X-Ray Diffraction Study of $MgCl_2$ in Methanol

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The structure of a concentrated solution of $MgCl_2$ in methanol has been studied by X-ray diffraction. The parameters for the ion-solvent interactions are in good agreement with those found in aqueous solutions. Both for Mg^{2+} and Cl^- the solvate shells are composed of 6 methanol molecules. An average octahedral arrangement of OH groups in the solvate shells of magnesium is probable. Octahedral symmetrical positions for CH_3 groups proved to be unlikely.

Introduction

Many X-ray studies on the structure of aqueous solutions have been performed with the aim to describe the ion-water, water-water and ion-ion interactions, but the method was very seldom applied for salts in organic solvents. Methanol may be a subject of special interest, because firstly it is a typical liquid with strongly H-bonded structure, and secondly each molecule contains also a significant hydrophobic part. Only two relevant X-ray works on the structure of methanolic solutions can be found in the literature: a more recent study of iron (III) chloride [1] and another one of mercury (II) chloride [2] as a part of a more extended examination of complex formaton with Hg^{2+}.

The structure of aqueous solutions of $MgCl_2$ was studied by X-ray diffraction [3], and also by X-ray diffraction combined with computer simulation (molecular dynamics) method [4]. In the latter work, beyond the description of the average structure by two consecutive hydration shells around the cations and one around the anions, a detailed analysis of the symmetry properties of the first ionic hydration shells and the many-particle distribution of the neighbouring water molecules were presented. The average orientation of the hydrate molecules was also studied by molecular dynamics [5]. The same average structure in the two cationic hydration shells was found in a $Mg(NO_3)_2$ aqueous solution [6]. As concerns the Cl^- ion, it is one of the ions most frequently studied in aqueous solutions, and a very similar structural picture of its hydration shell was found in various solutions [7, 8, 9].

An X-ray diffraction study of a highly concentrated $MgCl_2$ solution (1.44 molar) in methanol is reported here. $MgCl_2$ was chosen because the ion-solvent interactions were already exhaustively studied in its aqueous solutions, and the salt is highly soluble both in water and methanol without having a significant tendency to form ion-pairs. The aim of the work was to determine the structure of the solvation shells both for the Mg^{2+} and the Cl^- ions and to decide whether differences can be observed between the solvation and hydration structures.

Both pure water and methanol have strongly H-bonded structures, but with significant differences due to the number of sites offered by a molecule for H-bridges (4 in water, 3 in methanol). For decreasing eventual disturbing effects in the evaluation of the solvation, arising from the rest solvent, a high concentration was chosen where the original structure of methanol can be assumed as damaged (the so called "chains" disrupted with a high probability).

Experimental and Data Treatment

The solution was prepared from methanol of high purity and anhydrous $MgCl_2$ salt. The water content of the solution was less than 1%. The stoichiometric ratio $MgCl_2 : CH_3OH$ was 1 : 18.7. The density of the solution was 0.8412 gcm^{-3} at room temperature.

The X-ray diffraction experiment was performed using transmission geometry and Mo K_α radiation with a flat monochromator in the primary beam.

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The measurement technique as well as the details of the data elaboration were described elsewhere [10]. The plane-parallel windows of the specimen holder had been prepared from 75 μm thick mylar foils at a distance of 1.2 mm. The data registration extended over a range $0.1 \leqq k \leqq 15\ \text{Å}^{-1}$ with a scattering variable $k = (4\pi/\lambda) \sin \vartheta$, where $\lambda = 0.711$ Å is the wavelength of the incident radiation and 2ϑ the scattering angle. Two parallel measurements were performed. In the first one the measured intensities were collected in equidistant steps with an increment $\Delta k = 0.05\ \text{Å}^{-1}$ and $4 \cdot 10^5$ counts at each point. Afterwards it was repeated with $\Delta k = 0.1\ \text{Å}^{-1}$ and $2 \cdot 10^5$ counts. The reproducibility was excellent except the highest scattering angles. Therefore, the data above $k = 13\ \text{Å}^{-1}$ were not used for the structural interpretation, although all measured points were used in the elaboration of the data.

