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Abstract
Hydrogen/deuterium isotopic substitution neutron scattering techniques and
empirical potential structure refinement have been used to investigate the
structure in a 0.86 mole fraction solution of tertiary butanol in water. The
resulting model structure suggests that in this mixture, the relatively small
quantity of water molecules tend to associate in small hydrogen bonded clusters
of two or three molecules, solvated by the alcohol hydroxyl groups. An
interesting observation on investigating this novel local water environment is
that the tetrahedral hydrogen bonding motif of water still strongly influences
the location of both the water and alcohol first neighbours. The combination
of the small number of water molecules in the mixture and the bulky molecular
structure of the alcohol appears to result in the incomplete satisfaction of the
water molecule's full hydrogen bonding capabilities.

1. Introduction

Understanding the mixing state of the molecular components in alcohol–water solutions is
currently a considerable challenge in the area of the physical chemistry and chemical physics
of liquid systems. These mixtures tend to be widely used in the laboratory environment as
support media for diverse molecular processes and chemical reactions—firstly because their
amphiphilic nature is well suited to the in-solution support of both polar and non-polar solute
species, and secondly because many solutions possess thermodynamic characteristics that
make them ideal cryosolvents able to maintain their liquid state to low temperatures. Recent
work on a concentrated methanol–water solution highlighted the occurrence of molecular
scale segregation between the alcohol and water molecules in these mixtures, and it has been
suggested that this may be the key concept to assist us in understanding how their physico-
chemical properties arise [1]. Whether or not this incomplete mixing on the microscopic scale
was unique to the methanol–water system was not possible to establish from this single study;
however, recent work on a concentrated tertiary butanol–water solution [2] lends support to
the idea that this phenomenon may be ubiquitous to the alcohol–water system.

Structural studies of these amphiphilic solutions tend to revolve around the balance of non-polar (hydrophobic) and polar (hydrophilic) character that exists within these solvent mixtures. In the dilute alcohol range, it is widely accepted that hydrophobic interactions between the non-polar methyl groups of the alcohol molecules and the solvent water tend to dominate the mixing state [3]. This fact has been borne out by a number of experimental and computational studies [4–12] though some argument exists as to how these effects are manifested within the mixtures. The two principal models are based either on the existence of labile aggregates of alcohol and water in some kind of pseudo-stoichiometric unit [4–6, 8] or on some kind of pseudo-critical behaviour associated with concentration fluctuations in the mixture [7, 10, 11].

In contrast to the case for the dilute systems, at the concentrated alcohol end of the mixing scale few experimental studies have been undertaken, most probably due to the fact that the thermodynamic and volumetric properties of these mixtures tends to focus interest on the water-rich systems. The recent experimental investigations on both the concentrated methanol–water [1] and tertiary butanol–water [2] systems perhaps highlight that this was short-sighted and that it is in this concentrated regime where the structural foundations necessary for clarifying the understanding of the general alcohol–water solution state can be found. Here we investigate the alcohol–water interactions in a 0.86 mole fraction tertiary butanol–water solution and in particular we investigate the hydrogen bonding environment in which the small content of water molecules find themselves.

2. Experiment and data analysis

To investigate the structure of the concentrated (0.86 mole fraction) tertiary butanol–water solution we have used the technique of neutron diffraction with hydrogen/deuterium isotopic substitution. In this study the isotope exchange is used to enhance the structural contrast of the technique towards the tertiary butanol molecules in the solution by selective exchange on the methyl hydrogen sites of the alcohol molecules, the details of which have been presented elsewhere [2].

In the subsequent discussion the following labels have been assigned to the distinguishable atomic sites on the alcohol and water molecules. On the alcohol molecule, CC refers to the tertiary carbon atom, C to the methyl group carbon atoms, M to the methyl group hydrogen atoms, O to the hydroxyl group oxygen atom and H to the hydroxyl group hydrogen atom. On the water molecule, OW refers to the water oxygen atom and HW to the water hydrogen atoms.

The three isotopic substitution experiments that have been performed [2] allow us to directly obtain three structure factors that contain information on the atomic pair correlations between:

  (i) M atoms and other M atoms;
 (ii) M atoms and CC, C, O, H, OW and HW atoms;
(iii) CC, C, O, H, OW, HW atoms and other CC, C, O, H, OW and HW atoms.

