Structure Investigation into Acetonitrile Solutions of $Mg(ClO_4)_2$ by Neutron Diffraction

U. Hoppe * and W. Matz

Zentralinstitut für Kernforschung der AdW der DDR, Rossendorf

Z. Naturforsch. **39 a**, 437–440 (1984); received January 23, 1984

The structure of acetonitrile solutions of $Mg(ClO_4)_2$ at two concentrations ($c = 0.38$ mole/l and 0.74 mole/l) is studied by neutron diffraction. The results are interpreted by a simple structure model. A good description is achieved for $c = 0.38$ mole/l by an octahedral surrounding of Mg^{2+} by acetonitrile molecules. For the higher concentration the fit results in a mixture of tetrahedral and octahedral surroundings.

1. Introduction

In the last decade there was a rapid progress in the investigation of aqueous solutions by diffraction methods. Sophisticated models [1] for the interpretation of x-ray diffraction data have been used. In connection with the operation of powerful neutron sources it became possible to reach detailed information about the first sphere of hydration by means of isotopic exchange of solute ions [2].

In case of non-aqueous solutions, the use of diffraction methods is limited by the high portion of intramolecular scattering and the low accessible solute concentrations. For the highest concentrations there are many different associated ions in the solutions [3]. We have studied solutions of $Mg(ClO_4)_2$ in acetonitrile (AN). AN has a sufficiently simple molecular structure. There are no hydrogen bridges and consequently no strong intermolecular orientations. It seems that most of the structural effects in such solutions are caused by the big dipole moment of CD_3CN and the ionic charges of the solute. In order to prevent the difficulties mentioned above we did choose concentrations of 0.39 mole/l and 0.74 mole/l.

2. Experimental and Data Reduction

The solutions were prepared from deuterated acetonitrile (degree of deuterisation 99.2%) and $Mg(ClO_4)_2 \cdot 6\,H_2O$. The latter was dried until the weight remained constant. The measured densities of the two solutions are given in Table 1*. For the neutron diffraction experiments a cylindrical container of silica with an inner diameter of 9.2 mm and a wall thickness of 0.3 mm was used. The experiments were performed at room temperature with neutrons of $\lambda = 0.096$ nm. The measured intensities from $8° \leqq 2\vartheta \leqq 92°$ were converted into a Q-scale ($Q = 4\pi \sin\vartheta/\lambda$) with $\Delta Q = 1\ \mathrm{nm}^{-1}$. The averaged intensity per point was about 130 000 counts, where background and container scattering amounted to about 30 000 counts. After substracting background the attenuation correction was performed according to Paalman & Pings [4]. The multiple scattering was estimated after Blech & Averbach [5] to be about 25%. The curves corrected as described are displayed in Figure 1.

The existence of light atoms in the sample makes it impossible to estimate the dynamic correction for the self scattering contribution by the method given in [6]. The general form is $A + B\,Q^2$, where A/B can be calculated according to the law of the neutron detector. A parameter describing an effective mass was determined together with the calibration factor.

Table 1. Measured densities and concentrations of the samples (at 20 °C).

Moles $Mg(ClO_4)_2$ per mole acetonitrile	Density ($g \cdot cm^{-3}$)	Molecules AN per nm^3	Molarity (mole/l)
0.00	0.782	11.48	0.00
0.02	0.860	11.39	0.38
0.04	0.923	11.13	0.74

* The neutron measurements were performed on the research reactor RFR at Rossendorf.

* On leave from Wilhelm-Pieck-Universität Rostock.

Reprint requests to Dr. W. Matz, ZfK Rossendorf, DDR-8051 Dresden, PF 19.