The measured intensities were corrected for background, polarization, absorption and Compton scattering. The Compton intensities needed for the corrections were calculated with analytical formulas [11].

The experimental structure function, shown in Fig. 1, is given by

$$H_{\text{exp}}(k) = \left[I(k) - \sum_{\alpha} x_\alpha f_\alpha^2(k) \right] \Big/ \left[\sum_{\alpha} x_\alpha f_\alpha(k) \right]^2, \quad (1)$$

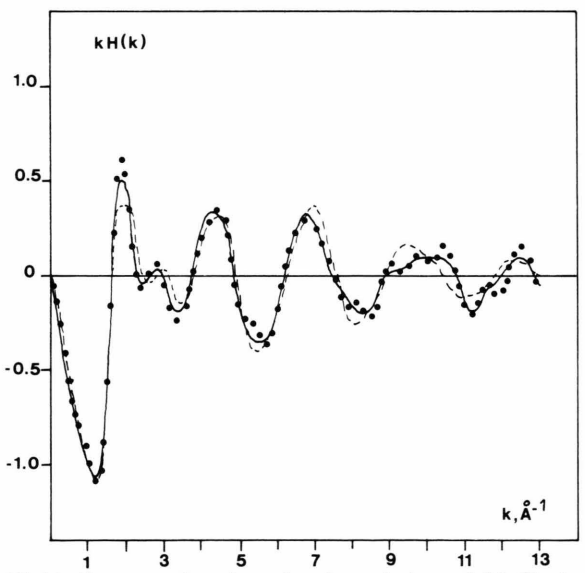

Fig. 1. Structure functions for the solution of $MgCl_2$ in methanol: experimental (dots) and theoretical (full line: LSF1, dashed line: LSF2).

where $I(k)$ is the corrected coherent intensity of the scattered beam in absolute units, and $f_\alpha(k)$ and x_α are the scattering amplitude and mole fraction, respectively, for a type α particle. The scattering amplitudes were computed in an analytical form, the parameters of which were taken from [12] for Mg^{2+} and Cl^-. Due to the small sensitivity of X-rays for the H atoms, the methanol molecule was assumed as consisting of two scattering centers, namely OH and CH_3, denoted in this paper by O and Me, respectively, for brevity. The parameters for the corresponding scattering amplitudes were taken from [13].

The experimental pair-correlation function, shown in Fig. 2, was computed from $H_{\text{exp}}(k)$ by Fourier transformation according to

$$G(r) = 1 + \frac{1}{2\pi^2 \varrho_0} \int_{k_{\min}}^{k_{\max}} k^2 H(k) j_0(k r)\, \mathrm{d}k, \quad (2)$$

where r is the interatomic distance, $k_{\min}$ and $k_{\max}$ are the lower and upper limits of the experimental data, ϱ_0 is the bulk number density of the stoichiometric units, and j_0 is the zeroth order spherical Bessel function. After repeated Fourier transformations when the nonphysical peaks present in the $G_{\text{exp}}(r)$ at small r values were removed, the structure function was corrected for residual systematic errors. In this process the peak due to the intramolecular Me–O distance, centered at about 1.45 Å, was also removed.

Determination of the Structural Parameters and Results

A pronounced and well resolved peak is present in the experimental pair correlation function at about 2.1 Å (Fig. 2). Since its position is in agreement with the magnesium-oxygen first neighbour distances found in aqueous solutions [3, 4], it is to be assign to the Mg–O interactions. For the quantitative evaluation of these interactions, a least-squares fit procedure was applied with the analytical formula for the corresponding theoretical correlation function (see Eq. (17) of [14]):

$$g_{\text{Mg-O}}(r) = \frac{\bar{c}_{\text{Mg-O}}}{\sqrt{32\pi^3}} \frac{n_{\text{Mg-O}}}{\varrho_0 x_{\text{O}} r_{\text{Mg-O}} l_{\text{Mg-O}}} \frac{1}{r} \cdot \left\{ \exp\left\{ -\frac{(r - r_{\text{Mg-O}})^2}{2 l_{\text{Mg-O}}^2} \right\} - \exp\left\{ -\frac{(r + r_{\text{Mg-O}})^2}{2 l_{\text{Mg-O}}^2} \right\} \right\} \quad (3)$$

