

# X-ray Diffraction Study of Aqueous Solutions of $\text{ZnSO}_4$

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Five aqueous solutions of  $\text{ZnSO}_4$  of concentrations ranging from 0.6 M to 3.1 M were examined by X-ray diffraction. In the correlation functions no concentration effect on structural phenomena is detectable. The same model was then successfully used for all cases, attributing two hydration shells to  $\text{Zn}^{2+}$  and one hydration shell to  $\text{SO}_4^{2-}$ . The reliability of the structural parameters obtained is discussed.

## Introduction

The hydration of transition metal ions has been extensively investigated by X-ray diffraction [1]. The solutions examined were mainly chloride solutions since  $\text{Cl}^-$  ions can now be treated with great confidence. However, the hydration cannot be studied in presence of  $\text{Cl}^-$  ions if the cation tends to form complexes with the chlorine ion. This is the case for the  $\text{Zn}^{2+}$  ion; indeed the investigations of Wertz et al. [2, 3] aimed at determining the degree of  $\text{Zn}^{2+}$ – $\text{Cl}^-$  complex formation. Information on the hydration of  $\text{Zn}^{2+}$  ions has been obtained in solutions of oxy-anions like  $\text{NO}_3^-$  (Bol et al., [4]),  $\text{ClO}_4^-$  and  $\text{SO}_4^{2-}$  (Ohtaki et al., [5]). However, these studies are not systematic and information on the hydration of  $\text{Zn}^{2+}$  is not as detailed as, for example, that concerning  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ .

Therefore we started an investigation on solutions of  $\text{ZnSO}_4$ , examining five samples of concentrations ranging from 0.6 M to 3.1 M. In a previous study [6], some of us have tried to understand if the structure of  $\text{SO}_4^{2-}$  ions is detectable when in presence of  $\text{Zn}^{2+}$  ions. In this paper attention is devoted to deducing structural parameters that describe the hydration of the cation and to following their eventual dependence on concentration.

## Experimental and Results

$\text{ZnSO}_4$  (Carlo Erba reagent grade) was dissolved in water and the composition of the solutions was determined by standard volumetric methods. The analytical results are given in Table 1.

The experimental X-ray apparatus and data collection procedures have been extensively described in previous papers [1, 7]. Experimental diffraction intensities, collected in the range of scattering angles  $4^\circ < 2\theta < 130^\circ$ , underwent conventional correction (background, polarization, absorption) and were normalized by standard procedures and deprived of independent atomic scattering.

From the structure functions  $s_i(s)$  thus obtained ( $s$  is the usual scattering variable), the correlation functions  $G(r)$  were calculated via Fourier Transform, using a damping factor  $e^{-0.005s^2}$  in order to reduce termination errors. The correlation functions evaluated in the five cases are reported in Figure 1. The sequence of the curves displays a regular behaviour of the main peaks, and this points to the correctness of the experimental results. (This regularity is also clearly shown by the structure functions shown in Figure 2: going from the water-like structure function of the 0.6 M solution to the one of the 3.1 M solution, maxima and minima vary monotonously). Three main peaks clearly emerge, centered at 1.45–1.50 Å, 2.10–2.15 Å and 2.85 Å respectively, which can easily be assigned. The peak at 1.45–1.50 Å is due to the S–O distances of the sulphate ions, as already found both in solutions and crystalline compounds [8]. The peak at 2.10–2.15 Å can be essentially attributed to  $\text{Zn}^{2+}$ – $\text{H}_2\text{O}$  distances, on the basis of previous diffraction studies

$M$	$x$
0.6	0.0099
1.0	0.0187
1.5	0.0270
2.0	0.0354
3.1	0.0558

Table 1. Molarity  $M$  and molar salt content expressed as  $x$  in the structural unit  $(\text{ZnSO}_4)_x(\text{H}_2\text{O})_{1-x}$ .

