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Water structure and solute association in dilute aqueous methanol

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Abstract. – The molecular structure of a dilute aqueous methanol solution (1 : 19 molar ratio) is studied using neutron diffraction with hydrogen/deuterium isotope substitution. The Empirical Potential Structure Refinement (EPSR) method is used to create a structural model of the solution which is consistent with the measured diffraction data. Direct evidence of methanol association is found with more than 80% of the methanol molecules in clusters of 3 to 8 molecules. Contrary to several previous studies, and conventional views on the hydrophobic interaction, no enhancement of the water structure surrounding the non-polar groups is observed. Consistent with results from other related systems, a compression of the second-neighbour water-water contact distance is observed that may be a structural feature of the hydrophobic driving force.

Introduction. – Dilute aqueous solutions of lower alcohols are recognised as important prototype hydrophobic systems [1]. Molecular-level models of their properties are especially valuable, as these may aid our understanding of more complex aqueous solutions of amphiphiles, including macro- and biomolecules.

Conventional models of hydrophobic hydration of non-polar molecules emphasise enhancement of the water structure in the vicinity of the solute [2]. Association of the solutes is argued to expel this structured water to the bulk solvent, resulting in a favourable entropy increase of the system. Moreover, thermodynamic data on dilute aqueous solutions of lower alcohols have been interpreted in terms of structural models without any significant solute association [3]. Most experimental studies aimed at testing these two hypotheses are indirect as they are based on calorimetric or spectroscopic data, the interpretation of which is often model dependent and ambiguous [4–6]. Surprisingly, there is no *direct* supporting evidence.

Methanol holds special status as the simplest amphiphile-like molecule. Dilute aqueous methanol is therefore an important model system for developing a molecular-level structural description to facilitate testing these hypotheses. However, direct experimental structural studies on this system are limited. The most detailed investigation to date is the neutron diffraction work of Soper and Finney [7] on a semi-dilute 1 : 9 mole fraction solution which revealed no discernible perturbation of the water structure in the hydration shell. Solute association was not explored. Structural studies on other aqueous mixtures with solutes like tetraalkyl ammonium ions and tert-butanol have supported the case for an unperturbed water structure [8–10]. Moreover, in tert-butanol, clear evidence for solute association was found [10, 11]. Very recent reports indicate modified second-neighbour water correlations [11] in a dilute aqueous tertiary butanol.

Computer simulations of several low-concentration aqueous methanol solutions show both various degrees of water structure enhancement and evidence of solute association [12–16]. Okazaki *et al.* [12] concluded that the slight exothermic mixing on adding small amounts of methanol to water is due to promotion of water structure around methanol. Laaksonen *et al.* [15] also report “significant” perturbation of the water structure evidenced by enhancement of first and second coordination structure and the disappearance of the signature of non-tetrahedral (interstitial) water molecules. Hernandez and Blake [14], using an *ab initio* parameterisation of non-additive potentials, conclude that water closer to the solute shows lowered local density. They also report evidence for hydrogen bonding between associated solutes.

There is therefore clearly a need to clarify both the water structure, particularly in the neighbourhood of the non-polar group, and the degree of solute association. We present the first comprehensive neutron diffraction measurements on a dilute methanol-water mixture (1 : 19 mole fraction). The results provide a clear picture of water structure and solute association that helps to resolve several conflicts about the structure of this important prototype system.

Neutron diffraction and data analysis methods. – Samples of methanol and water (natural and deuterated) were obtained from Sigma-Aldrich and used without further purification. Five independent measurements on isotopically different but otherwise identical solutions of 0.05 mole fraction methanol in water were performed. The following solutions were prepared: 1) CD₃OD in D₂O; 2) CD₃OH in H₂O; 3) a 1 : 1 mixture of CD₃OH/CD₃OD in H₂O/D₂O; 4) CH₃OH in H₂O; 5) a 1 : 1 mixture of CH₃OH/CD₃OD in H₂O/D₂O.

Hydrogen/deuterium substitutions were made on the hydrogen atoms of the —OH groups of methanol and water as indicated in solutions 1), 2) and 3) to provide hydroxyl hydrogen correlations. Substitutions on the methyl and —OH hydrogens using solutions 1), 4) and 5) yielded correlations between all hydrogen atoms in the solution including methanol-water correlations. An independent substitution only on the methyl groups is not possible since the mixture has a low concentration of methanol.