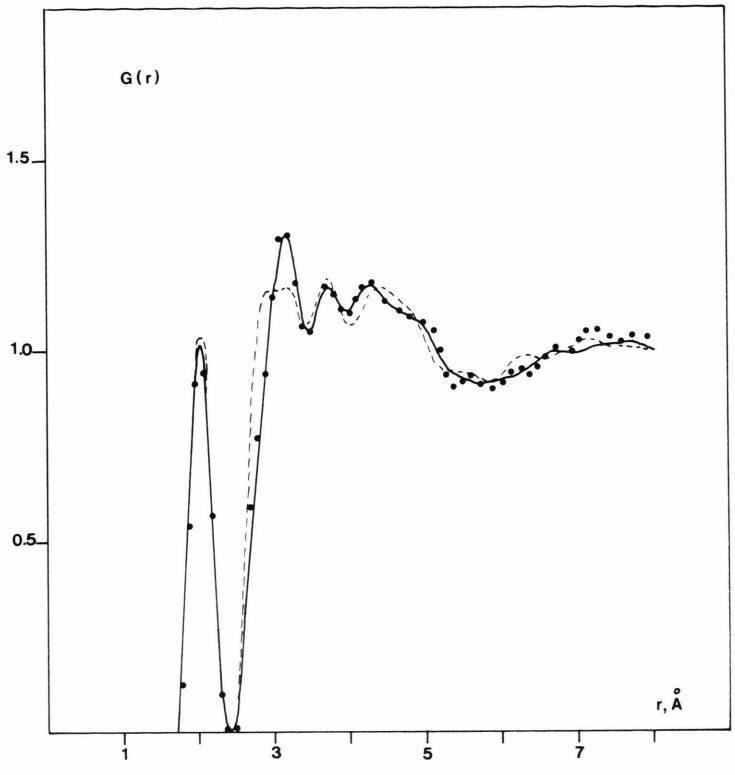

Fig. 2. Pair-correlation functions for the solution of $MgCl_2$ in methanol: experimental (dots) and theoretical (full line: LSF1, dashed line: LSF2).

where r_{Mg-O}, l_{Mg-O} and n_{Mg-O} are the mean distance, its root mean square deviation (rmsd) and the coordination number, respectively, and $\bar{c}_{Mg-O}$ is the average weight for the Mg–O contribution to the structure function. The k-dependent weights, and their averages are defined by

$$c_{\alpha\beta}(k) = \left[(2-\delta_{\alpha\beta})\, x_\alpha x_\beta f_\alpha(k) f_\beta(k)\right] \Big/ \left[\sum_\alpha x_\alpha f_\alpha(k)\right]^2,$$

$$\bar{c}_{\alpha\beta} = \frac{\int c_{\alpha\beta}(k)\,\mathrm{d}k}{\int \mathrm{d}k} \qquad (4)$$

and are given in Fig. 3, and Table 1, respectively, for the most important α, β pairs. Replacing the $c_{Mg-O}(k)$ function by its average $\bar{c}_{Mg-O}$ in order to avoid the deconvolution process invoked by the Fourier-transformation is satisfying due to the slight k-dependence of the given weight.

The resulting parameters are: $r_{Mg-O} = 2.068$ Å, $l_{Mg-O} = 0.124$ Å and $n_{Mg-O} = 5.95$. The contribution of the Mg–O interaction to the structure function was computed by

$$k\, h_{Mg-O}(k) = k\, \varrho \int (g_{Mg-O}(r) - 1)\, j_0(k\, r)\, \mathrm{d}r. \qquad (5)$$

A "distinct" structure function could then be derived as

$$k H_A(k) = k H_{exp}(k) - k\, h_{Mg-O}(k). \qquad (6)$$

Both $k\, h_{Mg-O}(k)$ and $k H_A(k)$ are shown in Figure 4. The high frequency ripples observed in $k H_A(k)$ at $k > 8$ Å^{-1} are without reliable structural information, the derivation of the above three parameters from the correlation function has to be regarded as relevant. Moreover, the given k-range is enough extended for the structural interpretation.