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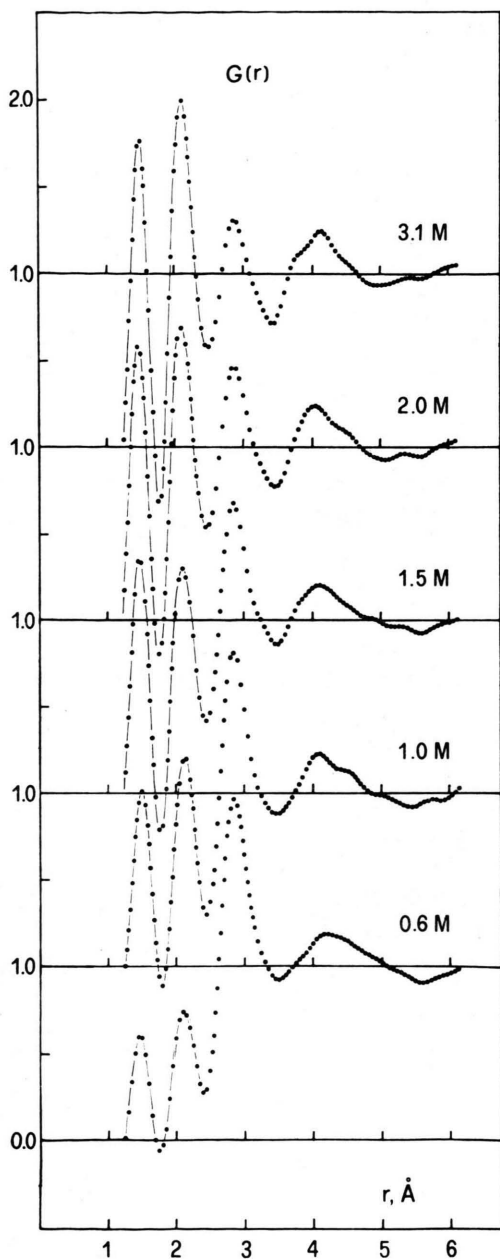


Fig. 1. Experimental correlation functions (● continuous line has been drawn through experimental points for clarity).

[2–6] and of ionic radii of  $\text{Zn}^{2+}$  and  $\text{H}_2\text{O}$ . These peaks originate from pair distances involving the solute and, accordingly, their height increases as the concentration increases. The peak at  $2.85 \text{ \AA}$  in aqueous solutions is generally connected with O–O interactions [1]. Here, it decreases as the

concentration increases, clearly as a consequence of the diminishing bulk water  $\text{H}_2\text{O} - \text{H}_2\text{O}$  interaction; however it is still present even at the highest concentrations, since interactions like O (from sulphate ion) –  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O} - \text{H}_2\text{O}$  between subsequent cation hydration shells, and  $\text{H}_2\text{O} - \text{H}_2\text{O}$  within polyhedra of cation first hydration shells contribute to it.

Besides the peaks mentioned, a broad and poorly defined one appears in the range  $3.75 - 4.75 \text{ \AA}$ . Though clearly composite, its maximum approaches  $4.10 - 4.20 \text{ \AA}$  in all the five cases. Arguing by analogy from results of other solutions of bi- and trivalent cations with radii close to the one of  $\text{Zn}^{2+}$  [1], the main contribution in this range can be