Neutron diffraction measurements were performed on the SANDALS time-of-flight diffractometer at the ISIS neutron spallation source at the Rutherford Appleton Laboratory, UK. The range of scattering vector Q used in the analysis of the data was $\approx 0.5^\circ \text{\AA}^{-1}$ to $50^\circ \text{\AA}^{-1}$, where $Q = 4\pi \sin \theta / \lambda$. The samples were placed in flat plate cells made from Ti-Zr alloy that gives negligible coherent scattering. The temperature was held constant at $25 \pm 1^\circ \text{C}$. The data were corrected for attenuation and multiple scattering using the ATLAS series of programs [17] and the differential scattering cross-section was calculated using a vanadium standard. Corrections for inelastic scattering were performed by the method outlined by Soper and Luzar [18].

Analysis of the measured data (after all necessary corrections) results in a total structure

factor $F(Q)$:

$$F(Q) = c_X^2 b_X^2 [S_{XX}(Q) - 1] + 2c_X c_H b_X b_H [S_{XH}(Q) - 1] + c_H^2 b_H^2 [S_{HH}(Q) - 1], \quad (1)$$

where $S_{HH}(Q)$ is the structure factor relating to isotopically labelled atoms and $S_{XH}(Q)$ and $S_{XX}(Q)$ are the two composite partial structure factors relating to the correlations between other types of atoms (X) and the labelled atom type (H).

The EPSR technique is a constrained Monte Carlo simulation of the mixture that generates assemblies of molecules consistent with the experimental data [19,20]. In this case, the charges and the Lennard-Jones constants from the SPC/E potential of Berendsen *et al.* [21] were used for the water molecules [20]. The H1 potential of Haughney *et al.* [22] was used for the methanol molecules. Methanol-water interactions were simulated by Lorentz-Berthelot mixing rules [23]. The cubic simulation box (side 26.0751 Å) contained 28 methanol and 532 water molecules with periodic boundary conditions. After equilibration, information from the diffraction data is introduced as a potential of mean force superimposed on the interaction potentials. The magnitude of the perturbation is determined from the difference between the measured and simulated composite partial structure factors [19,24] and its effect is to drive the simulated model towards consistency with all available experimental structural data. This process is iterated until a satisfactory fit to the experimental data is obtained. The ensemble of model structures obtained can then be examined to extract the full set of radial and orientational distribution functions [25].

Results and discussion. – In fig. 1 we show the experimentally determined partial structure factors and ensemble-averaged fits to the experimental data obtained from EPSR-generated structures. These structures are able to reproduce the salient features of the measured structure factors, specifically for Q values greater than approximately 2.5°Å^{-1} . Deviations between the measured data and the fits at low Q are due to imperfect removal of inelastic scattering contribution from hydrogen and do not affect the correlations at relevant intermolecular distances. The slight deviations seen at intermediate Q values for the XX composite partials are attributed to small errors in the inelastic scattering correction.

The methanol pair correlation function, $g_{CC}(r)$, is shown in fig. 2a. The distinct first coordination shell with a peak at 4.09 Å indicates solute (methanol) molecular contacts at this distance. Integrating under this peak gives an average CC coordination number of 1.33 ± 0.3 implying that an average methanol molecule is in contact with slightly more than one other methanol molecule, in agreement with the simulation results of Okazaki *et al.* [12]. The first peaks in $g_{OO}(r)$ and $g_{OH}(r)$ (where O and H denote the methanol hydroxyl oxygen and hydrogen) shown in fig. 2b,c, respectively, relate to hydrogen-bonded methanol molecules. Integration under these peaks yields very small coordination numbers (0.14 ± 0.1 and 0.07 ± 0.05 , respectively), indicating that this inter-methanol hydrogen-bond contact occurs rarely in solution. The dominant intermolecular methanol-methanol contact is therefore through the methyl head groups. This is confirmed by the orientational correlation functions obtained from the ensembles, and is also consistent with data on aqueous tert-butanol [10,11] and with the simulations of Okazaki *et al.* [12] but not with those of Hernandez and Ortega [14] who find hydrogen bonding between methanol molecules.