The short-range structural order does not extend beyond 5 Å, as it can be seen from the $G_{exp}(r)$ function. The highest peak is at about 3.2 Å, which corresponds to the first neighbour chloride-oxygen

Table 1. Average weights $\bar{c}_{\alpha\beta}$ for the main contributions to the structure function (in percentages).

Me–O	O–O	Cl–O	Me–Me	Cl–Me	Mg–O	Mg–Me	sum
32.77	31.84	12.97	12.51	9.79	3.89	2.89	96.66

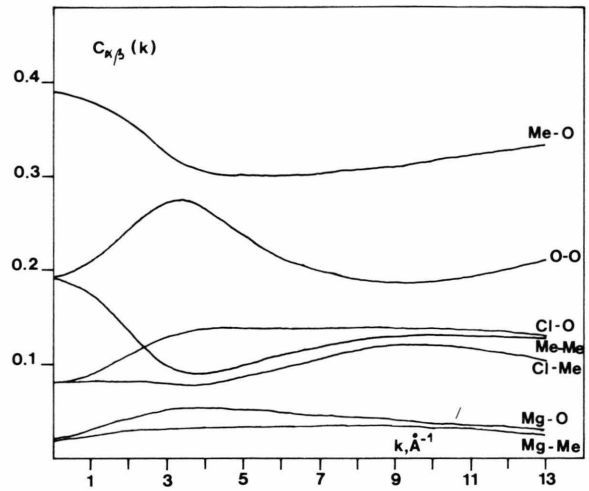

Fig. 3. Weighting functions $c_{\alpha\beta}(k)$ for the main contributions to the structure function as a function of the scattering variable.

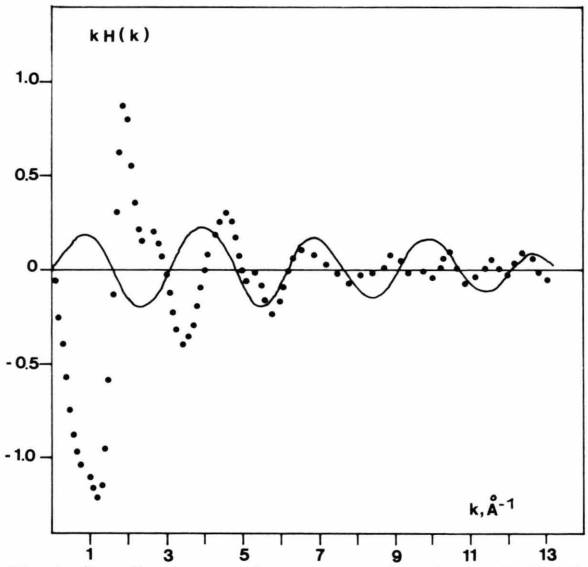

Fig. 4. Contributions to the structure function: calculated for the Mg–O interaction (full line) and distinct structure function $kH_{\Delta}(k)$ (dots).

interaction found in aqueous solutions. The remaining peaks are composite ones, their assignment is not obvious. It is striking that the predominant peak usually detected at about 2.7–2.85 Å in water and aqueous solutions as well as in methanol, due to the H-bonded oxygen-oxygen distances, is absent here. The slight left-wing broadening of the main peak can be attributed to some minor contribution from O–O interactions, but Mg-Me interactions can also fall into this region.

