WHY ALCOHOL AND WATER DON'T MIX

Hydrogen-Bonded Clusters Explain Low Increase in Entropy

Devotees of scotch and water should be advised they may never attain the perfect blend. A group of scientists has used x-ray absorption and selectively excited x-ray emission spectroscopy at the ALS to study the electronic states of liquid water mixed with the simplest type of alcohol, methanol. While methanol is not used in beverages (it's actually a poison), its molecular behavior when mixed with water is expected to be the same as that of ethanol, the drinkable form of alcohol. Beyond advances in mixology, however, the ability to determine the mixing properties of different liquids is of great importance: many vital chemical and biological processes take place in aqueous solutions. The emission spectra obtained in this study reveal that the water and alcohol molecules in solution form complex hydrogen-bonded networks and mix very little at the microscopic level. The results illustrate the technique's potential to provide new and valuable information about the microscopic origins of the properties of liquids and solutions.

Our knowledge about the geometry and electronic structure of molecules in the liquid phase is very limited. Not only do the molecular arrangements change rapidly — on the scale of picoseconds to femtoseconds — but the properties of the individual molecules are also constantly changing, and interactions between the molecules cannot be neglected. Thus it is not surprising that there is still much to learn about common and simple liquids.

One big mystery has involved the fact that, when alcohol and water mix, the disorder or entropy in the resulting system does not increase as expected for ideal solutions. This anomaly has traditionally been explained in terms of hydrophobic interactions involving alcohol molecules that induce a static, ice-like structure in the surrounding water. However, despite a great deal of effort spanning four decades, a convincing description of the details of the incomplete mixing is lacking, and no consensus on the correct explanation has been reached.

To shed light on this puzzle, researchers turned to ALS Beamline 7.0.1, where they studied the absorption and emission of x rays by liquid methanol in and out of solution with water. The spectra obtained reflect the local electronic structure; in particular, the oxygen line shape is sensitive to the hydrogen bonding configurations. Information about the molecular arrangements can therefore be obtained by comparison to theoretical predictions.

The results show that the structure of liquid methanol at room temperature is a combination of rings and chains, each made up of either 6 or 8 methanol molecules. When water is added, the methanol chains interact with varying numbers of water molecules. These “bridging” water molecules bend the chains into open-ring structures that are stable because their glue-like hydrogen bonds are saturated. This means that the mixing of alcohol and water on the microscopic level is incomplete no matter how long you wait.

The high degree of order in these clusters reduces the overall entropy of the liquid. Yet entropy must either stay the same or increase in the liquid. So to preserve the second law of thermodynamics, nature discourages the formation of too many such clusters in the liquid. Indeed, the measurements indicate that only a portion of the chains are being bridged. While the formation of clusters prevents full mixing, the second law of thermodynamics limits the degree of order in the system, suggesting a competition between increasing entropy and hydrogen bonding of clusters.

This study establishes a valuable tool for probing the molecular properties of liquids and solutions, something that until now has been difficult to do. The results have substantially refined both our knowledge of structure and order in methanol and methanol-water solutions and our understanding of the unusual thermodynamic properties of this common liquid mixture.

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J.-H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-E. Rubensson, D.K. Shuh, H. Agren, and J. Nordgren, “The Molecular Structure of Alcohol-Water Mixtures,” *Phys. Rev. Lett.* **91**, 157401 (2003).

