of x, given in percentages. The function reaches its minimum at $x=40\%$. The width of this minimum is surely due to the small weight of the newly introduced contributions. Indeed, $x \approx 70\%$ results in as good a fit as $x=0$ (model B). On the other hand, the shape of the $\sigma^2(x)$ curve suggests that the number of ion

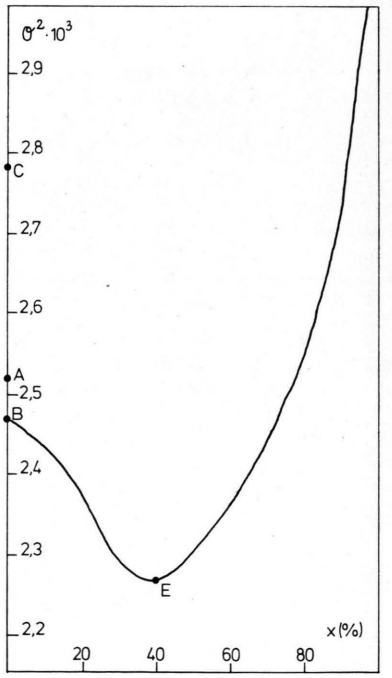

Fig. 3. The σ^2 values, defined in (1), for the different models as a function of the percentage of $[Zn(H_2O)_5SO_4]$ inner complexes. Model D is not reported because of its high σ^2.

pairs must be significantly smaller than for the 3 molar $CdSO_4$ solution, where $x = 100\%$, and so the complex formation abilities of Zn^{2+} and Cd^{2+} seem to be different.

The structural parameters had only negligible variations within the described procedure. Although the number of second shell water molecules around the inner-sphere complexes was not fixed at 10, it remained practically unchanged (10.4 when $x = 40\%$).

As for the ion-pair distance, $r_{Zn-SO_4} = 3.13$ Å was found. In the experimental $G_d(r)$ a slight asymmetry on the right hand side of the peak at 3.0 Å must be explained by its contribution. The parameter of the contact ion-pair distance of 3.13 Å is in good agreement with the value found for the anion-water distance 3.83 Å. Calculating an effective ion radius for the anion from the radius of the water molecules 1.4 Å and the ionic radius of the cation 0.7 Å, one can also arrive at 3.13 Å for the ion-pair distance.

Concerning the possibility for Zn ions to form complexes with more sulfate groups, its checking is beyond to the limits of the X-ray diffraction method. Indeed, an additional test with two sulfate groups in the inner-sphere of the cation, gave a $\sigma^2(x)$ curve not distinguishable from the $\sigma^2(x/2)$ one.

Concluding Remarks

The analysis of the X-ray data allows for the existence of both ion-pair formation and secondary hydration around the cation in the aqueous $ZnSO_4$ solution investigated. A comparison of the qualities of models B and C with those of B and E shows that the sensitivity of the X-ray data for ion-pair formation is no less than for secondary hydration. The occurrence of shortened H-bonds between the solvent molecules is verified, but there is only a slight indication to assign it to hydration shells of Zn^{2+} ions.

The treatment of the sulfate groups as five-site species is proved to be meaningless in the solution studied.

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[1] M. Eigen and K. Tamm, Z. Elektrochem. **66**, 93 (1962).
[2] W. Libuś, T. Sadowska, and Z. Libuś, J. Sol. Chem. **9**, 341 (1980).
[3] G. Licheri, G. Paschina, G. Piccaluga, and G. Pinna, Z. Naturforsch. in print.
[4] H. Ohtaki, T. Yamaguchi, and M. Maeda, Bull. Chem. Soc. Japan. **49**, 701 (1976).
[5] I. M. Shapovalov and I. V. Radchenko, Zh. Strukt. Khim. **12**, 769 (1971).
[6] G. Pálinkás, T. Radnai, W. Dietz, Gy. I. Szász, and K. Heinzinger, Z. Naturforsch. **37a**, 1049 (1982).
[7] R. Caminiti, G. Licheri, G. Piccaluga, G. Pinna, and T. Radnai, J. Chem. Phys. **71**, 2473 (1979).
[8] R. Caminiti, Chem. Phys. Lett. **86**, 214 (1982).
[9] R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, J. Appl. Cryst. **12**, 34 (1979).
[10] R. Caminiti, Chem. Phys. Lett. 88, 103 (1982).
[11] T. Radnai, G. Pálinkás, Gy. I. Szász, and K. Heinzinger, Z. Naturforsch. **36a**, 1076 (1981).
[12] I. D. Brown, Acta Cryst. **A32**, 24 (1976).
[13] G. Pálinkás, T. Radnai, and F. Hajdu, Z. Naturforsch. **35a**, 107 (1980)
[14] R. E. Hester and R. A. Plane, Inorg. Chem. **3**, 769 (1964).
[15] H. Yokoyama and H. Yamatera, Bull. Chem. Soc. Japan **54**, 2286 (1981).
[16] A. Lo Surdo and P. J. Millero, J. Sol. Chem. **9**, 163 (1980).
[17] R. Larsson, Acta Chem. Scand. **18**, 923 (1964).
[18] R. Näsänen, Suomen Chem. **B26**, 67 (1957).
[19] S. Katayama, J. Sol. Chem. **4**, 241 (1976).
[20] H. Yokoyama and H. Yamatera, Bull. Chem. Soc. Japan **48**, 2719 (1957).