To extract structural information from the three partial structure factors determined by the experiment, we have used the technique of empirical potential structure refinement (EPSR) developed by Soper [13, 14]. Essentially the method combines Monte Carlo computer modelling procedures with constrained refinement against the measured experimental data. The result is the production of an ensemble of model structures that reproduce the measured neutron partial structure factors and that can then subsequently be interrogated to extract any structural function of interest. A particular advantage of this method is that it becomes possible to investigate the structural pair correlations between atom sites that were not explicitly

substituted in the original series of neutron diffraction measurements. This is feasible because the components that contribute to the structural model, i.e. the molecular units, are constrained to retain the known shape and size of each species, here tertiary butanol molecules and water molecules. In addition, the overall density of the model structures is maintained at the experimentally known atomic density of the solution.

For this study, the EPSR procedure was initialized using a cubic box of side length 27.75 Å containing 108 tertiary butanol molecules and 18 water molecules at an atomic density of 0.098 atoms Å^{-3} [15]. The box was seeded using a reference set of potentials for each of the two molecular species. The OPLS set of potentials of Jorgensen and co-workers [16, 17] was used for the tertiary butanol molecules and the SPC/E potentials of Berendsen *et al* [18] for the water molecules. During the EPSR procedure the model box is allowed to develop under standard Monte Carlo procedures, but with the novel feature of driving the structures towards agreement with the neutron scattering data by a perturbation to the reference potentials. This is implemented via a potential of mean force derived from the experimental diffraction data. Tests of the method [14, 19] have shown that given the molecule and density constraints, and those provided by the available neutron scattering data sets, the refined structures prove to be quite insensitive to perturbations arising from the initial seed potentials. The final structural functions extracted by the procedure arise from the analysis of the Monte Carlo produced ensemble averaged configurations of the simulation box. Typically many millions of atomic and molecular moves are performed in the generation of this ensemble which consist of individual atom displacements, molecule displacements and rotations, and lastly rotations of any appropriate molecular groups. The structural functions are thus analogous to any produced by conventional simulation methods and attempt to capture the essence of the infinite set of possible molecular configurations of liquid state systems, through the generation of this ensemble. Further details of the EPSR refinement performed on this 0.86 mole fraction solution are given elsewhere [2].

Although in the ideal scenario for the structural study of this 0.86 mole fraction alcohol system it would be desirable to also perform isotopic exchange on the water hydrogen sites in the solution, at this concentration this is not practical. This is because they are present in too dilute a proportion for accurate structure determination with current neutron scattering facilities. Tests of the EPSR technique however, i.e. a comparison of the results of [9] and [12], gives us confidence that even in this non-ideal case the method is robust enough to provide useful information on the water-centred hydrogen bonding interactions in the mixture.

3. Results

In figure 1 we show the partial distribution functions corresponding to pair correlations involving the water molecules and the alcohol molecule hydroxyl groups. The characteristic shape of $g_{OW-OW}(r)$, heavily weighted to correlations between the water molecules at separations below 5 Å, is illustrative of strong clustering of the water molecules within the solution. This hallmark of association of like species can also be seen in the $g_{HW-HW}(r)$ and $g_{OW-HW}(r)$ partial pair distribution functions. Integration of $g_{OW-OW}(r)$ between 2.0 and 5.5 Å tells us that each water molecule has 1.5 ± 0.4 neighbouring water molecules in this range, partitioned as 0.8 ± 0.3 neighbours between 2.0 and 3.5 Å and 0.7 ± 0.3 between 3.5 and 5.5 Å.