0340-4811 / 84 / 0500-0437 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

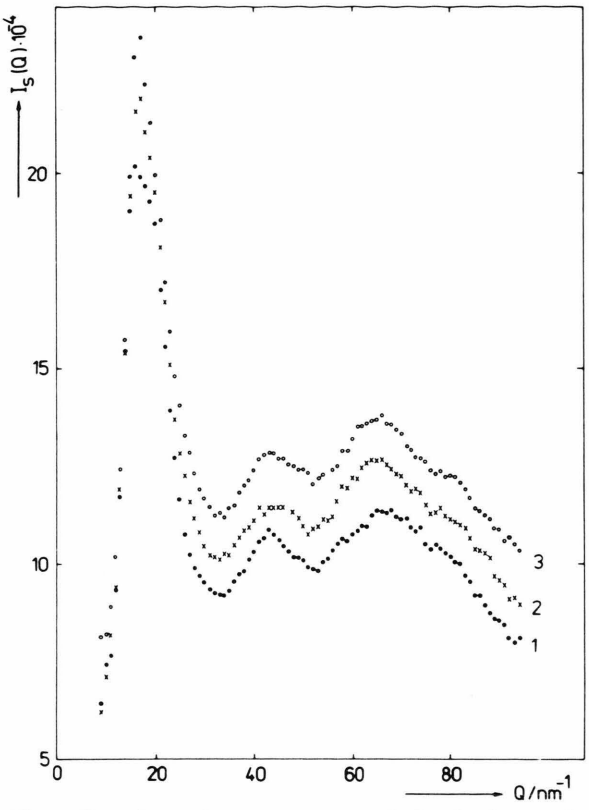

Fig. 1. Experimental spectra corrected for background, absorption and multiple scattering for the solvent (1) and the solutions with 0.38 mole/l (2) and 0.74 mole/l (3). Curves 2 and 3 are shifted by 1 and 2 units of abszissa scale, respectively.

Small oscillations in the dynamical correction, caused by intramolecular interferences [7] have been neglected. Calibration was done by adapting the curves of Fig. 1 in the region from 65 to 84 nm^{-1} to a model for the static structure factor. For this procedure the structural data for CD_3CN [8] and ClO_4^- [9] have been fixed, because the measured Q-region is too limited for the determination of the molecular structure too. The calculations were performed with a quantity $F(Q)$ which is proportional to the structure factor

$$F(Q) = F_{AN}^{intra}(Q) + 2\,C\,F_{anion}^{intra}(Q) + \langle b_{Mg}^2 \rangle \quad (1)$$

with

$$F_\chi^{intra}(Q) = \sum_{i \neq j} [\langle b_i \rangle \langle b_j \rangle j_0(Q r_{ij}) \cdot \exp(-Q^2 \gamma_{ij}^2/2)] + \sum_i \langle b_i^2 \rangle ,$$

where c is the mole ratio solute-solvent, b_i the scattering length, γ_{ij} the r.m.s. deviation, r_{ij} the distance between atoms i and j, and $j_0(x) = \sin x/x$. The sum runs over all atoms of the AN molecule and the ClO_4^--ion, respectively.

3. Analysis of the Experimental Results

Because of the small differences in the structure factor and the limited Q range of the measurements a Fourier transform seems to give no new information. So we will discuss a simple model in terms of the structure factor.

Suppose that at higher Q the structure of the molecule only describes the structure factor. For lower Q there are also interferences from neighbouring molecules. The interaction of the solvent's dipoles with the smaller Mg^{2+} ions will be substantially greater than with the single charged greater perchlorat ions.