A snapshot of the simulation box (fig. 3) reveals significant solute association. A quantitative measure of solute association can be obtained from a cluster analysis of the EPSR-generated configurations. We define two methanol molecules as belonging to the same cluster if they are within 5.8 Å of each other (first minimum in the CC pair distribution function of fig. 2a). Only about 20% of the methanol molecules occur singly, and about 80% of the

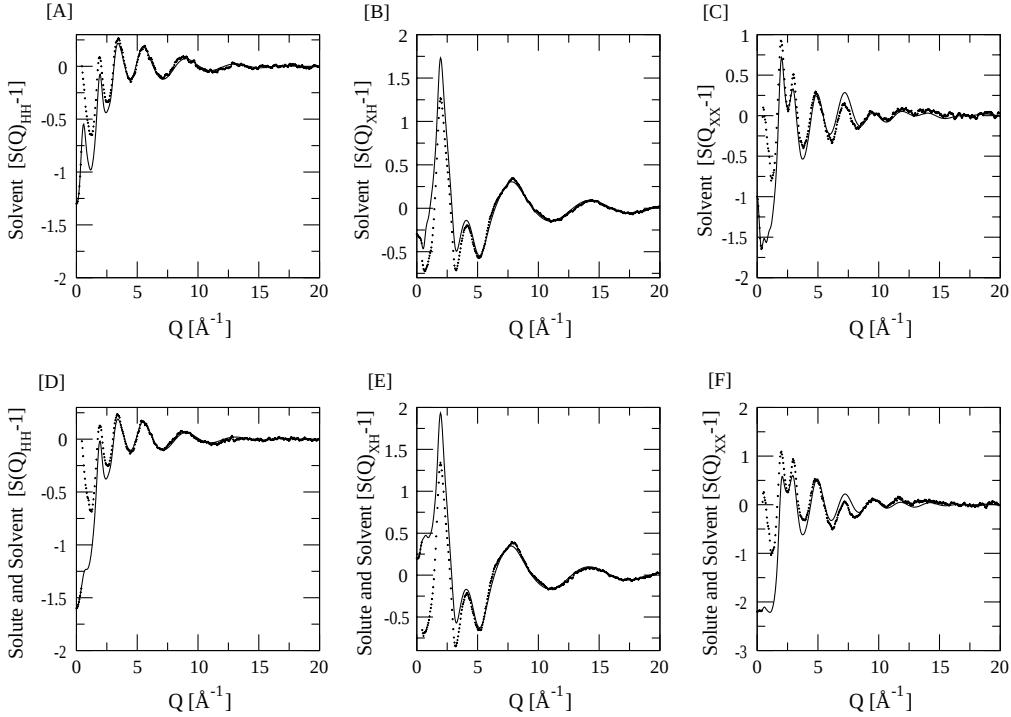


Fig. 1 – Experimental data (line) and the EPSR fits (filled circles) for 0.05 mole fraction of methanol in water. Frames A to F show the $S_{HH}(Q) - 1$ [A, D], $S_{XH}(Q) - 1$ [B, E] and $S_{XX}(Q) - 1$ [C, F] for the solvent-solvent and solute+solvent - solute+solvent series of isotopic substitution data.

methanol molecules are found to exist in clusters of 3 to 8 methanol molecules. Such cluster sizes are unexpected on the basis of the accepted model of homogeneous mixing in this system.

Water correlations (HwHw, OwHw and OwOw) are shown in fig. 4 for both pure water and the 1 : 19 methanol/water mixture. It is clear from figs. 4a, b that there is negligible perturbation in the HwHw and OwHw correlations, confirming in this system the conclusions drawn in the earlier work on the more concentrated aqueous methanol solution [7] and related systems [8–10]. However, the results here show a striking inward shift (by 0.3 Å) of the second coordination shell in the OwOw correlations in the mixture relative to pure water fig. 4c.

