X-Ray Diffraction Study of Methanol-Water Mixtures

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Z. Naturforsch. **49a**, 967–972 (1994); received August 18, 1994

X-ray diffraction patterns of methanol-water mixtures with mole fractions of methanol molecules of 0.1, 0.25 and 0.9 have been measured. The experimental structure functions of mixtures are compared with those of pure solvents and with recent Molecular Dynamics results. Difference structure functions similar to thermodynamic excess functions are introduced for the analysis of methanol-water interactions. The comparison of the total and the difference structure functions from experiments and simulations shows an overall good agreement.

1. Introduction

Recently considerable attention has been given to computer simulation studies of methanol-water mixtures [1–5]. Among them we have performed a series of Molecular Dynamics (MD) simulations with flexible models for water [6] and methanol [7] in order to study peculiar excess properties of these mixtures. In these studies the structure of mixtures with three methanol mole fractions ($x_m = 0.1$, 0.25 and 0.9) has been compared in detail with that of the pure solvents, simulated with the same molecular models. The structural changes relative to the pure solvents have been discussed with the help of radial distribution functions and the geometrical arrangement of nearest neighbor molecules [3]. It has also been shown that the pair potentials employed in the simulations reproduce reasonably several excess thermodynamic and dynamic properties of the mixtures. The methanol-water mixture with $x_m = 0.25$, resulting in extreme values for most of the excess properties, has been found to be characterized by the highest number of molecules with a maximal number of H-bonded neighbors [5].

In this paper we present the results of X-ray diffraction measurements on the same methanol-water mixtures and provide a comparison between the experimental and MD structure functions.

The interpretation of diffraction data of multicomponent liquids is confronted with some general problems [8]. Special difficulties arise for the analysis of X-ray data of alcohol-water mixtures, as X-rays do not distinguish between oxygen atoms of methanol and water molecules and as the scattering amplitudes of carbon and oxygen are not very different [9]. Moreover, the nearest neighbor O–O distances are the same for water-water and methanol-methanol interactions [3].

Therefore, the aim of this work was twofold. Firstly, we wanted to perform a check of the reliability of results calculated from recent MD simulations by the comparison of experimental and simulated structure functions. The detailed information on the structure of mixtures which can be derived from a computer simulation goes significantly beyond that derived from a X-ray measurement. The additional information is, of course, only reliable if the data which result from the diffraction experiments are reproduced by the simulations. Secondly, owing to the difficulties mentioned above for the direct analysis of X-ray data, we wanted to perform a check on the method of analysis introduced for experimental data by analysing the MD structure functions in the same way.

The organization of the paper is as follows: Section 2 describes the details of the X-ray diffraction experiments. In Sect. 3 the excess intermolecular structure functions for the mixtures are introduced, which are similarly defined as the thermodynamic excess functions. Both the total as well as the difference structure functions from the experiments will be compared with those from the MD simulation. The

Reprint requests to Dr. K. Heinzinger.

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methanol-water interactions will be parameterized with the help of synthetic difference structure functions. Finally, in Sect. 4 conclusions will be drawn on the reliability of the potentials used in the simulations and on the method employed for the analysis of experimental X-ray data.

2. Experimental

The X-ray experiments have been performed on mixtures with $x_m = 0.1$, 0.25, and 0.9. The solutions have been obtained from high purity methanol and water. The mixtures contained 0.0302, 0.262, and 0.0158 molecules/Å^3 for the 1:9, 1:3, and 9:1 methanol:water mixtures, respectively.

The experiments were carried out at room temperature on flat plane-parallel specimens using transmission geometry and MoK_α ($\lambda = 0.711$ Å) radiation, monochromated by a flat LiF crystal in the primary beam. The scattering data were measured in the range $0.2 \leq k \leq 14.5$ Å^{-1} of the scattering variable $k = \frac{4\pi}{\lambda} \sin(\theta)$. The measured intensities were corrected for polarisation, absorption, volume of the irradiated sample and for Compton scattering.

The intensity of the scattered X-rays was collected at equidistant steps with an increment $\Delta k = 0.05$ Å^{-1} and $3 \cdot 10^5$ impulses at each point. The details of the data processing and correction procedure are discussed in [10]. The coherent and the incoherent X-ray amplitudes of the atoms were used in their analytical form [11]. For both the corrections and the further analysis of the experimental data the methanol molecules were regarded as three site molecules, treating the scattering of the CH_3 group in the united atom approximation [12].

The experimental X-ray structure function of pure methanol and of pure water used for comparison in this work were taken from [12] and from our recent measurement [13], respectively.

