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## The structure of aqueous solutions of tertiary butanol

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**Abstract.** Using neutron diffraction with isotopic substitution, the structures of aqueous solutions of tertiary butanol have been studied as a function of concentration. As the behaviour of this system is thought to be driven by hydrophobic interactions, particular attention was paid to the hydration of the non-polar headgroups and the nature of the intermolecular contacts. As concentration is increased from 0.06 to 0.16 mole fraction tertiary butanol, there is evidence for the growth of small clusters of the alcohol molecules, with butanol–butanol coordination of two to three even at the lowest concentration. Orientational pair correlation functions show that the dominant intermolecular contacts between alcohol molecules are between the non-polar head groups, as would be expected for a system driven by hydrophobic interactions. As concentration increases, however, there is evidence of mixed polar–non-polar contacts. The alcohol group's hydrogen bonding requirements appear to be fully met by polar contacts with water molecules: there is no evidence for significant butanol–butanol hydrogen bonding.

### 1. Introduction

The structures of solutions depend on the balance between the various intermolecular forces. In the case of aqueous solutions of bifunctional molecules such as alcohols, not only are hydrophobic interactions thought to be an important factor in determining the solution structure, but also the degree to which the solute alcohol molecules hydrogen bond to each other rather than to the solvent water. This in turn will depend on the relative strengths of the water–alcohol OH, water–water, and alcohol OH–alcohol OH hydrogen bonds. In simulations of such systems, small errors in the potential functions may therefore lead to erroneous structural predictions. Similar considerations apply to more complex systems such as the free energy difference between a folded and an unfolded protein. It is therefore important to obtain good quality experimental data on such systems, against which simulation calculations can be tested.

Neutron diffraction using multiple isotopic substitution is now sufficiently powerful to enable us to measure, in unprecedented detail, the structures of such solution systems. Taken together with recent developments in data interpretation, in particular the empirical potential structure refinement procedure (ESPR) [1], we are able to construct models of the solution structure that are consistent with a number of experimental data sets. These models can then be interrogated to obtain detailed structural information at the partial pair correlation function level. Comparisons with models generated using 'standard' potential functions may then suggest how these potentials may need to be modified to reproduce more closely the experimental results (for example in pure tertiary butanol [2]).

We present here results of measurements of the structures of three concentrations of tertiary butanol in water. These are presented in terms of a number of partial pair distribution functions, which are discussed in terms of what they tell us of the local structures in this system, and how they change with concentration. Particular attention is paid to the interactions of (a) the non-polar head group of the solute molecule, in the context of the hydrophobic interaction, and (b) the polar alcoholic OH group. Comparison with the structure of the pure solute indicates how the presence of the aqueous solvent perturbs the intermolecular solute–solute interactions.

## 2. Experimental details

Neutron diffraction experiments were performed on the SANDALS diffractometer at the ISIS pulsed neutron spallation source at the Rutherford Appleton Laboratory. For each of the three concentrations studied (0.057, 0.1071 and 0.167 mole fractions of alcohol, corresponding respectively to alcohol:water molecular ratios of approximately 1:17, 1:8 and 1:5), data were taken on each of the three isotopic mixtures  $(\text{CH}_3)_3\text{COH}$  in  $\text{D}_2\text{O}$ ,  $(\text{CD}_3)_3\text{COD}$  in  $\text{D}_2\text{O}$  and a 1:1 mixture of these two solutions. The samples were contained in 2 mm thick flat plate TiZr cells of composition chosen to give zero coherent scattering. The data were corrected for absorption and multiple scattering and normalized to vanadium using the ATLAS programs [3]. Corrections for inelastic scattering were made as outlined in [4].