For a more complete description of the structure two least-squares fit procedures were applied, referred to as LSF1 and LSF2, respectively. In both procedures theoretical structure functions with adjustable parameters were computed according to the formulas

$$H_{\mathrm{th}}(k) = H_{\mathrm{d}}(k) + H_{\mathrm{c}}(k),$$

$$H_{\mathrm{d}}(k) = \sum_{\alpha\beta i} \varrho_0 c_{\alpha\beta}(k) \frac{n_{\alpha\beta i}}{x_{\beta}} \Delta_0(k r_{\alpha\beta i}, l_{\alpha\beta i}),$$

$$H_{\mathrm{c}}(k) = -\sum_{\alpha\beta} \frac{4\pi\varrho_0}{k} R_{\alpha\beta}^2 c_{\alpha\beta}(k) \Delta_1(k R_{\alpha\beta}, L_{\alpha\beta}),$$

$$\Delta_m(k r, l) = j_m(k r) \exp[-\tfrac{1}{2} l^2 k^2], \qquad (6)$$

where α, β refers to scattering centers of different chemical types, i is the sequence number of interactions of α, β type involved in the procedure, and j_m is the mth order spherical Bessel function. The subscripts d and c stand for the "discrete" and the "continuum" parts usually applied in the X-ray structural analysis of liquids. The adjustable parameters were the $r_{\alpha\beta i}$ distances, their $l_{\alpha\beta i}$ rmsd-s, the $n_{\alpha\beta i}$ coordination numbers for the $H_{\mathrm{d}}(k)$ function, and $R_{\alpha\beta}$ and $L_{\alpha\beta}$ for defining the boundary of the uniform distribution of α, β type distances and its rmsd, respectively, for the $H_{\mathrm{c}}(k)$ function.

The minimum condition for the least-squares fits was fixed as

$$U = \sum_{k} [k H_{\mathrm{exp}}(k) - k H_{\mathrm{th}}(k)]^2 = \text{minimum}. \qquad (7)$$

In LSF1 no starting geometrical picture was assumed for the structure. An examination of the weights of the contributions to the structure function shows that the ion-ion type interactions are negligible compared with the other ones. Their ignoration is also supported by the known slight tendency of $MgCl_2$ to form ion-pairs in solutions. Thus, in LSF1, one contribution for each type was involved both in $H_{\mathrm{d}}(k)$ and $H_{\mathrm{c}}(k)$, i.e. $i = 1$, with the exclusion of the ion-ion types. As a consequence of the not prefixed geometry, the $n_{\alpha\beta}$ coordination numbers were free parameters.

The resulting $kH_{\mathrm{th}}(k)$ and $G_{\mathrm{th}}(r)$ functions are shown in Figs. 1 and 2, respectively. The structural parameters are given in Table 2.

A possible model interpretation of the results from the LSF1 procedure seems to be plausible because: i) each Mg^{2+} ion is surrounded by 6

Table 2. Structural parameters for the $MgCl_2$ solution in methanol derived from the LSF1 procedure with the estimated errors in the last digits. The distances and rmsd values are given in Å.

	$r_{\alpha\beta}$	$l_{\alpha\beta}$	$n_{\alpha\beta}$	$R_{\alpha\beta}$	$L_{\alpha\beta}$
Mg–O	2.065(3)	0.109(5)	5.9(1)	3.35(8)	1.1(3)
Mg–Me	2.78(1)	0.12(2)	6.4(2)	3.50(5)	0.6(1)
Cl–O	3.15(2)	0.20(2)	6.0(1)	3.90(5)	0.05(2)
Cl–Me	4.33(3)	0.22(2)	6.7(2)	6.5(2)	0.02(1)
O–O	3.77(2)	0.24(2)	4.4(1)	4.2(1)	0.15(2)
Me–Me	4.83(5)	0.24(2)	5.8(2)	5.1(3)	0.60(5)
Me–O	3.33(3)	0.39(4)	1.1(1)	2.9(1)	0.8(2)

Table 3. The same as in Table 2, for the LSF2 procedure. Distances and coordination numbers derived from the independent parameters and the assumed geometry are given in parenthesis. The subscripts + and − refer to the solvation shells of the cation and anion, respectively.