3. Results and Discussion

The total experimental structure functions of the mixtures were constructed according to the equation

$$H(k) = \frac{I_{\text{norm}}(k) - \sum_{i=1}^{3} x_i f_i^2(k)}{M(k)}, \tag{1}$$

where $I_{\text{norm}}(k)$, $f_i(k)$, and x_i are the normalized coherent intensity, the coherent scattering amplitudes for the sites O, H, CH_3 and the molar fractions of the different sites in the given mixture, respectively. $M(k)$ is a modification function defined by

$$M(k) = \left(\sum_{i=1}^{3} x_i f_i(k) \right)^2. \tag{2}$$

The total structure functions derived from the experiments can be written as the sum of two terms:

$$H(k) = H_m(k) + H_d(k), \tag{3}$$

where m and d indicate the intramolecular and the distinct part of the scattering, respectively. In $H_d(k)$ only contributions from intermolecular correlations are included. The total radial distribution functions have been calculated from the total structure functions by Fourier transformation:

$$G(r) = 1 + \frac{1}{2\pi^2 \varrho_0 r} \int_0^{k_{\max}} k H(k) \sin(k r) \, dk, \tag{4}$$

where ϱ_0 is the average number density of all sites for the given mixture.

The distinct structure functions and the radial distribution functions (RDFs) for the mixtures and the pure solvents from the X-ray experiments and the simulations are compared in Figs. 1 and 2, respectively. The MD distinct structure functions have been calculated as weighted sums of the partial structure functions $h_{\alpha\beta}(k)$ obtained by Fourier transformations from the site-site RDFs [3, 5].

The comparison of the experimental with the simulation results shows an overall good agreement for each mixture. It can be concluded that the MD data reproduce very well the changes both of the structure functions and the RDFs caused by an increasing mole fraction of methanol molecules. This agreement between experiments and MD simulations demonstrates that the flexible three-site models for water and methanol used in the simulations lead to a basically correct description of the structure of these mixtures. The small differences observable between experimental and MD structure functions can be attributed to experimental uncertainties except for the small phase shift between MD and experimental structure functions for pure methanol at large k, which is due to the fact that the experiment leads to a slightly shorter nearest neighbor O–O distance than the simulation (Figure 2). The decrease in the height of the first peak in the RDFs in

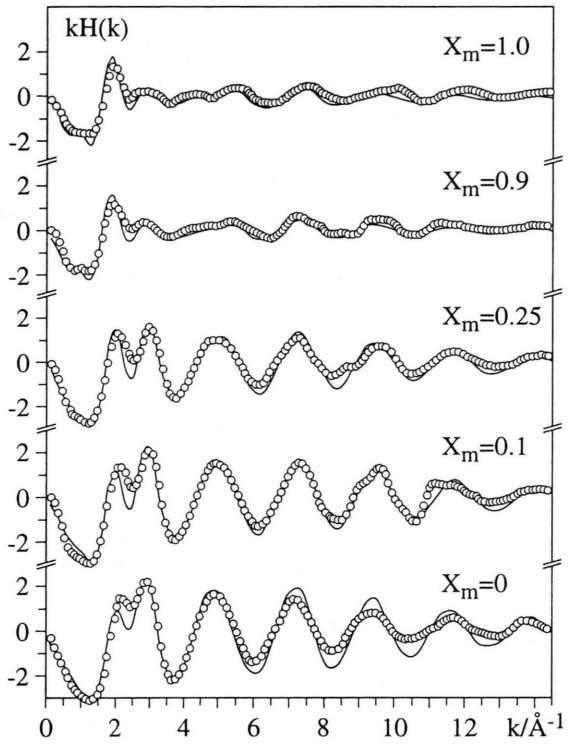

Fig. 1. Comparison of the structure functions from Molecular Dynamics (MD) simulations (——) and experiments (ooo) for various methanol-water mixtures with the mole fractions of methanol as indicated.