## 3. Theory and data interpretation

### 3.1. Isotope substitution neutron scattering

As described elsewhere (see e.g. [2]), from such an isotopic substitution measurement we can extract three partial structure factors  $S_{HH}(Q)$ ,  $S_{HX}(Q)$  and  $S_{XX}(Q)$ , where  $S_{HH}(Q)$  is the hydrogen–hydrogen partial structure factor, and the correlations involving all other (non-substituted) atoms are labelled with the subscript  $X$ .  $Q$  is the magnitude of the neutron scattering vector, given by  $Q = 4\pi \sin \theta / \lambda$  where  $\lambda$  is the neutron wavelength and  $2\theta$  the scattering angle. The partial structure factors are related to the interatomic partial pair distribution functions  $g_{HH}(r)$  etc through the normal Fourier transform relationship.

### 3.2. Data modelling

We use the recently developed empirical potential structure refinement procedure (EPSR) of Soper [1]. In this method, a set of experimentally determined radial distribution function data  $g_{\alpha\beta}^D(r)$  is used to constrain a Monte Carlo simulation. The method is based on the development of a potential of mean force  $\Psi_{\alpha\beta}(r) = -kT \ln g_{\alpha\beta}(r)$  between atoms  $\alpha$  and  $\beta$ . Starting from a model fluid with the correct temperature and density, and using assumed potentials  $U_{\alpha\beta}^O(r)$  between sites  $\alpha$  and  $\beta$ , an estimate of the pair distribution function  $g_{\alpha\beta}(r)$  can be made. A new potential energy function  $U_{\alpha\beta}^N(r)$  is then estimated from

$$U_{\alpha\beta}^N(r) = U_{\alpha\beta}^O(r) + (\Psi_{\alpha\beta}^D(r) - \Psi_{\alpha\beta}(r)) = U_{\alpha\beta}^O(r) + kT \ln(g_{\alpha\beta}(r)/g_{\alpha\beta}^D(r)).$$

This new potential is then fed back into the simulation, and particles within the simulation box moved. This process continues until such time as

$$U_{\alpha\beta}^N(r) \cong U_{\alpha\beta}^O(r)$$

and hence

$$g_{\alpha\beta}(r) \cong g_{\alpha\beta}^D(r).$$

In other words, the simulated data now shows good agreement with that measured experimentally.

The Monte Carlo process is now continued, and ensemble averages of various partial distribution functions are extracted. These can include the full set of interatomic partial pair distribution functions. Intermolecular orientational function information can also be evaluated through a spherical harmonic expansion of the orientational pair correlation functions  $g(\mathbf{r}, \omega_1, \omega_2)$  [5]. This function relates the relative position vector  $\mathbf{r}$  of molecules 1 and 2 with their orientations  $\omega_1$  and  $\omega_2$  in the laboratory reference frame.

In this case, the 'seed' potentials used were, for the alcohol molecules, the OPLS potentials of Jorgensen *et al* [6, 7] and, for water, the SPC/E potentials of Berendsen *et al* [8].

#### 4. Results

In the t-butanol–water system, we identify seven distinctly different atomic sites as follows:

- CC, tertiary butanol central carbon;
- C, tertiary butanol methyl group carbon;
- M, tertiary butanol methyl group hydrogen;
- O, tertiary butanol hydroxyl group oxygen;
- H, tertiary butanol hydroxyl group hydrogen;
- OW, water molecule oxygen; and
- HW, water molecule hydrogen.