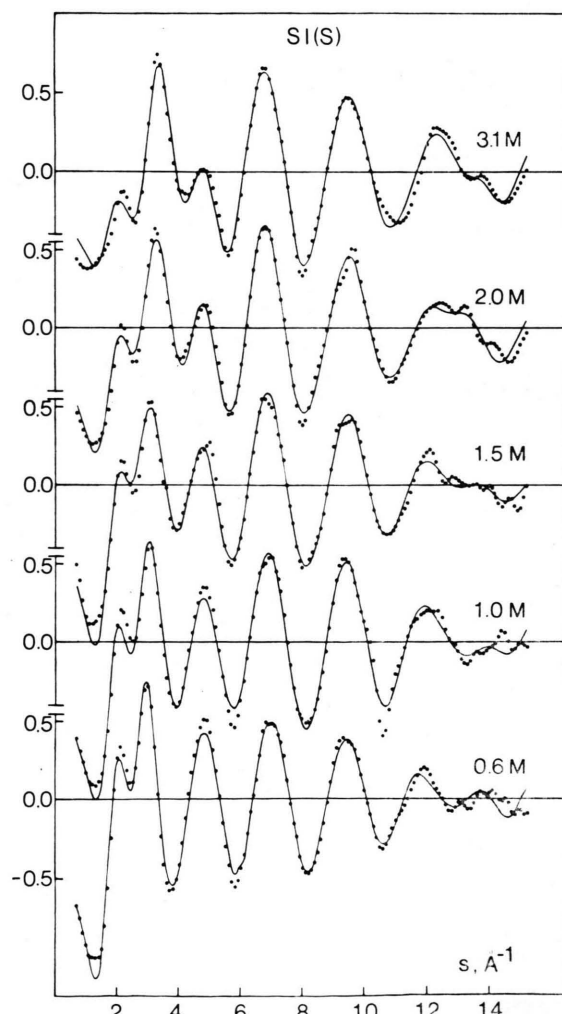


Fig. 2. Experimental (·····) and model (—) structure functions.

thought to come from interactions between Zn<sup>2+</sup> ions and water molecules in a second coordination shell.

An overview of the correlation functions obtained gives important information: no concentration effect on structural phenomena is detectable, except the obvious height variations in connection with the different amount of the various pair interactions.

A last consideration regards the sulphate ion. The five  $G(r)$  functions do not show evidence of sulphate-water or sulphate-cation interactions, thus suggesting that sulphate ions may only be involved in rather weak and poorly defined structural units. Undoubtedly, the various pair interactions contribute with different weight to the observed diffracted intensities and, as a consequence, are differently observable. As an example, we may notice that not even O—O interactions within the sulphate ion (at about 2.45 Å) give rise to a resolved peak in the correlation function, but they mingle with the right side of the Zn<sup>2+</sup>—H<sub>2</sub>O peak at 2.10 Å, making it slightly asymmetrical and preventing it from approaching zero around  $r = 2.5$  Å. In any case, it is quite clear that it will be very difficult to obtain reliable information on the sulphate ion structuring. This is in full agreement with the results obtained in a previous investigation [6] on the state of the sulphate ion in a ZnSO<sub>4</sub> 2 M aqueous solution.

## Discussion and Conclusions

For the quantitative analysis of the data, synthetic structure functions, calculated for the structural models adopted, were tested against experimental ones and systematically refined by least squares.

The synthetic structure functions were defined as:

$$i(s) = \sum_{i=1}^m \sum_{j=1}^{n_i} x_i f_i f_j \left( \sum_{i=1}^m x_i f_i \right)^{-2} \exp\left(-\frac{1}{2} \sigma_{ij}^2 s^2\right) \cdot \frac{\sin(s r_{ij})}{s r_{ij}} + 4\pi \rho_0 \sum_{i=1}^m \sum_{j=1}^m x_i x_j f_i f_j \left( \sum_{i=1}^m x_i f_i \right)^{-2} \cdot \exp\left(-\frac{1}{2} \sigma_{0ij}^2 s^2\right) \frac{s r_{0ij} \cos(s r_{0ij}) - \sin(s r_{0ij})}{s^3} \quad (1)$$

where

$m$  = number of atoms in the stoichiometric unit.

$n_i$  = number of atoms with discrete structure "seen" by an origin atom of the  $i$  type.

$r_{ij}$  = mean radial distance of  $j^{\text{th}}$  atom from an origin atom of the  $i$  type.

$\sigma_{ij}$  = mean square deviation for the distance  $r_{ij}$ .

