Hydration of Methanol in Aqueous Solution

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We present neutron diffraction data on a 1:9 molar ratio methanol-water mixture in which isotope substitution is used to isolate the methyl hydrogen (M) to water hydrogen (H) pair correlation function. Spherical harmonic analysis of the data confirms the existence of a definite hydration shell of water molecules at a distance of ~3.7 Å from the carbon atom in the methanol molecule. The water molecules in this shell form a disordered cage but retain the roughly tetrahedral local coordination found in pure water. Some degree of polarization of the water molecules in this shell is also apparent.

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One of the more intriguing questions in the physics of aqueous solutions concerns the structure and dynamics of water cages around so-called "hydrophobic" headgroups in solution. It is a widely held view [1] that apolar headgroups such as the methyl group $-CH_3$ in solution must enhance water structure compared to the pure liquid if the observed heats of mixing and negative excess entropy of solution are to be explained. Bearing in mind that pure water is conventionally regarded as a "hydrogen-bonded" structure, with specific orientational (roughly tetrahedral) correlations between neighboring molecules, it has often been speculated that normal water structure is significantly enhanced by a hydrophobic entity, resulting in a more ordered structure near the headgroup, sometimes misleadingly referred to as "icelike." The loss of entropy associated with generating a cage of water molecules around hydrophobic headgroups [2] has frequently been cited as the principle driving mechanism responsible for the folding of proteins.

Because of the difficulty of obtaining direct structural information from experiment, computer simulation has been used extensively to study the effect of hydrophobic entities [3–6] in solution. For systems such as methanol (CH_3OH) in water a slight sharpening of the water pair correlation functions is seen in solution, compared to those in the pure liquid [3], although the effects are sufficiently small to be difficult to verify in a neutron or x-ray diffraction experiment. In addition there is a prediction that a shell of water molecules forms around the methanol molecule [3,4] in solution. Computer studies of other hydrophobic entities in aqueous solution [5,6] also suggest that a hydration sphere exists in these systems as well.

In order to study the structure of *real* water around a dissolved methanol molecule we have performed a neutron diffraction experiment on the methanol-water system (mole ratio 1:9), using hydrogen isotope substitution to extract particular methanol-water correlation functions (specifically the methyl hydrogen to water hydrogen correlation function) directly from the data and independently from the water-water correlations. With isotope labeling on the hydrogen species and three different isotope contrasts, three composite partial structure factors (CPSFs) can be obtained in a neutron diffraction experiment [7]; hydrogen to hydrogen H_{YY}, unlabeled atoms to hydrogen H_{XY}, and unlabeled atoms to unlabeled atoms H_{XX}, each CPSF being in general a neutron-weighted average of several partial structure factors, $H_{\alpha\beta}(Q)$. These are related by Fourier transform to the corresponding partial pair correlation functions $g_{\alpha\beta}(r)$, between atomic species α and β,

$$H_{\alpha\beta}(Q)=\int_0^\infty 4\pi\rho r[g_{\alpha\beta}(r)-1]\sin Qr\,dr\,.$$

For methanol in water, although nominally a three-component system (O,C,H), neutrons can distinguish between hydrogens on the methyl group ($-CH_3$) and those on the water or hydroxyl ($-OH$) groups. This is because hydroxyl protons, which are labeled here as "H," exchange readily with hydroxyl deuterons, whereas the methyl protons, labeled "M," do not exchange. Thus to neutrons a methanol-water mixture will appear as a four-component system (O,C,M,H) with ten distinct partial structure factors.

For this experiment two sets of samples were made up as follows. In the first set (a) the isotope substitution was made only on the H hydrogens. Samples of methanol with deuterated methyl group were measured in three combinations of heavy and light water: pure light water H_2O, pure heavy water D_2O, and a 50:50 mixture of heavy and light water HDO. Analysis of the three diffraction patterns yields the CPSF $H_{YY}^{(a)}$, where

$$H_{YY}^{(a)}=H_{HH}(Q)\,. \tag{1}$$

Note that this result is particularly simple to interpret as it consists only of correlations between hydroxyl hydro-

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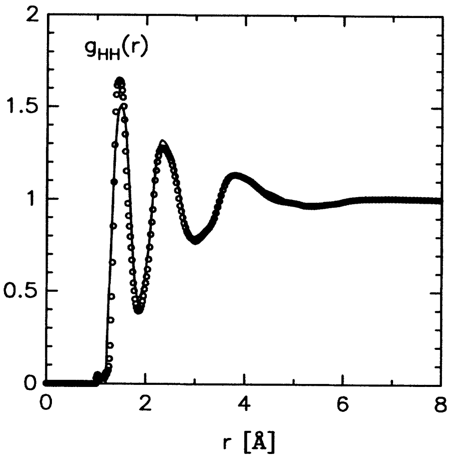

FIG. 1. The hydrogen-hydrogen correlation function for a 1:9 mole ratio methanol/water mixture (line) compared to the same function for pure water (circles) [15]. The intramolecular peak at $r \sim 1.5$ Å, the hydrogen bond peak at $r \sim 2.3$ Å, and a third characteristic peak near $r \sim 3.8$ Å are all clearly visible in both cases.

gens and is therefore related closely to the $H_{HH}(Q)$ partial structure factor in pure water.

