Probing how alcohol affects the structure of water

Water, despite its ubiquity, is an extraordinarily complex substance. The structure of water on a molecular level is defined by the interactions, “hydrogen bonds”, that individual molecules have with each other. These are the reason that upon turning to solid ice, water takes up more space that it does as a liquid. The addition of other substances to water can dramatically alter these interactions and hence the properties of water. The impact of adding alcohols to water is particularly interesting. Not only are alcohol/water mixtures widely used in chemical processes, for example as solvents, but they provide an excellent model system for considering how more complex species such as proteins influence the structure of water. The same interactions also take place in alcoholic beverages where ethanol is mixed with water and hence play a key role in the properties of those, perhaps influencing their flavour.

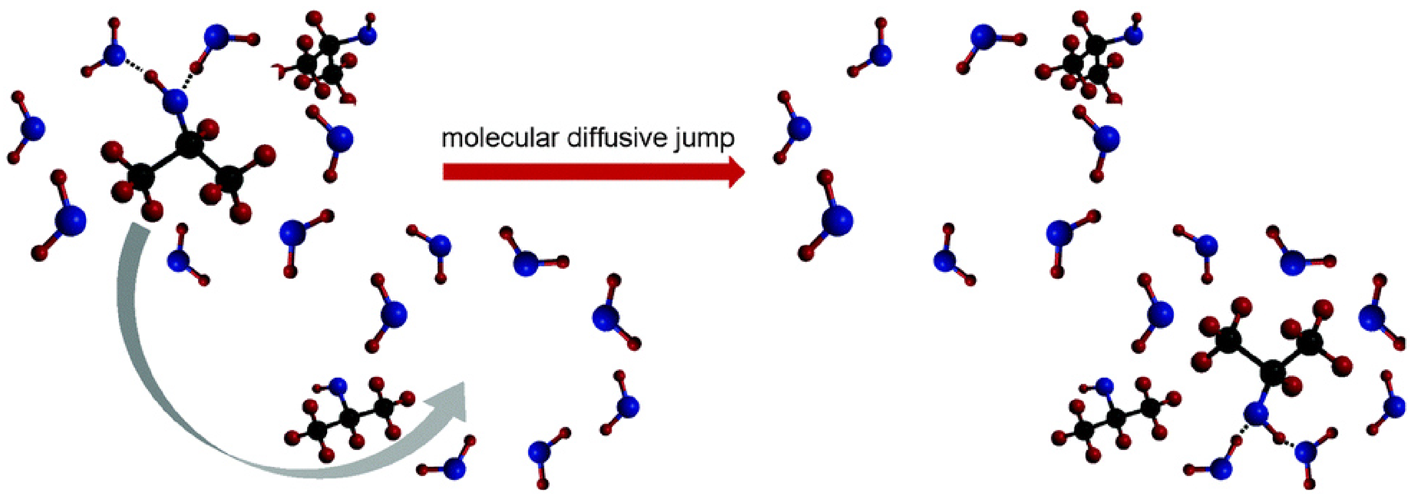

Fig. 1. Schematic showing a “molecular diffusive jump” of 2-propanol in water.

In order to probe the structure of alcohol/water mixtures it is necessary to apply a range of advanced techniques. In this work we have utilised NMR relaxation time analysis, terahertz time-domain spectroscopy and neutron diffraction. These techniques are ideally suited for probing the structure of alcohol/water structures on the most relevant lengthscales: NMR relaxation time analysis can provide the energy barrier for a molecule to break its interactions with its neighbours and form new ones with other molecules; terahertz time-domain spectroscopy can probe the hydrogen-bonding interactions and give a measure of the average number of water molecules surrounding an alcohol molecule in solution’ while neutron diffraction probes the structure of the solutions, yielding data on the number, type and strength of hydrogen bonds present. The results of this study show that even the addition of a small quantity of alcohol, in this case 2-propanol, has a significant impact on the structure of water.

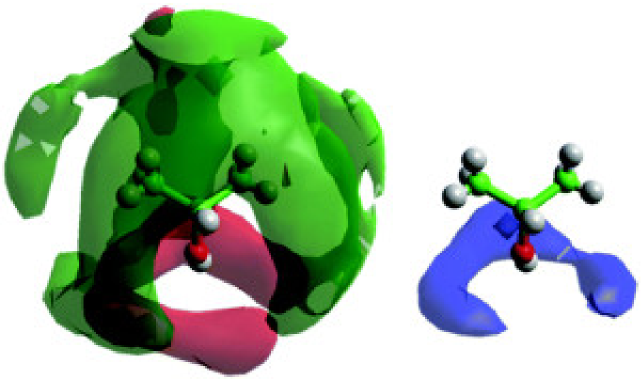

Fig. 2. Spatial probability densities of 2-propanol (methyl group – green; oxygen – red) and water (blue) at 90 mol % H2O.

Specifically, at a composition ratio of nine water molecules to one 2-propanol molecule, the mixture shows the greatest deviation from ideality; i.e. deviation from what would be expected from a simple additive mixture of the two components. By employing the range of advanced techniques described above we have shown that there are four-to-five water molecules in the immediate surroundings of an alcohol molecule. The alcohol molecules are therefore intimately mixed throughout the water, altering its hydrogen bonding structure and hence its properties. For example, this directly impacts on the mobility of hydrogen through the liquid media – a key step in many chemical processes including hydrogenation reactions; the viscosity of the mixture; and other related properties such as the velocity of sound through the mixture. Figure 1 shows a schematic representation of a 2-propanol molecule moving through water, the energetics of which are directly probed in this study, while Figure 2 shows Spatial probability densities of 2-propanol and water in a 90% water / 10% 2-propanol mixture as derived from neutron diffraction studies.

Understanding the impact of additives, e.g. 2-propanol, has the potential to have a significant impact in any area where water finds application: from catalysis, to fuel cells, to biological processing to alcoholic beverages. The knowledge of the meso-scale structure of such mixtures directly informs the design of such processes and products. A similar approach could be applied to, for example, understand the impact of salts on the structure and dynamics of water. Water surrounds us, and plays a crucial role in supporting life, however we are only now beginning to understand the properties of this highly complex substance.

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Publication

Structure and dynamics of aqueous 2-propanol: a THz-TDS, NMR and neutron diffraction study.
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