$r_{0ij}$  = mean radius of the discrete structure of  $j$  atoms around one of the  $i$  type.

$\sigma_{0ij}$  = mean square deviation for  $r_{0ij}$ .

The first term in (1) derives from the discrete interactions within the model; interatomic distances, their mean-square deviations and, when unknown, their frequency factors are the parameters refined in this term. The second term accounts for the transition to a continuous distribution of distances; in it, the radii of the discrete structure around the different chemical species and their mean square deviations are the adjustable parameters.

The "experimental" structure functions here used are not the ones from which the correlation functions of Fig. 1 were obtained. In fact, at this point, the contribution of S—O interactions at 1.45–1.50 Å was removed from the structure functions, as this contribution is obvious and not important to the aims of the present study. As discussed elsewhere [9] this procedure allowed the structure functions to be corrected effectively for systematic errors.

As the overall inspection of the  $G(r)$  functions did not suggest the existence of concentration effects on the structure, the same model was used for all cases. According to literature information [4–5] and to results already obtained in our laboratory, a first coordination shell composed of six water molecules ( $w_1$ ) octahedrally arranged was assigned to the cation. In addition, a second shell of a non-fixed number  $N_{\text{Zn}^{2+}-w_2}$  of water molecules ( $w_2$ ) was included. Since the conformation of  $w_1$  water molecules is unknown, the distances  $r_{\text{Zn}^{2+}-w_1}$ ,  $r_{\text{Zn}^{2+}-w_2}$  and  $r_{w_1-w_2}$  were refined independently, together with their mean square deviation. When treating cationic hydration, another major contribution comes from water-water interactions within the first hydration shells; however, the corresponding distance is not an adjustable parameter, as it is related to  $r_{\text{Zn}^{2+}-w_1}$  in a way fixed by the geometry adopted, whereas its mean square deviation has been refined.

As far as the anion is concerned, there is the obvious contribution from intramolecular distances between the oxygen atoms of the tetrahedral sulphate ion (O<sub>S</sub>—O<sub>S</sub>). It seemed right to add an intermolecular contribution. In fact, though the experimental  $G(r)$ 's do not show evidence of intermolecular in-



teractions due to the anion, these have been found in some cases, for example in solutions of  $(\text{NH}_4)_2\text{SO}_4$  [10], so it does not seem realistic to replace them with a purely random distribution of distances. As a first attempt, the coordination shell around the sulphate ion was built with only water molecules. In fact, investigations on some sulphates ( $\text{Fe}_2(\text{SO}_4)_3$  [8],  $\text{In}_2(\text{SO}_4)_3$  [11],  $\text{CdSO}_4$  [12]), in which a noteworthy amount of ion pairs has been found, showed cation-S distances in peaks clearly observable in the total  $G(r)$ 's. In the cases in which the radii of the atomic species had values close to the one of  $\text{Zn}^{2+}$ , such peaks fell at 3.3–3.4 Å.  $\text{Zn}^{2+}$ -S contribution should then be expected around this distance, that is, where the  $G(r)$  functions show a deeper and deeper minimum with increasing concentration. A hydration shell has then been considered around the sulphate ion, and cation and anion hydration shells have been treated as independent one from the other. This approach is unlikely to give reliable structural parameters for sulphate-water interactions, but assuming a likely simulation of the structuring around the sulphate should permit in turn a more reliable study of the other interactions. In the hydration model of the sulphate the number of water molecules  $w_A$  around the central ion and the geometric arrangement were not fixed. Thus, each S atom interacts with  $N_{S-w_A}$  water molecules and each  $\text{O}_S$  atom in the anion interacts with  $N_{S-w_A}/4$  water molecules; distances and mean square deviations of the pairs S– $w_A$  and  $\text{O}_S$ – $w_A$  were refined.