	$r_{\alpha\beta}$	$l_{\alpha\beta}$	$n_{\alpha\beta}$	$R_{\alpha\beta}$	$L_{\alpha\beta}$
Mg–O	2.068(3)	0.112(5)	(6)	3.39(7)	0.011(4)
Mg–Me	2.78(1)	0.07(1)	(6)	3.30(5)	0.01
Cl–O	3.18(3)	0.25(3)	(6)	3.19(4)	0.20(5)
Cl–Me	4.47(3)	0.39(3)	(6)	6.79(9)	0.01
$(O-O)_+$	(2.93)	0.16(2)	(4)	3.05(2)	0.01
$(O-O)_-$	(4.51)	0.35(3)	(4)	–	–
$(Me-Me)_+$	(3.93)	0.07(1)	(4)	3.24(2)	0.04(2)
$(Me-Me)_-$	(6.32)	0.35(4)	(4)	–	–
$(Me-O)_+$	3.68(2)	0.04(1)	2.28(5)	4.17(4)	1.5(2)
$(Me-O)_-$	5.25(5)	0.26(3)	0.84(7)	–	–

methanol molecules turning with their oxygens towards to the cation, ii) a relatively rigid octahedral structural unit for the cationic solvate shell is supported by the sixfold coordination, the small rmsd values and the number of the closest Me–O between the neighbouring methanol molecules (1.1), iii) each Cl^- ion is also solvated by 6 methanol molecules as to be seen from the Cl–O and Cl–Me parameters, iv) the chemical type of the Cl–O interactions (via the hydrogens of the OH groups) as well as the larger distances and rmsd values make the regular octahedral geometry for the anionic solvate shells less probable.

For the sake of an additional reliability check of the Mg–O interaction, the LSF1 procedure was repeated for the distinct $kH_A(k)$ function, with the omission of the Mg–O contribution to $kH_{th}(k)$. The same quality of fit was reached without significant changes in the structural parameters. This indicates that the other contributions do not influence really the upper k range beyond $k = 8$ Å^{-1}.

In LSF2 an octahedral geometry was assumed for the solvate shells both of the cation and the anion. Accordingly, the O and Me centers should occupy the vertices of two octahedra around each ions. Therefore, new O–O and Me–Me type interactions had to be introduced with distances calculated from the adjusted Mg–O, Mg–Me, Cl–O and Cl–Me distances and from the supposed geometry. Since the corresponding coordination numbers were also fixed, only two new rmsd values were taken as free parameters. Moreover, due to the different sizes of the cationic and anionic solvate shells, two contributions were included for the Me–O interactions of closest contacts between the neighbouring solvate molecules instead of the one in LSF1, with 3 additional parameters. Further on, 4 new rmsd values were attributed to the O–O and Me–Me trans-distances of the octahedrons, respectively.

The resulting $kH_{th}(k)$ and $G_{th}(r)$ functions are also shown in Fig. 1 and 2, respectively. The structural parameters are given in Table 3.

Discussion and Conclusions

In spite of the additional 9 independent parameters introduced in LSF2 compared with LSF1, the least-squares sum is significantly higher (the usual R-factor 0.29 instead of 0.14) and the agreement between the theoretical and experimental structure and correlation functions is considerably worse. These observations already indicate that the assumption of a prefixed octahedral symmetry is too rigorous.

The parameters describing the cation-solvent first neighbour interactions from the two LSF procedures are in fairly good agreement. The Mg–O parameters are the same within the limit of standard errors as obtained from the direct evaluation of $G_{exp}(r)$. The average sixfold coordination is confirmed. The r_{Mg-O} distance is somewhat less than usually found in aqueous solutions (2.07 Å instead of 2.10–2.12 Å), which is certainly of physical significance, taking into account that it could be determined rather exactly because of the high resolution of the first peak in $G_{exp}(r)$ and the self-consistency in the procedures applied. The distance shortening can be explained by the different electrostatic interactions between the Mg^{2+} and CH_3OH molecules on one hand, and between the Mg^{2+} and H_2O molecules, on the other hand, due to the difference in the dipol moments in magnitude and in position relating to the lone pairs. A deeper explanation can only be

given by studying the orientation of the methanol molecules around the cations. An estimate for the average Mg–O–Mg angle can only be deduced from the r_{Mg-O} and r_{Mg-Me} values, and assuming that the intramolecular O–Me distance is equal to 1.42 Å, as obtained from a neutron diffraction study of liquid methanol [15], which will result in about 104 degrees, somewhat lower than the tetrahedral angle.