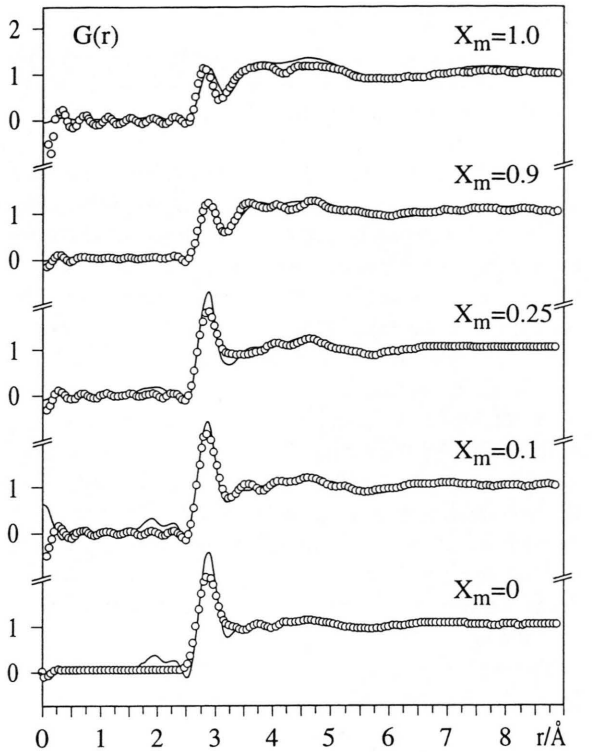

Fig. 2. Comparison of the total radial distribution functions from MD simulations (——) and experiments (ooo) for various methanol-water mixtures with the mole fractions of methanol as indicated.

Fig. 2 at 2.85 Å – assigned to nearest neighbor O–O distances – with increasing mole fraction of the methanol component can be understood as a result of a decreasing coordination number and a decreasing weight of the O–O interactions in the total RDFs [3, 5].

The further analysis of the total structure functions is very difficult. For a more detailed comparison of experimental and MD data and also for the introduction of a method usefull for the analysis of X-ray data of any kind of mixtures, a difference structure function, describing excess structures in mixtures, has been introduced by the equation

$$\Delta H(k) = H_d(k) - x_m H^0_{mm}(k) - x_w H^0_{ww}(k), \qquad (5)$$

where $H^0_{mm}(k)$ and $H^0_{ww}(k)$ are the structure functions of pure methanol and pure water, respectively, renormalized for the density of the mixture and for the modification function M:

$$H^0_{ss}(k) = \frac{\varrho_s}{\varrho_{0s}} \frac{M^{pure}(k)}{M(k)} H_{pure,s}(k), \qquad (6)$$

where ϱ_s and ϱ_{0s} indicate densities of the components in the mixture and in the pure solvent at the same temperature, respectively. The difference functions are composed of all methanol-water interactions and of the contributions due to changes in methanol-methanol and water-water interactions in the mixture compared to those in pure liquids:

$$\Delta H(k) = H_{mw}(k) + \Delta H_{mm}(k) + \Delta H_{ww}(k), \qquad (7)$$

where

$$\Delta H_{ss}(k) = H_{ss}(k) - x_s H^0_{ss}(k) \qquad (8)$$

and ss stands either for methanol-methanol or water-water interactions. The corresponding difference radial

distribution functions

$$\Delta G(r) = G_{mw}(r) + \Delta G_{mm}(r) + \Delta G_{ww}(r) \qquad (9)$$

can then also be calculated by Fourier transformation of the $\Delta H(k)$.

The difference structure function $\Delta H(k)$ has been introduced in order to simplify the analysis of the X-ray structure functions by leaving out much of the non-interesting contributions and enhancing the weights of the contributions for unlike pairs of molecules. The $\Delta H(k)$ from the experiments are compared in Fig. 3 with those from the MD simulations. The comparison shows good agreement between experimental and MD difference functions for all mixtures in almost the whole range of the scattering variable. The MD functions for the above mixtures reproduce the splitting of the first peak in the range of $2 \leq k \leq 3$ Å^{-1}. The small deviations at higher scattering variables may also be due to experimental uncertainties and a slightly greater damping of the experimental functions with increasing k.

This is a very important result as it strongly confirms the conclusion, which had been drawn already from the agreement of the total structure functions shown in Fig. 1, that the pair potentials employed in the simulations describe the structure of the water-methanol mixtures correctly. It follows that the detailed analysis of the structure of the methanol-water mixtures presented in [3] is highly reliable. Experimentally the three terms in (7) cannot be separated. But the reliability of the pair potentials as demonstrated by Figs. 1 and 3 allows to calculate the excess solvent-solvent structure functions ΔH_{mm} and ΔH_{ww} from the simulations with a high degree of confidence. The resulting ΔG_{mm} and ΔG_{ww} are depicted in Fig. 4 for various concentrations. The excess methanol-methanol and water-water functions for the mixtures $x_m = 0.1$ and $x_m = 0.9$, respectively, were not calculated because of negligible weights of these interactions in the corresponding total structure functions.