Finally, the water not involved in hydration was accounted for by using a structure function ob-

tained from pure water and weighted according to the stoichiometric composition of the solution. This procedure, although quite common in this type of analysis, presents questionable aspects, as recently discussed by Pálkás et al. [13]. However, we verified that the replacing of the pure water structure function with  $\text{H}_2\text{O}$ – $\text{H}_2\text{O}$  contributions from aquo-complexes  $\text{H}_2\text{O}(\text{H}_2\text{O})_n$  does not modify the results about cation hydration significantly [6]. Furthermore, the problem of bulk water does not exist in the concentrated solutions at all, as in them the whole water is engaged in cationic and anionic hydration.

Calculations showed that the model proposed was consistent with experimental data in all the five solutions examined, thus confirming the lack of structural evolution with changing concentration. The structure functions obtained from best fit calculations in Fig. 2 together with the experimental ones; it can be seen that the agreement is quite good. The best fit values of the parameters describing the discrete interactions are reported in Table 2. The usual [14] agreement factor  $R$  is also reported for each case.

A close examination of the parameters reveals that in the case of the  $\text{Zn}^{2+}$  ion the values obtained for the different concentrations are very similar, not only as far as distances are concerned, but also regarding their mean square deviations as well. The only parameter that changes significantly is the number of water molecules forming the second hydration shell, namely  $N_{\text{Zn}^{2+}-w_2}$ . This number tends to decrease with increasing concentration, as expected as the number of water molecules available

	3.1 M	2.0 M CA	1.5 M	1.0 M	0.6 M
$r_{\text{Zn}^{2+}-w_1}$	2.125 (2)	2.115 (2)	2.121 (3)	2.144 (3)	2.131 (5)
$\sigma_{\text{Zn}^{2+}-w_1}$	0.101 (2)	0.098 (2)	0.113 (2)	0.089 (4)	0.107 (5)
$\sigma_{w_1-w_1}$	0.092 (7)	0.116 (8)	0.12 (1)	0.09 (2)	0.11 (2)
$r_{\text{Zn}^{2+}-w_2}$	4.22 (1)	4.212 (9)	4.25 (2)	4.22 (3)	4.26 (4)
$\sigma_{\text{Zn}^{2+}-w_2}$	0.24 (1)	0.258 (9)	0.33 (2)	0.4 (2)	0.34 (5)
$r_{w_1-w_2}$	2.764 (7)	2.803 (5)	2.794 (6)	2.777 (7)	2.792 (8)
$\sigma_{w_1-w_2}$	0.02 (3)	0.03 (2)	0.014 (9)	0.037 (9)	0.037 (9)
$N_{\text{Zn}^{2+}-w_2}$	7.6 (2)	9.9 (3)	10.3 (4)	13.2 (6)	12.5 (7)
$r_{\text{O}_S-\text{O}_S}$	2.489 (3)	2.471 (3)	2.487 (5)	2.54 (1)	2.54 (1)
$\sigma_{\text{O}_S-\text{O}_S}$	0.04	0.03	0.09	0.08	0.08
$r_{\text{O}_S-w_A}$	2.797 (7)	2.79 (2)	2.82 (1)	2.826 (9)	2.80 (1)
$\sigma_{\text{O}_S-w_A}$	0.038 (9)	0.14 (2)	0.08 (2)	0.06 (2)	0.07 (2)
$r_{S-w_A}$	3.84 (1)	3.88 (1)	3.91 (2)	3.95 (4)	3.83 (5)
$\sigma_{S-w_A}$	0.17 (1)	0.156 (8)	0.20 (1)	0.27 (2)	0.28 (2)
$N_{S-w_A}$	7.6 (4)	7.3 (4)	7.8 (6)	14.3 (8)	12.4 (9)
$R$	16.88	15.14	17.54	17.81	13.98

Table 2. Mean distances  $r(\text{\AA})$ , mean square deviations  $\sigma(\text{\AA})$  and frequency factors  $N$  for the discrete interactions, used in the final calculations of the synthetic structure functions, are given for the five solutions. Standard errors for the refined parameters are given in parentheses. In the last line the values of the agreement factor  $R$  are also reported.