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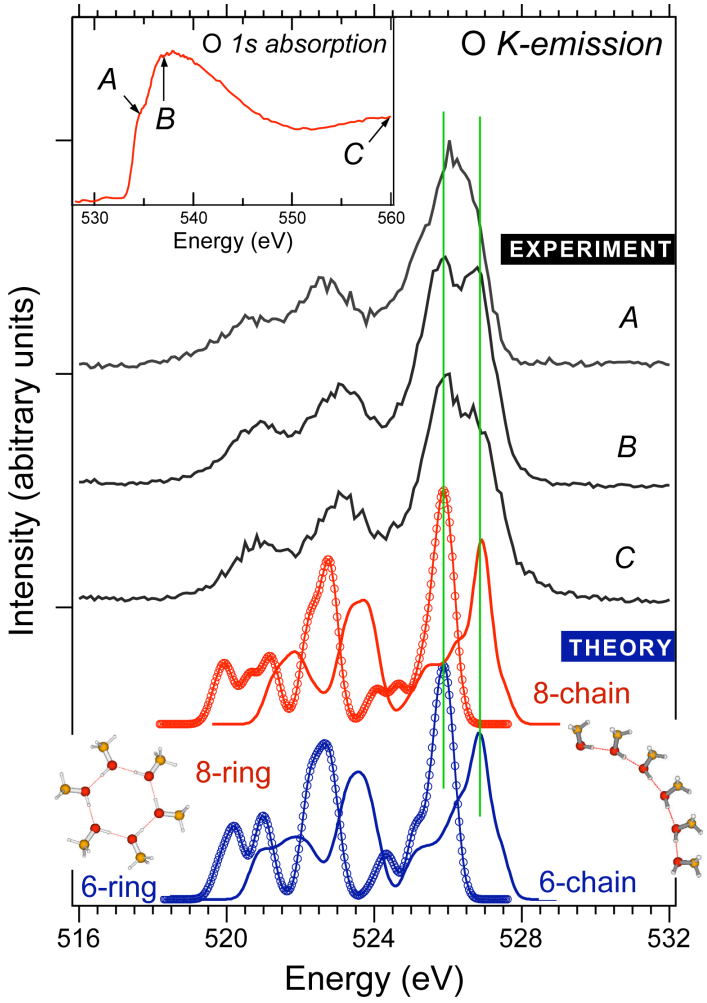


- **Still much to learn about simple, common liquids**
  - *Molecular structure dynamically changing*
  - *Time scale: picoseconds to femtoseconds*
  - *Interactions between molecules important*
- **Spectroscopy of liquids at ALS Beamline 7.0.1**
  - *X-ray absorption and emission reflect local electronic structure*
  - *Oxygen line shape sensitive to H-bond configurations*
  - *Comparison to theoretical predictions gives geometry*

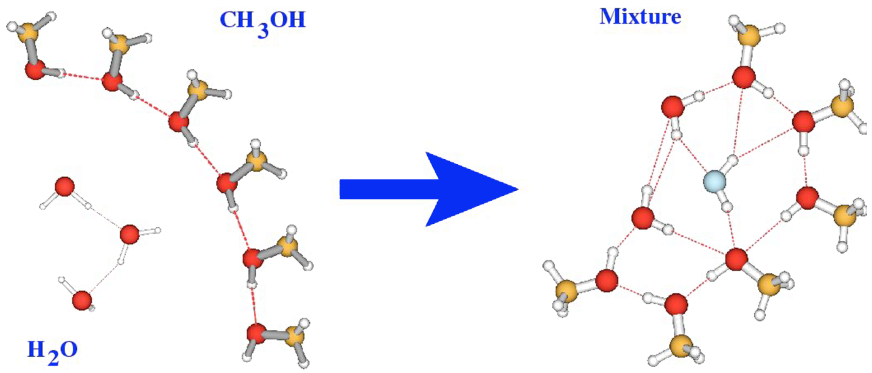
Experimental oxygen emission spectra recorded at three excitation energies (A, B, and C) compared with theoretical emission spectra of chain and ring structures in methanol.

J.-H. Guo and D.K. Shuh (Berkeley Lab); Y. Luo, S. Kashtanov, and H. Agren (Royal Institute of Technology, Sweden); A. Augustsson, J.-E. Rubensson, and J. Nordgren (Uppsala University). [*Phys. Rev. Lett.* **91**, 157401 (2003)]

WHY ALCOHOL AND WATER DON'T MIX

Hydrogen-Bonded Clusters Explain Low Increase in Entropy

- **Many chemical and biological processes involve alcohol–water mixtures**
  - *Methanol: simplest type of alcohol, behavior can be generalized*
  - *40-year controversy over molecular structure*
  - *Anomalously low increase in entropy when mixed with water*
- **Results: pure methanol forms 6- to 8-molecule rings and chains**
  - *Clusters "bridged" by water molecules in methanol–water mixture*
  - *Highly ordered structures lower entropy*
  - *Thermodynamics limits number of water-bridged clusters*



Methanol molecules react with water molecules to form stable open-ring structures.

J.-H. Guo and D.K. Shuh (Berkeley Lab); Y. Luo, S. Kashtanov, and H. Agren (Royal Institute of Technology, Sweden); A. Augustsson, J.-E. Rubensson, and J. Nordgren (Uppsala University). [*Phys. Rev. Lett.* **91**, 157401 (2003)]