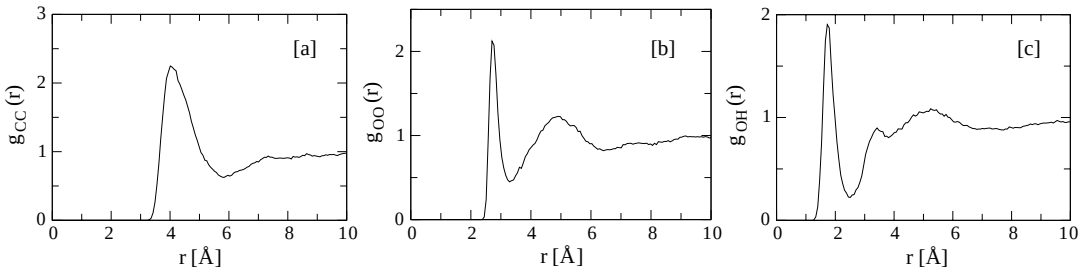


Fig. 2 – Intermolecular solute-solute partial radial distribution functions determined by the EPSR method: (a) CC, (b) OO and (c) OH for 0.05 mole fraction of methanol in water.

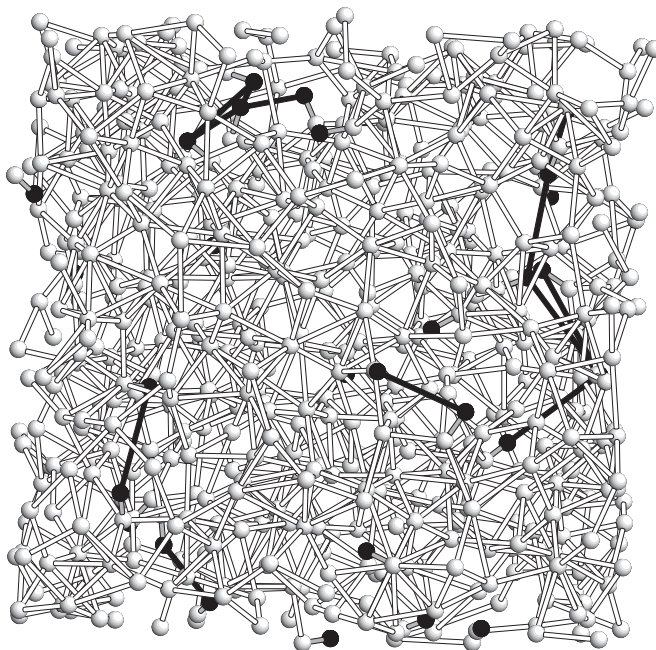


Fig. 3 – One of the simulated molecular boxes. Water and methanol oxygens are shown as white atoms. The methanol carbon atom is shown in black. Black bonds indicate methanol carbons in the first coordination shell, $r \leq 5.8 \text{ \AA}$. Grey bonds join a carbon and oxygen atom of a methanol molecule. White bonds join all oxygen atoms. Note that the snapshot shows just one face of the cubic simulation box. Thus, some water molecules are seen to be surrounded by only water molecules in all directions. However, as one moves away from such a water molecule, even if there are relatively few methanol molecules within the first Ow-Ow coordination shell (*i.e.* within $3.5 \text{ \AA}$), there is a high probability of finding a methanol molecule in the second coordination shell which peaks around $4.5 \text{ \AA}$. Since a methanol molecule can be anywhere up to $\approx 5 \text{ \AA}$ from the second-shell water molecule for the latter to be in the hydration shell of the former, we conclude that most of the water molecules are within the first hydration shell of at least one methanol molecule.

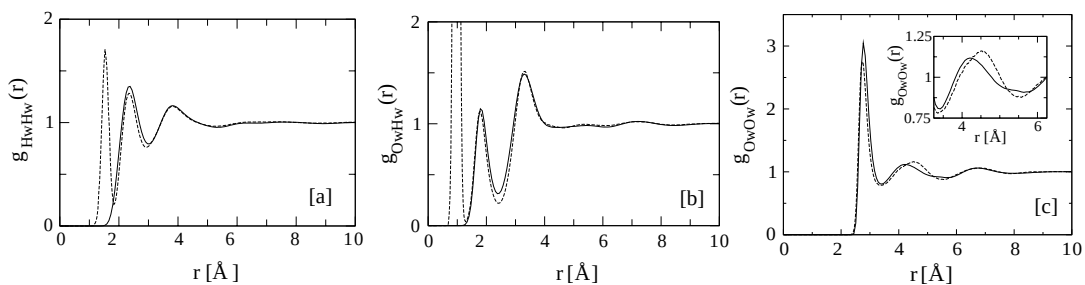


Fig. 4 – Intermolecular solvent-solvent partial radial distribution functions determined by the EPSR method for 0.05 mole fraction of methanol in water: (a) HwHw, (b) OwHw and (c) OwOw. In all three plots the full line corresponds to the mixture and the dashed line corresponds to pure water. Intramolecular peaks are shown only in the reconstructed radial distribution functions for pure water since they will be identical for the methanol-water results.