For the second set of samples (b) the substitution was made on the methyl protons as well as the hydroxyl protons. In this case because the methyl protons do not exchange the *intramolecular* contribution to the *M*-*M* partial structure factor does not appear in the H_{YY} CPSF:

$$H_{YY}^{(b)} = 0.746 H_{HH} + 0.236 H_{MH}^{\text{inter}} + 0.068 H_{MH}^{\text{intra}} + 0.019 H_{MM}^{\text{inter}} . \quad (2)$$

(See [8] for the definition of $H_{\alpha\beta}^{\text{intra}}$.)

A simple combination of the two results (1) and (2) then yields

$$H_{YM} = 0.929 H_{MH}^{\text{inter}} + 0.268 H_{MH}^{\text{intra}} + 0.073 H_{MM}^{\text{inter}} . \quad (3)$$

This result is dominated by the important cross correlations between the methyl group and water molecules —the water-water correlations (H-H), which are heavily weighted in (1) and (2), have cancelled completely. A final step in the analysis is to remove the contribution from H_{MH}^{intra}, which can be estimated from the molecular geometry.

Neutron scattering data were recorded on the LAD diffractometer at ambient pressure and temperature (20 °C) at the ISIS pulsed spallation neutron source. The data were corrected according to standard techniques and Fourier transformed to real space.

Figure 1 shows the pair correlation function corresponding to $H_{YY}^{(a)}$. It will be noted that the result is remarkably similar to what has been measured previously for bulk water [9] and confirms that the underlying water structure is not greatly affected by the presence of methanol molecules at this concentration.

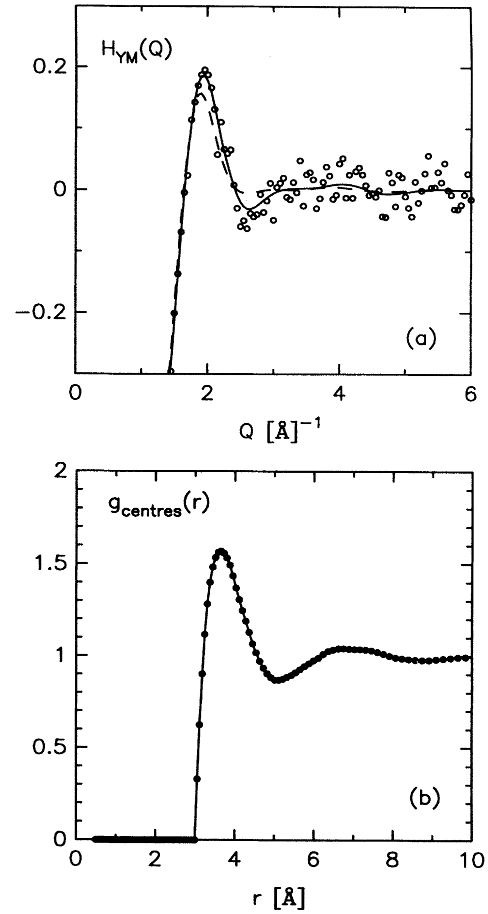

FIG. 2. (a) The measured H_{YM} composite partial structure factor for a 1:9 molar ratio mixture of methanol and water. The dashed line shows the fit to these data assuming isotropic orientations between methyl headgroup and surrounding molecules. The full line shows the fit using the full spherical harmonic expansion. (b) The molecular centers (methanol carbon to water oxygen) correlation function obtained after averaging over all molecular orientations. A clear peak is seen at about ~ 3.7 Å and indicates a definite shell of water molecules around the methanol molecule in solution.

The CPSF H_{YM} is shown in Fig. 2(a) and is quite different from the two parent functions [Eqs. (1) and (2), not shown here] from which it is derived. To analyze these data further we adopted the technique of spherical harmonic reconstruction described elsewhere [10], in order to estimate the extent that orientational correlations exist between methyl headgroup and surrounding water molecules.

The site-site (*M*H) partial structure factor is expanded in a series of products of spherical harmonic functions using a standard formula [11], with coefficients $H(l_1 l_2 l; n_1 n_2; Q)$ related by Fourier-Bessel transform to their real space counterparts $h(l_1 l_2 l; n_1 n_2; r)$. Once found, the latter can be used to reconstruct the orientational pair correlation function, $g(\mathbf{r},\omega_1,\omega_2)$ (see [11] for details). The l and n are integers whose values are determined by the molecular symmetries of the methanol and water molecules, and by the symmetry properties of the spherical harmonic functions themselves.