Around the anions there should be no well defined arrangements. The cations can be symmetrically surrounded by 3, 4, 6 or 8 CD_3CN. The nitrogen of CD_3CN is directed to the cation, so that the latter lies in the direction of the molecular axis. The intermolecular structure factor of the solvent not included in solvation spheres is assumed to be the same as in the pure solvent. Then the model is described by

$$F_{mod}(Q) = F_{AN}^{exp}(Q)\,(1 - K\,C) + 2\,C\,F_{anion}^{intra}(Q) + C\,F_{solv}(Q) + K\,C\,F_{AN}^{intra}(Q) . \quad (2)$$

$F_{AN}^{exp}(Q)$ is derived from the experimental data of the solvent; K is the number of AN-molecules in the arrangement around the cations. The intermolecular part of the cation complex is given by

$$F_{solv}(Q) = \langle b_{Mg}^2 \rangle + \sum_{i \neq j} \langle b_i \rangle \langle b_j \rangle j_0(Q r_{ij}) \cdot \exp[-(\delta Q r_{ij})^2/2] . \quad (3)$$

The sum runs over all intermolecular distances between Mg, C, and N, respectively. The distances to the deuterium were summed up only with respect to Mg^{2+}. The other distances are not properly fixed because the rotations around the molecular axes are not hindered. All the r_{ij} can be derived from r_{MgN} according to the symmetry. δ is the ratio of the r.m.s. deviation γ_{ij} and the distance r_{ij}. δ was assumed to be equal for all distances. This simple statement was used by other authors also [10]. For different K ($K = 0$ included) the figures for r_{MgN}

Table 2. Best parameters from the fit procedure.

c	K	r_{MgN} (nm)	δ
0.02	6	0.225(1)	0.028
0.04	4	0.195(1)	0.023
0.04	6	0.222(1)	0.067

and at the minimum of ε, where

$$\varepsilon = \left\{ \sum_Q [F_{exp}(Q) - F_{mod}(Q)]^2 / \sum_Q F_{exp}^2(Q) \right\}^{1/2},$$

have been calculated. The fit was performed in the region from 30 to 94 nm^{-1}. Table 2 gives the parameters of the models.

Figure 2 shows $\Delta F_{exp}(Q)$ and $\Delta F_{mod}(Q)$ for the tetrahedral and octahedral arrangements of AN in the solution with $C = 0.04$

$$\Delta F_{exp}(Q) = F_{exp}(Q) - (1 - KC)\, F_{AN}^{exp}(Q),$$

$$\Delta F_{mod}(Q) = C\,(2\,F_{anion}^{intra}(Q) + K\,F_{AN}^{intra}(Q) + F_{solv}(Q)).$$

A better fit to the experimental results can be obtained by a mixture of both types of AN arrangements around the cation. The contribution of the tetrahedral solvation sphere is 0.6 (1) with $r_{MgN} =$ 0.199 (1) nm and $\delta = 0.03$.

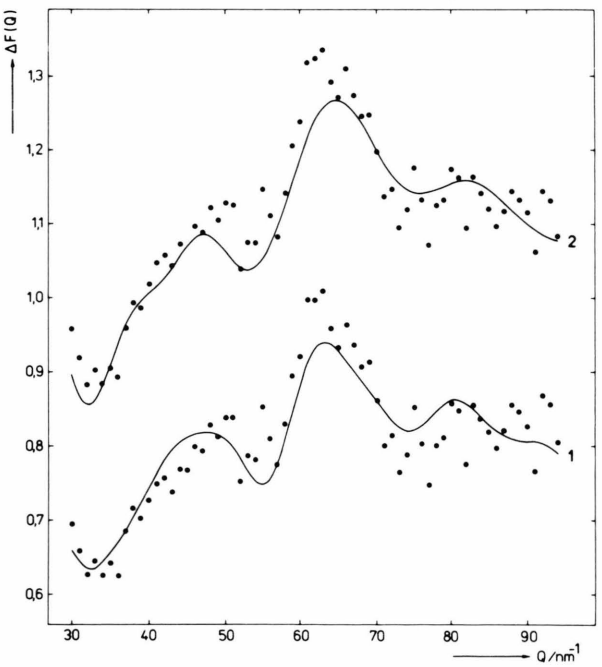

Fig. 2. Experimental scattering contribution ΔF of the ions and the solvation spheres (points) for the solution with 0.74 mole/l. The lines were calculated for tetrahedral (1) and octahedral (2) arrangements of AN around Mg^{2+}, respectively.