Turning our attention to $g_{OW-HW}(r)$ we find that the function displays two principal peaks, the first corresponding to intermolecular hydrogen bonding OW–HW interactions between 1.2 and 2.4 Å, and the second to those between 2.4 and 5.5 Å, corresponding to non-bonding configurations. If we integrate this function in these ranges we find that each water oxygen
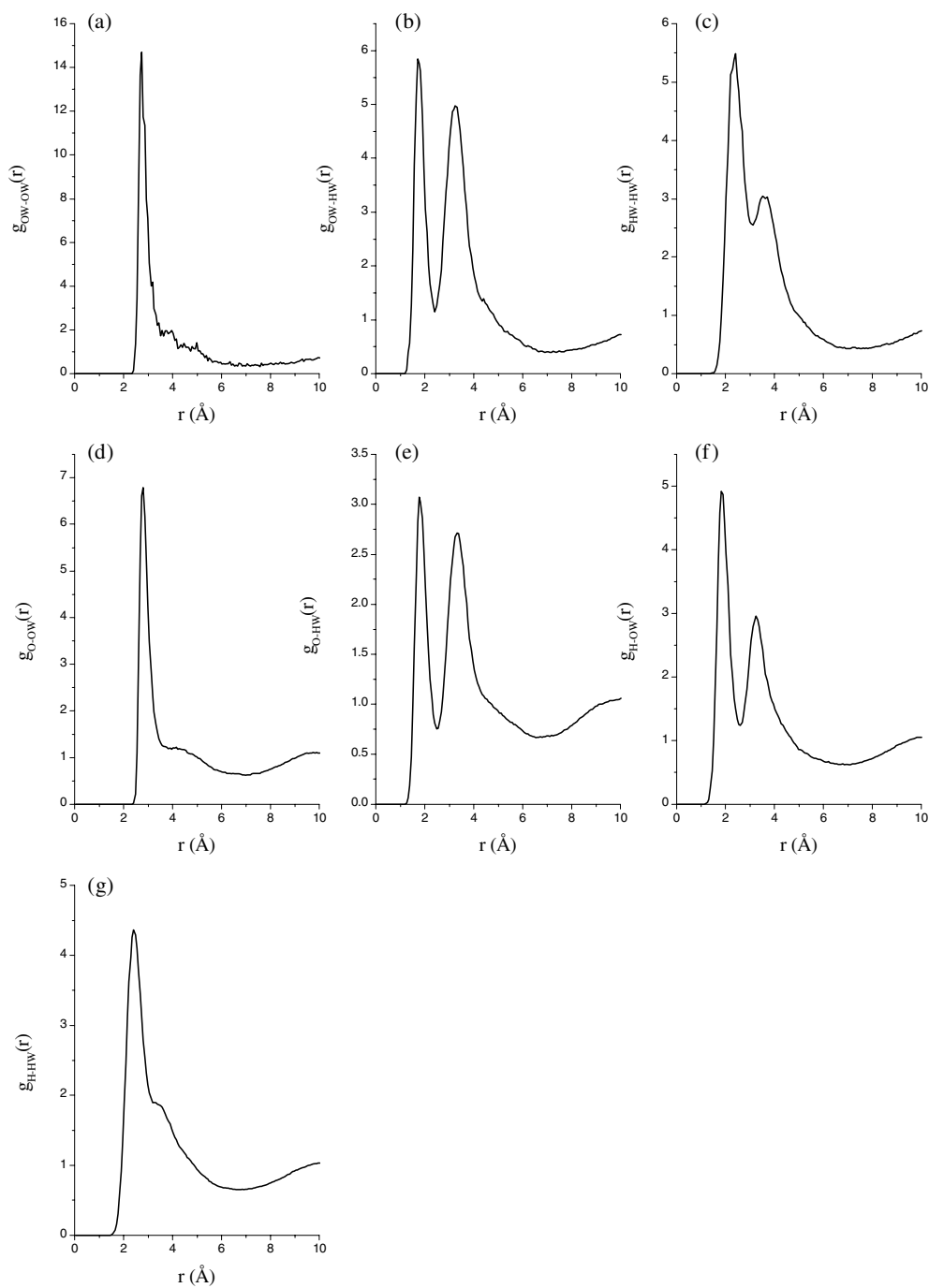
Figure 1. The intermolecular partial distribution functions corresponding to hydrogen bonding interactions between water molecules themselves and between water and alcohol molecules: (a) $g_{OW-OW}(r)$, (b) $g_{OW-HW}(r)$, (c) $g_{HW-HW}(r)$, (d) $g_{O-OW}(r)$, (e) $g_{O-HW}(r)$, (f) $g_{H-OW}(r)$ and (g) $g_{H-HW}(r)$.