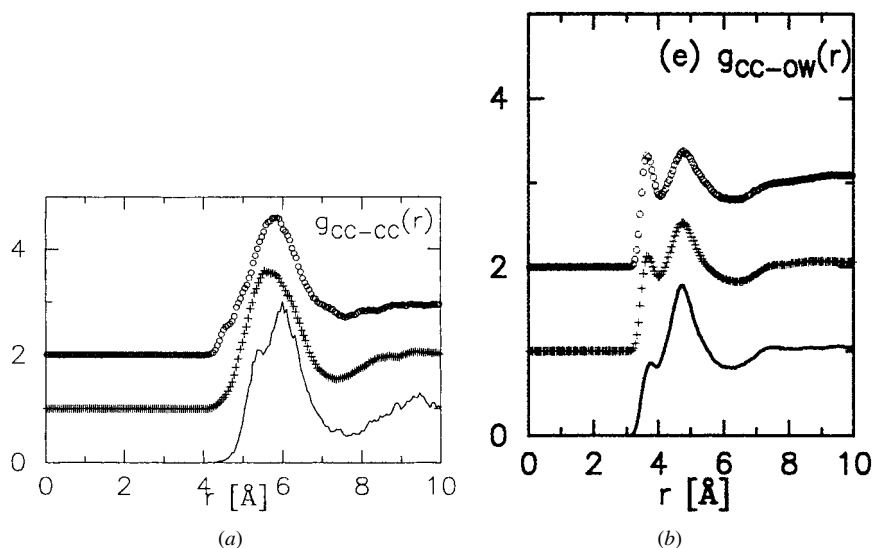
Thus, to characterize the solution structure fully, we require 28 partial pair distribution functions. These can be extracted from the EPSR modelled ensemble. Each of these 28 partial functions will contribute with different weights to the experimentally measured HH, HX and XX partial distribution functions (see table 1 in [9]).

These 28 partial pair distribution functions were extracted for these three concentrations of aqueous tertiary butanol [9], from which a great deal of structural information can be extracted concerning the solute–solute, solute–solvent, and solvent–solvent structures. Furthermore, orientational correlation function data can be extracted to give information on, for example, the relative orientations of solute molecules in contact. We limit ourselves here to a few salient points that are of particular interest with respect to (a) the hydrophobic interaction and (b) the solute–solute and solute–solvent hydrogen bonding.

##### 4.1. Solute–solute correlations

Figure 1(a) shows the solute–solute molecular centres correlation functions  $g_{CC-CC}(r)$  for the three concentrations. The fact that the functions peak between 5.5 and 6.0 Å tells us that the t-butanol molecules at all three concentrations are in contact: this distance is too short to allow any intervening water molecules, as would be the case for a solvent-separated association. The area under this peak rises from  $2.8 \pm 0.6$  neighbouring alcohol molecules at the lowest ( $\sim 0.06$  mole fraction) concentration, to  $4.4 \pm 0.6$  and  $5.5 \pm 1.3$  direct solute–solute contacts for the  $\sim 0.11$  and  $\sim 0.16$  mole fraction concentrations, respectively (see also table 1). Thus, as we increase the concentration, it seems that each t-butanol molecule is, on the average, surrounded by two to three contacting molecules at the lowest concentration, rising to five to six at the highest concentration studied.

What are the chemical natures of these intermolecular solute–solute contacts? This question can be answered by looking at the orientational correlation functions obtained from



**Figure 1.** (a) The molecular centres partial pair distribution functions for (○) 0.16; (+) 0.11; and (−) 0.06 mole fraction concentrations of t-butanol in water. (b) The central carbon–water oxygen partial pair distribution functions for (○) 0.16; (+) 0.11; and (−) 0.06 mole fraction concentrations of t-butanol in water. Functions are offset vertically for clarity.

**Table 1.** Selected coordination numbers obtained from integration of the features observed in various partial distribution functions at the three different concentrations used (0.06, 0.11 and 0.16 mole fractions).

Correlation	$R_{min}$ (Å)	$R_{max}$ (Å)	Coordination number (atoms)		
			0.06 mole fraction	0.11 mole fraction	0.16 mole fraction
CC–CC	4.0	7.0	$2.8 \pm 0.6$	$4.4 \pm 0.6$	$5.8 \pm 1.3$
CC–OW	3.0	4.0	$2.1 \pm 0.4$	$2.2 \pm 0.3$	$2.0 \pm 0.2$
O–OW	4.0	6.2	$21.0 \pm 1.2$	$16.4 \pm 0.9$	$12.8 \pm 0.6$
O–HW	2.3	3.3	$2.2 \pm 0.4$	$2.3 \pm 0.3$	$2.1 \pm 0.3$
O–H	1.4	2.5	$1.2 \pm 0.3$	$1.3 \pm 0.2$	$1.2 \pm 0.2$
O–O	2.4	3.25		$0.12 \pm 0.10$	$0.2 \pm 0.1$
O–H	2.5	3.5		$0.07 \pm 0.07$	$0.06 \pm 0.06$
H–H	1.6	3.0		$0.17 \pm 0.11$	$0.3 \pm 0.1$