It can be seen from Fig. 4 that the major contributions to the MD excess solvent-solvent radial distribution functions are found in the range of the nearest neighbor O–O distances. The $\Delta G_{ss}(r)$ show at $r = 2.85$ Å an excess in the number of water-water interactions and a lack of methanol-methanol interactions compared to the corresponding pure solvent at the density of the mixtures. The integration over the first peaks in the ΔG_{ss}results in an increase of the coordination number of water with increasing x_m and a decrease of that of methanol with decreasing x_m, as can be seen from Table 1. Almost no excess contributions are observable beyond the nearest neighbor shell of solvent molecules except for $\Delta G_{ww}(r)$ at $x_m = 0.25$, where a slight effect is observable in the range of the

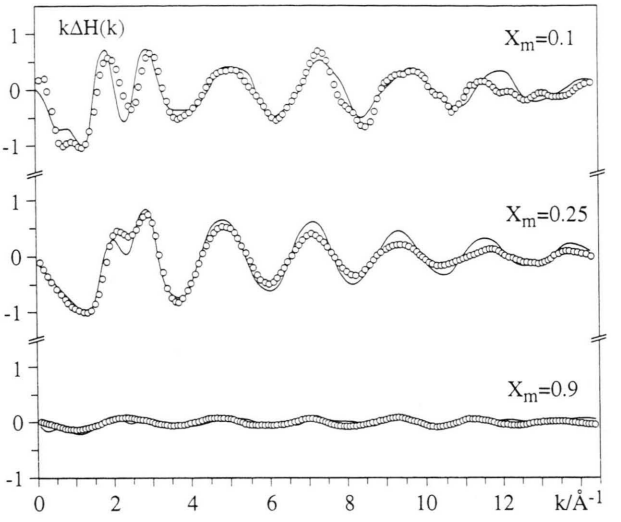

Fig. 3. Comparison of the difference structure functions from MD simulations (——) and experiments (ooo) for various methanol-water mixtures with the mole fractions of methanol as indicated.

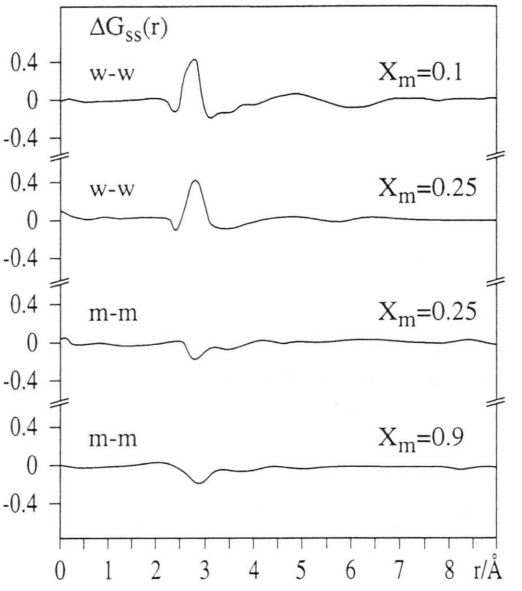

Fig. 4. The excess solvent-solvent radial distribution functions for methanol-water mixtures at various mole fractions of methanol as indicated.

Table 1. Excess water-water and methanol-methanol coordination numbers in different mixtures with the methanol mole fractions x_m.

x_m	0.1	0.25	0.9
ΔN_{ww}	0.1	0.4	
ΔN_{mm}		−0.4	−0.3

second neighbors. From this discussion of the $\Delta G_{ss}(r)$ it can be concluded that the measurable difference structure function $\Delta H(k)$ is approximately equal to $H_{mw}(k)$, which means that the experiment is able to provide the structure functions which describes all and only the water-methanol interactions in those mixtures.

In order to deduce further information on the structural parameters for methanol-water interactions in the mixtures, the $\Delta H(k)$ difference structure functions of the water rich mixtures have been analysed with parameterised synthetic structure functions. The analysis was achieved by fitting the synthetic functions to the experimental difference functions.

The synthetic structure functions were composed of discrete contributions of nearest neighbor O_m-O_w and $C-O_w$ interactions, and the contributions beyond the first shell were approximated by continuum distributions. Interactions including H-sites in $\Delta H_D(k)$ have been neglected owing to their low X-ray weights c_{ij} in the difference functions. However, in the continuum part of the synthetic difference functions the $C-H_w$ and O_m-H_w interactions have to be taken into account because of their considerable contributions to the difference structure functions in the range of $0 \leq k \leq 2$ Å^{-1}. Thus

$$\Delta H(k) = \Delta H_D(k) + \Delta H_C(k)\,, \tag{10}$$

with the first neighbor structure function

$$\Delta H_D(k) = \varrho_0 \sum_{i,j} c_{ij}(k)\, N_{ij}\, j_0(k r_{ij}) \exp(-l_{ij} k^2/2) \tag{11}$$

and the structure function for the continuum

$$\Delta H_C(k) = \frac{4\pi \varrho_0}{k} \sum_{i,j} j_1(k R_{ij}) \exp(-L_{ij} k^2/2)\,, \tag{12}$$

where r_{ij}, N_{ij}, and l_{ij} are the mean nearest neighbor distance between particles i and j, the mean coordination number and the root mean square deviations from the mean distance, respectively. j_l in the expressions (11) and (12) stands for l-th order spherical Bessel function, ϱ_0 and c_{ij} denote the average number density and X-ray weights in the given mixture, respectively. The parameters R_{ij} and L_{ij} are characteristic for the boundary of the structureless environment.