The coefficients were determined by a maximum-entropy-like process which requires them to be as *smooth* as possible [10], while also requiring them to fit the diffraction data. Furthermore, a superposition of all trial sets of coefficients was formed, and this set of average coefficients is also a valid set of coefficients which will fit the data. This procedure allows a range of possible orientational correlation functions which are compatible with the neutron data to be explored.

The initial step in the reconstruction is to estimate the $h(000;00;r)$ term. This corresponds to the distribution of water molecule centers around methanol molecule centers, after averaging over all orientations. [The small contribution from the MM term in Eq. (7) is assumed to appear only in the molecular centers term, since there are not likely to be strong orientational correlations between methanol molecules, at least at the concentration of this experiment.]

The contribution of the zeroth order term to the MH partial structure factor is shown as the dashed line in Fig. 2(a). A small but significant discrepancy between fit and experimental data is seen, and this could not be removed by further refinement of the (000;00) term alone. To understand how this might be, it will be noted that the Q-space spherical harmonic expansion involves a sum of products of the form $j_{l_1}(Qd_M)j_{l_2}(Qd_{\mathrm{H}})\mathrm{H}(l_1l_2l;n_1n_2;Q)$ [11], where $j_l(x)$ is the spherical Bessel function of order l, and d_M and d_{H} are the intramolecular carbon-hydrogen and oxygen-hydrogen distances, respectively. Both these

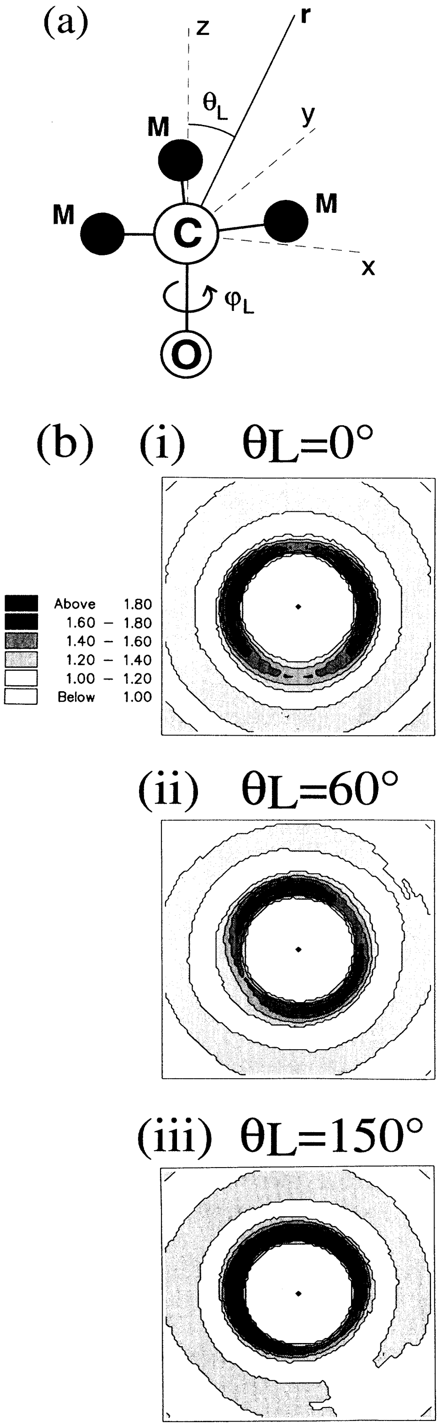

FIG. 3. (a) Diagram of the coordinate system used to define the maps of orientational pair correlation function. The carbon atom is at the center of the coordinate axes, with the OC bond pointing along the positive z axis. The hydroxyl hydrogen on the methanol molecule is not shown here as its contribution has been eliminated from the measured structure factor. (b) Density maps of the orientation pair correlation function, $g(\mathbf{r},\omega_1,\omega_2)$, for water molecules around methanol in aqueous solution. The pair correlation function for water molecules is shown as a function of radial distance r away from the central carbon atom (central black dot in each map), after averaging over rotations, ϕ_L, of the methanol molecule about the z axis. For the particular set of maps shown here the H-O-H plane of the water molecule lies *perpendicular* to the plane of the diagrams, with the water molecule's H-O-H bisector (i.e., the dipole moment vector) in the same plane. The direction within each plot corresponds to the *angle* that the dipole moment vector in the water molecule makes with the positive laboratory z axis. Each map is plotted on a 15 Å×15 Å square. The three maps correspond to (i) moving away from the carbon atom vertically upwards (i.e., along the positive z axis, $\theta_L = 0°$), (ii) moving at an angle of 60° to the z axis ($\theta_L = 60°$), and (iii) moving at angle of 150° to the same axis ($\theta_L = 150°$). It will be seen that the brightest lobes occur in directions where the H-O-H bisector is roughly tangential to the carbon-water axis, but a slight polarization of the water molecules is also discernible. (The dipole moment of the methanol molecule runs along the positive z axis after the average over ϕ_L.)