the EPSR fits. The main conclusions that can be drawn from an analysis of these (which are discussed in details elsewhere [9]) are as follows.

At the lowest (0.06 mole fraction) concentration, the dominant direction of approach of a neighbouring solute molecule is through direct methyl group–methyl group (‘head-to-head’) contacts. This is what we might expect for a system whose interactions are dominated by the hydrophobic interaction. At this lowest concentration, the particular strength of this non-polar–non-polar interaction is underlined by the existence of a distinct low- $r$  shoulder on the centres–centres correlation function show in figure 1(a). The orientational analysis [9] shows this is quite clearly the case: this shoulder is *not* due to a closer approach consequent upon hydrogen bonding through the alcohol OH groups.

As we increase the concentration, the coordination number increases, as shown in table 1. However, as we increase the coordination number, there will come a point at which it is no

longer possible to accommodate all the intermolecular solute–solute contacts through the non-polar–non-polar headgroup interaction. Thus, we would expect other kinds of interactions to be observed, the most obvious we might expect to be direct hydrogen bonding between the alcohol OH groups of two neighbouring molecules. However, the orientation analysis is not consistent with such an expectation [9]: as the concentration increases, and it no longer is possible to accommodate all the interactions through a clear non-polar headgroup contact, we find an increasing number of polar group–non-polar group contacts. Put slightly differently, as we move around the ‘central’ t-butanol molecule from the non-polar headgroup region towards the polar ‘tail’ region where we find the alcoholic OH group, there is a tendency for a neighbouring t-butanol molecule to point towards this alcohol group *with its non-polar head rather than its polar tail*. Initially, this may seem to be counterintuitive. It can be rationalized perhaps by considering that the loss of a potential hydrogen bond resulting from this apparently sub-optimal intermolecular interaction is possibly compensated by the ability of the interacting neighbour to maintain its hydrogen bonding interaction of its alcoholic polar tail to a water molecule or water molecules in the solvent.

As we move to the highest concentration examined (0.16 mole fraction), the intermolecular orientational correlations begin to resemble those found in the pure liquid alcohol [2]. At these concentrations, the structural perturbations caused by the presence of the water solvent become less. At the 0.16 mole fraction, however, there is still much less in the way of direct polar–polar solute–solute interaction through the hydroxyl groups than there is in the pure solvent. The water seems to want to grab all the t-butanol hydroxyl groups that it can, rather than share them with other t-butanol molecules. This conclusion is confirmed by inspecting the essentially zero coordination numbers shown in the last three rows of table 1.

#### 4.2. Solute–solvent correlations

The solute hydration is best illustrated through considering the pair correlations between the central carbon (CC) and the water oxygen (OW) centres, namely the  $g_{CC-OW}(r)$  shown in figure 1(b).

In the 0.06 mole fraction case,  $g_{CC-OW}(r)$  has a main peak at 4.8 Å, with a shoulder at 3.6 Å. At the higher concentrations, this shoulder develops into a more significant peak. Integration of these partials yields  $2.1 \pm 0.4$  water oxygens at distances between 3.0 Å and 4.0 Å, and  $21.0 \pm 1.2$  water oxygens between 4.0 Å and 6.2 Å at the 0.06 mole fraction concentration (see also table 1). At the two higher concentrations, these water oxygen coordinations are found to be  $2.2 \pm 0.3$  and  $16.4 \pm 0.9$  (0.11 mole fraction) and  $2.0 \pm 0.2$  and  $12.6 \pm 0.6$  (0.16 mole fraction). Thus, the shorter range correlations, which (as is verified by an analysis of the relevant orientational correlation functions [9] and is also consistent with the O–OW correlation—see table 1) correspond to water molecules hydrogen bonded to the hydroxyl group of the alcohol, are constant over the concentration range studied. Changes in the hydration structure occur only in the remainder of the alcohol hydration shell. As the average size of t-butanol clusters increases, the number of water molecules contributing to the second feature in the partial distribution functions at 4.8 Å necessarily decrease.