atom is hydrogen bonded to 0.3 ± 0.1 water hydrogen atoms in the short range with 2.6 ± 0.4 water hydrogen atoms in the range allocated to the second peak. This finding suggests that the alcohol hydroxyl hydrogen atoms are more likely to be the dominant species bonding with each water oxygen atom. This hypothesis can be tested by interrogating the $g_{H-OW}(r)$ ($\equiv g_{OW-H}(r)$) and g_{O-HW} ($\equiv g_{HW-O}(r)$) functions. These two functions can be seen to essentially mirror the peak positions found in $g_{OW-HW}(r)$ ($\equiv g_{HW-OW}(r)$) which is indicative of the fact that the nature of the interaction between the water molecule and this functional group on the alcohol are, as expected, of similar kind. Integrating $g_{H-OW}(r)$ to find out how many alcohol hydroxyl hydrogen atoms can be found in the two relevant distance ranges from the water oxygen tells us that in the first peak from 1.2 to 2.5 Å, one finds on average 1.0 ± 0.2 alcohol hydroxyl hydrogen atoms directly hydrogen bonded to each water oxygen atom. In the second peak, there are 5.3 ± 0.5 hydroxyl group hydrogen atoms from 2.5 to 5.5 Å. Conversely, integrating the first and second peaks of $g_{HW-O}(r)$ tells us that each water hydrogen atom is on average bonded to 0.6 ± 0.1 alcohol oxygen atoms, with 5.1 ± 0.4 in the longer range from 2.5 to 5.5 Å.

What is apparent is that each water oxygen atom as an intermolecular hydrogen bond acceptor in this 0.86 mole fraction tertiary butanol solution does not have its hydrogen bonding potential fully utilized. If this were the case, the mean number of intermolecular hydrogen atoms that would be found within 2.4 Å of each water oxygen atom would be 2.0 and not 1.3. If we look at the total number of alcohol hydroxyl groups that can be found within the region within 5.5 Å of each water oxygen atom we find that there are approximately six. These are partitioned as 2.8 ± 0.4 between 2.3 and 3.8 Å and 3.0 ± 0.4 between 3.8 and 5.5 Å, as can be found on integrating the function $g_{O-OW}(r)$.