distances are of order 1 Å, and so for the zeroth order term $l_1 = l_2 = l = 0$ the product of Bessel functions decays quite rapidly with increasing Q, and in fact goes to zero near $Q \approx 3$ Å^{-1}. Therefore it is not possible to fit the full Q range with only this one term, no matter how much structure is introduced in the centers correlation function. Higher order terms are needed. The full calculation involving terms up to order $l = 4$ (66 coefficients in all) is shown as the solid line in Fig. 2(a).

The estimated centers correlation function, Fig. 2(b) shows a well-defined peak at about 3.7 Å, corresponding to approximately 10 water molecules around the methyl headgroup. It shows good qualitative agreement with what computer simulations have predicted [3,4].

Some maps of the estimated orientational pair correlation function are shown in Fig. 3. Broad but pronounced lobes appear in these distributions and confirm that on the whole the plane of the water molecule prefers to lie tangential to the methanol-water axis. This we believe is the first direct *experimental* evidence that water molecules form a disordered hydrogen bonded cage around the methanol molecule. Apparently this can form without a high degree of hydrogen bond breaking between water molecules (Fig. 1). The direction of these orientation lobes indicates that the hydrogens on the water molecule tend to lie closer to the carbon atom in the bottom diagram than in the top, implying a weak alignment of the water molecule's dipole moment with that of the methanol molecule.

To summarize, we have observed, by neutron diffraction and isotope substitution, the water hydration shell around a methanol molecule in solution. The results confirm the existence of a shell of water molecules around the methanol molecule at a carbon to water distance of ~3.7 Å, as has been seen in several computer simulations. Spherical harmonic analysis of the data suggests that this shell is achieved without a significant modification of the orientational order between water molecules, which form a loose hydrogen bonded cage around the methanol molecule. This direct measurement of water structure in methanol aqueous solution therefore contradicts much previous speculation that water structure is enhanced by the dissolved alcohol molecule. There is also some preliminary evidence here for a weak polarization of the water molecules around the methanol molecule. The detailed description of the hydration shell of water around the methanol molecule that has been possible here is due in no small measure to being able to isolate the partial MH structure factor by isotope substitution.

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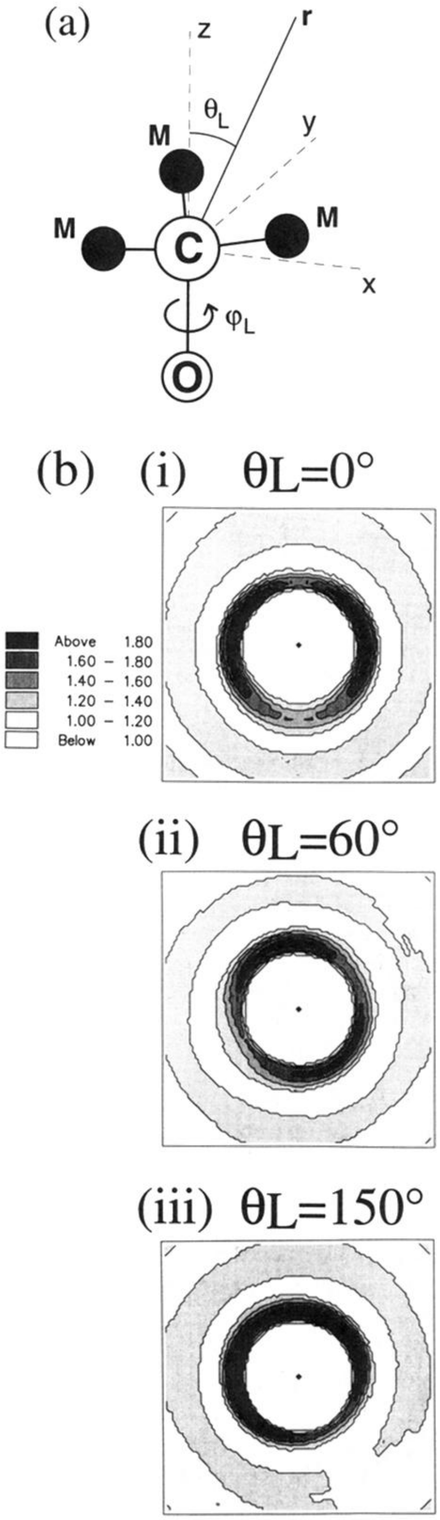

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