### 5. Concluding summary

These measurements, as interpreted using the EPSR modelling procedure, support a model for the structures of aqueous t-butanol solutions (0.06–0.16 mole fraction) in which the preferential mode of association of solute molecules is through their non-polar headgroups. *There is no significant solute–solute hydrogen bonding*: the alcohol’s polar tendencies are satisfied by

water molecules. This preference for alcohol OH group–solvent water interactions seems to be sufficiently strong that a t-butanol prefers to lose *both* of its water molecules and to point its polar tail towards a *non-polar* part of a neighbouring solute molecule than for both participating t-butanol molecules to each lose both of their water molecules and hydrogen bond to each other. This perhaps says something about the relative effective strengths of the solute–water and solute–solute hydrogen bonds that may be particularly relevant to a range of solution processes such as protein folding.

We can compare the conclusions drawn with a number of computer simulation calculations of this and related alcohol systems, and through such a comparison discriminate between such simulations and perhaps the assumptions they make, for example of the potential functions used. For example, our results are consistent with those of a Monte Carlo study of t-butanol in water (0.03 mole fraction) [10], which also found no evidence for hydrogen bonding interactions between alcohol molecules.

On the other hand, the same simulation study found evidence for solvent-separated ‘contact’ configurations, whereas our experimental results fails to show such evidence. This conclusion itself is consistent with a more recent simulation of ethanol–water, which suggests that direct solute association is the preferred mode of solute contact [11].

The experimental results for all three concentrations display a single feature at about 5.5 Å that is indicative of direct alcohol molecule contact. This suggests that models in which aggregates of clathrate-like hydrates are present in the mixture beyond a concentration of 0.04 mole fraction [12–14] need revision.

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### References

- [1] Soper A K 1996 *Chem. Phys.* **202** 295
- [2] Bowron D T, Finney J L and Soper A K 1998 *Molec. Phys.* **93** 531
- [3] Soper A K, Howells W S and Hannon A C 1989 ATLAS *Rutherford Appleton Laboratory Report RAL 89–046*
- [4] Soper A K and Luzar A 1992 *J. Chem. Phys.* **97** 1320
- [5] Soper A K 1994 *J. Chem. Phys.* **101** 6888
- [6] Jorgensen W L, Madura J D and Swenson C J 1984 *J. Am. Chem. Soc.* **106** 6638
- [7] Jorgensen W L 1986 *J. Phys. Chem.* **90** 1276
- [8] Berendsen H J C, Grigera J R and Straatsma T P 1987 *J. Phys. Chem.* **91** 6269
- [9] Bowron D T, Finney J L and Soper A K 1998 *J. Phys. Chem. B* **102** 3551
- [10] Tanaka H, Nakanishi K and Touhara H 1984 *J. Phys. Chem.* **81** 4065
- [11] Nishi N, Takahashi S, Matsumoto M, Tanaka A, Muraya K, Takamuku T and Yamaguchi T 1995 *J. Phys. Chem.* **99** 462
- [12] Iwasaki K and Fujiyama T 1977 *J. Phys. Chem.* **81** 1908
- [13] Nishikawa K, Hayashi H and Iijima T 1989 *J. Phys. Chem.* **93** 6559
- [14] Nishikawa K, Koderia Y and Iijima T 1987 *J. Phys. Chem.* **91** 3694