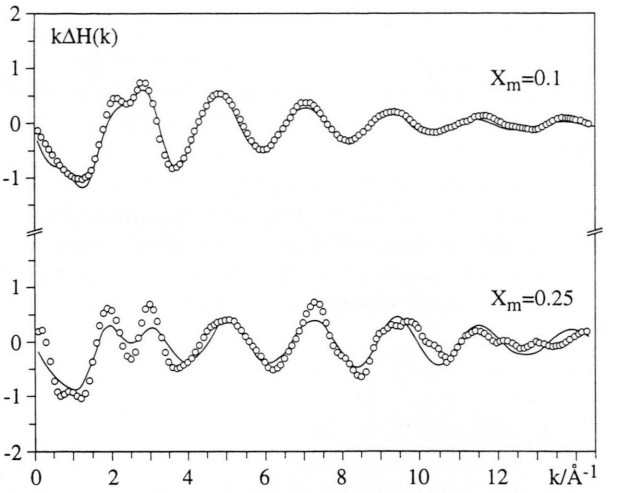

Fig. 5. Comparison of the synthetic difference structure functions (——) and the experimental ones (o o o) for methanol-water mixtures with the mole fractions of methanol as indicated.

Table 2. Mean distances r [Å], r.m.s. variations l [Å] and coordination numbers for nearest neighbor interactions obtained by least squares fits from experimental and MD difference structure functions of mixtures. The values in the columns MD* are determined by direct calculations from the corresponding radial distribution functions. The estimated errors for the mean distances, the r.m.s. variations, and the coordination numbers are 0.03 Å, 0.04 Å, and 10%, respectively.

	$x_m = 0.1$			$x_m = 0.25$		
	exp	MD	MD*	exp	MD	MD*
O_m-O_w						
r	2.83	2.83	2.83	2.87	2.85	2.85
l	0.14	0.15		0.17	0.15	
N	3.1	3.1	2.9	2.2	2.1	2.2
$C-O_w$						
r	3.7	3.71	3.65	3.55	3.63	3.60
l	0.7	0.52		0.51	0.55	
N	10.7	10.6	10.7	7.7	7.6	7.8

Least squares refinement of structural parameters were performed by minimizing the differences between synthetic and experimental difference functions. The comparison of the experimental difference functions with the final calculated synthetic functions is shown in Figure 5. The resulting structural parameters are given in Table 2.

To provide a basis for control of the method of analysis, synthetic structure functions were also fitted to the MD difference functions by the same method. The resulting parameters, together with the mean neighbor distances and coordination numbers calculated directly from the MD pair correlation functions, are also given in Table 2 for comparison. It is obvious from the numbers in Table 2 that a direct determination of the parameters describing the structure of methanol-water mixtures is possible from X-ray measurements.

4. Conclusions

Good agreement has been found between X-ray measurements and MD simulations for the total structure functions of methanol-water mixtures at various concentrations. This agreement indicates that the three-site flexible models for methanol and water employed in the simulations describe the interactions correctly and that the structure of these mixtures resulting from such simulations as presented in [3] can be considered highly reliable. A difference structure function is introduced by which the structure of the mixture is separated into the three contributions: (i) methanol-water interactions, $H_{mw}(k)$, (ii) changes in the water-water, $\Delta H_{ww}(k)$ and (iii) methanol-methanol, $\Delta H_{mm}(k)$, structure functions relative to the pure solvents. Again good agreement has been found for these difference structure functions between X-ray measurement and the simulations for all three water-methanol mixtures investigated.

On the basis of the simulations, the $\Delta H_{ww}(k)$ and $\Delta H_{mm}(k)$ – which are not accessible experimentally – are shown to be relatively small. This means that in a good approximation the methanol-water interactions in the mixtures can be determined solely by the experiments. Finally, it is demonstrated that by the fitting of a synthetic structure function to the $H_{mw}(k)$ the structural parameters of the mixtures can be deduced from the experiments with a high degree of reliability.

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