to form a second shell decreases. The existence of quite ordered second hydration shells is supported by the present results. In fact, the distances  $r_{\text{Zn}^{2+}-\text{w}_2}$  and  $r_{\text{w}_1-\text{w}_2}$  appear to have surprisingly constant values. The latter distance, though superimposed on 0-0 distances from different interactions, tends to assume values shorter than 2.80 Å, that is, shorter than the water-water distance in pure water, thus suggesting the formation of quite strong and directional H-bonds (see also the low value of the relative  $\sigma$ ). All these observations are in good agreement with previous results obtained in solutions of di- and trivalent ions [1].

The parameter values describing anion structure are on the whole less satisfactory. In particular: a)  $\text{O}_\text{S}-\text{O}_\text{S}$  distances undergo variations that can hardly be thought as connected to true structural modifications within sulphate ions; b) the hydration number  $N_{\text{S}-\text{w}_A}$  appears poorly defined. The results coming from the more dilute solutions are the most singular ones, also when compared with literature information [8, 11, 12]. Here, the uncertainty of the results is surely due to the light weight of the terms in the structure functions that describe the solute (it is worth noting that the investigation here presented extends to solutions of concentration less than 1 M, for which diffraction data are essentially non-existing). This uncertainty, however, is not surprising. In a study on the observability of the sulphate ion in a 2 M solution of  $\text{ZnSO}_4$  [6], some of us reached the conclusion that "the X-ray diffraction method is unable to provide results capable of unambiguous modelling of the  $\text{SO}_4^{2-}$  coordination; even the complete omission of sulphate-water interactions does not lead to unsatisfactory synthetic structure functions". Besides, "some characteristics of the best models can be affected by differences in experimental data that are within the limits of experimental uncertainties". This considered, attributing precise meaning to the parameters which describe the anion, seems, in our opinion, a little rash. This statement may seem in contradiction with the rather low values obtained for the standard errors associated with the parameters. But, as already remarked [15], the standard errors obtained from computer programs are not completely indicative of the reliability of the structural parameters. The parameter uncertainty is better determined by the variations that the parameters undergo when repeating data collections or when

examining sets of data collected in various laboratories, and the previous observations [6] point to a not negligible uncertainty as far as the anion is concerned.

The quality of the results seems not to be affected by the way in which bulk water has been taken into account, when present. The R values are in fact randomly distributed, and, anyway, the best result has been obtained in the case of the most dilute solution where a rough treatment of bulk water should have given rise to a poor agreement.

The consistency of the model used with the experimental data does not rule out alternative models. In particular, a model in which ion pairing is taken into account deserves to be tested. In fact, there are some physico-chemical and spectroscopical investigations which predict inner or outer sphere complex-formation in aqueous transition metal sulphate solutions; the lack in the  $G(r)$ 's of peaks which specifically indicate  $\text{Zn}^{2+}$ -S distances, might come from the poor resolution of the total correlation functions. These tests showed that even models including complex-formation are consistent with experimental data, but there is no reason to prefer them to those previously adopted. In fact: a) the variation of the agreement factor R is not sufficiently great; b) the number of independent parameters increases without eliminating the anomalies observed in some parameters. Clearly, these anomalies do not come from the need of a better model but from the intrinsic difficulty in defining the less important parameters. This again shows the difficulty of describing exhaustively the state of the sulphate ions.

In conclusion we summarize the information obtained by the present study: The first coordination shell of  $\text{Zn}^{2+}$  ions has been described with noteworthy reliability both as regards  $\text{Zn}^{2+}$ -O distances and mean square deviations. The existence of order beyond the first cationic coordination shell is a necessary condition for reaching good agreement between model and experimental data. The hydration of sulphate ions is certainly consistent with experimental data but the relative parameters appear rather uncertain. Finally the occurrence of complex formation neither can be confirmed nor ruled out.

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