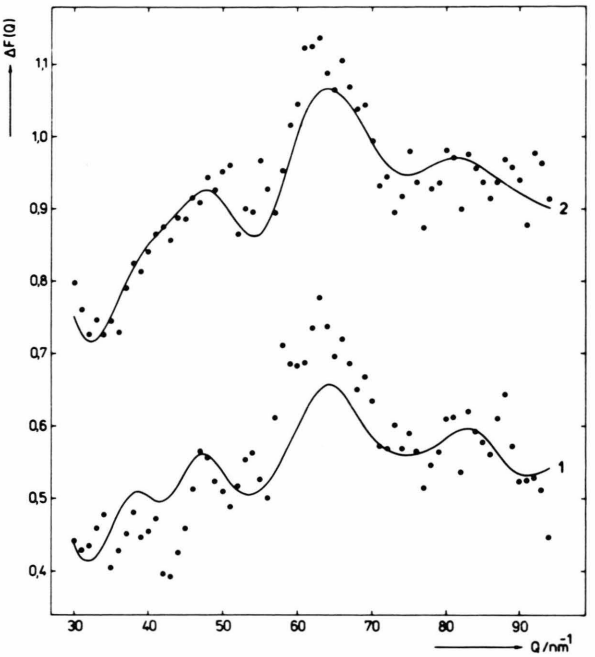

Fig. 3. Comparison of the experimental scattering contribution ΔF of the ions and the solvation complexes (points) with the best model fits for 0.38 mole/l (1) and 0.74 mole/l (2).

The remaining Mg^{2+} ions are surrounded by an octahedral arrangement with $r_{MgN} = 0.219$ (2) nm and $\delta = 0.05$. The corresponding curve for the optimal mixture of the two types of neighbourhood is shown in Fig. 3 (curve 2). For the solution with $c = 0.02$ a reasonable fit was achieved with octahedral arrangements only (Fig. 3, curve 1).

The ε-values vary in the range from 0.009 to 0.018. The small differences follow from the low contribution to the structure factor from cations with their solvation spheres at the given concentrations. On the other hand, ε is not very sensible against small variations of structural parameters because of the moderate statistical accuracy of the experimental data.

4. Conclusion

The available experimental results allow for the study of simple models of the structure of non-

aqueous solutions only. The investigation of more sophisticated models calls for higher experimental accuracy (higher neutron fluxes) and more exact correction procedures.

The interpretation of x-ray diffraction data from nonaqueous solutions is also difficult. Nevertheless x-ray experiments are desired in order to use the different contrast to get detailed information about the structure of such solutions.

Acknowledgement

We thank Drs. Kelm and Tutschhu for advices on the preparation of the samples.

[1] G. Pálinkás, T. Radnai, and F. Hajdu, Z. Naturforsch. **35 a,** 107 (1980).
[2] J. E. Enderby and G. W. Neilson, Rep. Prog. Phys. **44,** 593 (1981).
[3] D. W. James and R. E. Maves, Aust. J. Chem. **35,** 1775 (1982), and 1785 (1982).
[4] H. H. Paalman and C. J. Pings, J. Appl. Phys. **33,** 2635 (1962).
[5] I. A. Blech and B. L. Averbach, Phys. Rev. **137,** 1113 (1965).
[6] J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, Phys. Rev. **A7,** 2130 (1973).
[7] L. Blum and A. H. Narten, J. Chem. Phys. **64,** 2804 (1976).
[8] H. Bertagnolli, P. Chieux, and M. D. Zeidler, Molec. Phys. **32,** 759 (1976).
[9] R. Caminiti and G. Johansson, Acta Chem. Scand. **A35,** 373 (1981).
[10] N. Ohtomo and K. Arakawa, Bull. Chem. Soc. Japan **51,** 1649 (1978).