The Cl–O distance, its rmsd as well as the sixfold coordination are in good agreement with the corresponding parameters in aqueous chloride solutions, both for LSF1 and LSF2. As concerns the Cl–Me interaction, there are some inconsistencies between the parameters obtained with the two LSF procedures. The increased l_{Cl-Me} when going from LSF1 to LSF2 makes the octahedral symmetry assumption for the Me groups less convincing. Further, both n_{Mg-Me} and n_{Cl-Me} became greater than six when they were allowed to vary freely in LSF1. The excess can arise from outer molecules, for which it is sterically allowed to get in the neighbourhood of the molecules strongly bonded to the ions.

The parameters for the interactions between the scattering centers representing the solvent molecules exhibit much more uncertainties. There is an interesting rough agreement between the $n_{O-O} = 4.4$ from LSF1 and the fixed values of 4 from LSF2, as well as between the $r_{O-O} = 3.77$ Å and the average of the two O–O distance from LSF2, equal to 3.72 Å. These facts, however, do not give further argument for the octahedral geometry. On the contrary, the distribution of the O–O distances from LSF1 characterized by l_{O-O} cannot be substituted by the other two ones since the O–O distance with a value of 3.77 Å obtained by the LSF1 procedure, having a rmsd of 0.24 cannot be really interpreted in terms of average of the $(O-O)_+$ and $(O-O)_-$ distances of Table 3. From the other side, the necessary introduction of two different O–O contributions in LSF2 turned out to be strongly artificial. This is demonstrated by the corresponding overcompensations in $G(r)$. A possible explanation is that some of the solvate molecules at the high concentration have to be shared between the cations and anions, leading to a significant distortion in the octahedra.

In the Me–Me interactions the discrepancy between the two LSF parameter sets becomes too deep for a reliable comparison. The Me–O interactions are very poorly determined, as it can be seen from the high l_{Me-O} value in Table 2; moreover, the LSF2 procedure let to an unreasonably small $l_{(Me-O)+}$ value.

A further argument in favour of LSF1 results is arising from an internal consistency of the parameters, very rarely found in the literature. Namely, the boundaries of the uniform distribution of distances are not penetrating into the corresponding discrete regions with the only exception of the very uncertain Me–O contribution.

A methodical remark should be made here. The Mg–O contribution which has a relatively small $c_{Mg-O}(k)$ weight is the most precisely determined one in this study. On the contrary, the Me–O contribution with the highest overall weight in the system is the most uncertain one. This is due to the special "distance spectrum", i.e. the distribution of the distances in the $G(r)$ function, and to the highly different physical nature of the interactions between the corresponding particles. This means that the weights of the contributions, connected with the stoichiometric composition and the scattering factors of the particles do not correlate strongly with the possibility of extracting of structural information, and deviations in a wide range can occur.

From the above arguments, the following conclusions can be drawn: (i) both the cation and the anion have a solvation shell composed of six methanol molecules in average, (ii) the structural parameters describing the ion-methanol interactions and ion-water interactions are similar for the $MgCl_2$ solutions, (iii) since a much better fit with higher internal consistency could have been reached without preliminary assumption for geometry than with a maximum constraint, the symmetries within the solvate shells have to be strongly broken, and (iv) the success of the LSF1 procedure compared with the failure of the LSF2 with the heavy constraints in the symmetry assumptions suggests qualitatively that the assumption for an average octahedral arrangement is less probable for the anionic solvate shell than for the cationic one, and that the methyl groups have much less tendency to occupy symmetrical positions than the OH groups.

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