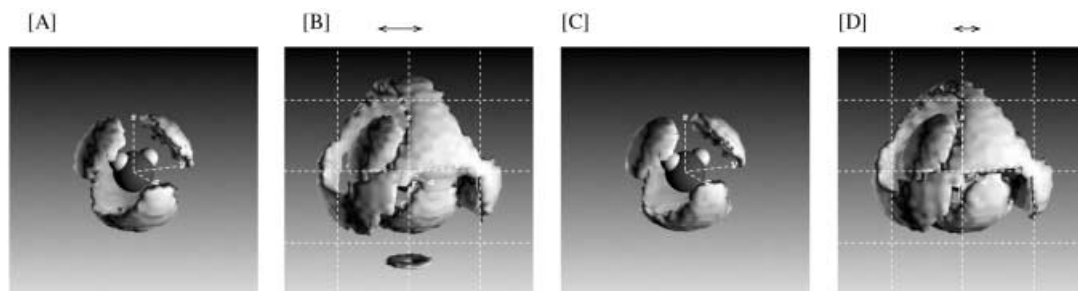


Fig. 5 – Water-water intermolecular spatial density maps after averaging over water molecule rotations. Frames A and B show the first and second coordination shells, respectively, for pure water. Frames C and D show the first and second coordination shells, respectively, for the 0.05 mole fraction methanol-water mixture.

A similar shift was observed in an aqueous solution of tertiary butanol at an equivalent concentration [11].

Three-dimensional spatial density maps of the water structure are shown in fig. 5 for pure water and for the 1 : 19 methanol/water mixture. The spatial density function is defined as the density of neighbouring molecular centres as a function of distance and direction away from a central molecule [26]. In these figures the spatial densities have been averaged over water molecule rotations. The characteristic tetrahedral structure of the first shell is evident in both cases, *i.e.* in frame A of fig. 5 for pure water and in frame C of fig. 5 for the 1 : 19 methanol/water mixture, confirming that there is no disruption of the immediate water-water contacts.

Subtle perturbations are visible in the second-neighbour lobes as seen in frames B and D of fig. 5 for pure water and the 1 : 19 methanol/water mixture, respectively. In the bulk water case, the second coordination shell is broad and well defined, indicative of the characteristic tetrahedral water network. By contrast, the second coordination shell is significantly compressed in the mixture, particularly in the direction directly above the central water molecule (*i.e.* along the vertical z -axis of fig. 5[D]) where it also has a narrower spatial density distribution (see arrows above frames [B] and [D]).

None of these experimental results support the traditional view of enhanced water structure in the nearest neighbourhood of non-polar groups. At the concentration of this experiment (1 : 19) there are on average 17.6 ± 0.8 water molecules in the hydration shell of a methanol molecule. This hydration number is determined from the carbon-water oxygen (COW) radial distribution function (not shown here). Thus, there is relatively little free water and all the observed structural features come from water in close proximity to a methanol molecule.

Similar effects were noted by Bowron *et al.* in a 0.06 mole fraction sample of tertiary-butanol in water [11]. Thus, the present results provide confirmation of this initially unexpected effect, here in a simpler system having a much smaller non-polar head group where the hydrophobic driving force is likely to be smaller.

To our knowledge, no simulation of this system replicates the structural response of the water that we have observed here. Moreover, the OwOw pair distribution function in most of those simulation reports shows the second coordination shell in the OwOw correlations moving *outwards* to larger distances; this is exactly *opposite* to what we observe experimentally.

Conclusions. – From the results of these neutron diffraction measurements the following picture emerges. First, even in the dilute concentration regime, methanol shows a significant

tendency for self-association into clusters in contact via methyl groups rather than through hydrogen bonds. The response of the water structure to the presence of these solutes is not an ordering of the hydration shell of the non-polar group as might be expected from the standard model of the hydrophobic interaction. Rather, a compression of the second shell is observed that is accompanied by a sharpening of the second-neighbour water correlations. It is tempting to suggest that this reduction in the structural freedom of the water molecules may contribute to the entropic driving force of the hydrophobic interaction.

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