4. Discussion

The results for the hydrogen bonding interactions of the water molecules between themselves and with the hydroxyl group on the tertiary butanol molecules suggest that the combination of the dilute presence of water in the solution and the steric effects limiting the packing of the bulky alcohol molecules transpire to prevent the full hydrogen bonding of the water molecules in this concentrated alcohol solution environment. The spatial distribution function [20] of the first and second shell of water molecules about an arbitrarily selected water molecule in the solution, and the corresponding first-and second-shell distributions of alcohol molecules, are shown in figure 2. What can be seen from figure 2(a) is that the favoured spatial distribution of water molecules around water is essentially identical to what would be found in pure water [15]. This indicates that the close-to-tetrahedral hydrogen bonding nature of this important molecule is still dominant in this water-poor solution. We know from our coordination number analysis (0.8 ± 0.3 neighbours between 2.0 and 3.5 Å) that each probability lobe has only partial occupancy. The second distribution shell, figure 2(b), containing 0.7 ± 0.3 water molecules between 3.5 and 5.5 Å, shows us that these water molecules can adopt a very broad range of possible configurations with respect to a water molecule centre. We note however that there are gaps in this second-shell distribution corresponding to the directions of direct hydrogen bonding indicated in the first shell. Figure 2(c) shows the distribution of alcohol molecules around water, albeit at a greater distance allowing for the offset of the alcohol molecule centre (the tertiary carbon, CC) from the water bonding hydroxyl group. The resulting spatial density map tells us that the first shell of alcohol molecules also manages to adopt a spatial distribution very similar to that of the first water shell. This finding further emphasizes the importance of the intrinsic nature of the hydrogen bonding to the accommodation of the water molecules within this alcohol-rich solution. The probability distribution of the second-neighbour shell of alcohol
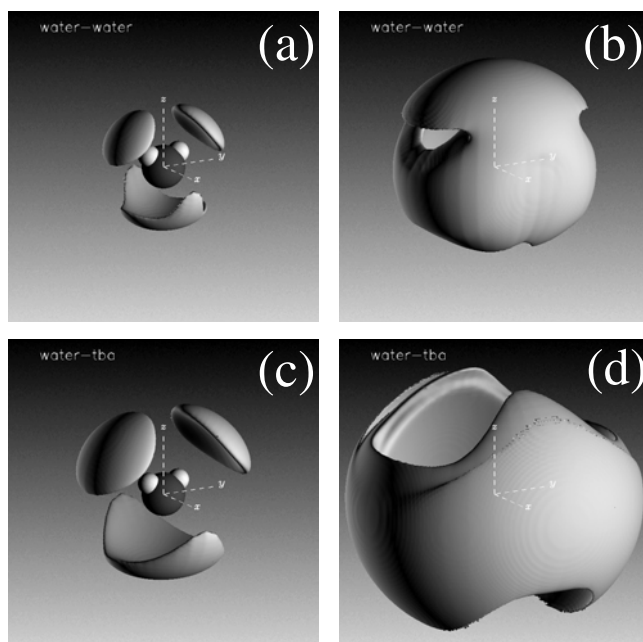
Figure 2. The spatial density functions [20] of ((a), (b)) water around a central water molecule, $g_{OW-OW}(r, \Omega)$, and ((c), (d)) tertiary butanol around a central water molecule, $g_{OW-CC}(r, \Omega)$, in the 0.86 mole fraction tertiary butanol–water solution. This function represents a three-dimensional map of the density of ((a), (b)) water or ((c), (d)) alcohol molecules as a function of radial distance, r, and orientation, Ω ($=\theta, \phi$), about a central water molecule in the liquid. Panel (a) shows the distribution of water oxygen atoms around the central water molecule in the shell from 2.0 to 3.5 Å. Panel (b) shows the shell of the most probable neighbouring water molecule distribution in the distance range from 3.5 to 5.5 Å. Panel (c) shows how the alcohol coordination of the water molecules mirrors the water–water case but at a larger distance, reflecting the greater distance between the central water oxygen atom and the tertiary carbon of the solvating alcohol molecules. The shell radius is set to include the distance range from 3.4 to 4.9 Å, i.e. scaled by the known intramolecular CC–O ($\approx$1.4 Å) distance for tertiary butanol. Panel (d) shows the second distribution shell of alcohol molecule centres; this covers the distance range from 4.9 to 6.9 Å. The viewports for each plot are set to $\pm$7 Å about the oxygen atom of the central water molecule. The contour level is set so as to plot the regions in spatial density corresponding to the most probable 50% of the total number of molecule centres (OW or CC) for each selected radial shell from the water oxygen centre.

molecules, figure 2(d), is similarly diffuse, as is found for the second shell of water molecules, though there appear to be larger holes in the direction above the central water hydrogen atoms and below the water oxygen. These larger holes are indicative of the greater quantities of steric hindrance and packing effects experienced by the more bulky alcohol molecules as compared to those which affect the smaller water molecules in their second-shell environment.

5. Conclusions

The average picture of this concentrated alcohol solution to emerge from this structural model is one in which we find water molecules clustering together in groups of two or three molecules on a length scale defined by a sphere of 5.5 Å around a centre situated on a water oxygen atom. This volume of space is also shared with approximately six tertiary butanol molecule hydroxyl groups which is the expected proportion given the 6:1 molecular ratio of

the solution components. The tetrahedral hydrogen bonding motif of the water molecules is the dominant factor organizing the likely location of both near-neighbour water molecules and alcohol molecules. The average hydrogen bond complement for each water oxygen is, at 1.3 (1.0 alcohol hydroxyl hydrogen, 0.3 water hydrogen), lower than would be expected for complete satisfaction of the bond forming capabilities of the molecule. This suggests that the combination of the small quantity of water in the solution and the bulky nature of the alcohol molecules inhibits the ability of the water molecules to reach complete connectivity. The orientational preferences of second-neighbour non-bonded interactions around the water, that must complete the solvation volume to be consistent with the solution atomic density, are found to be of a considerably more diffuse nature.

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