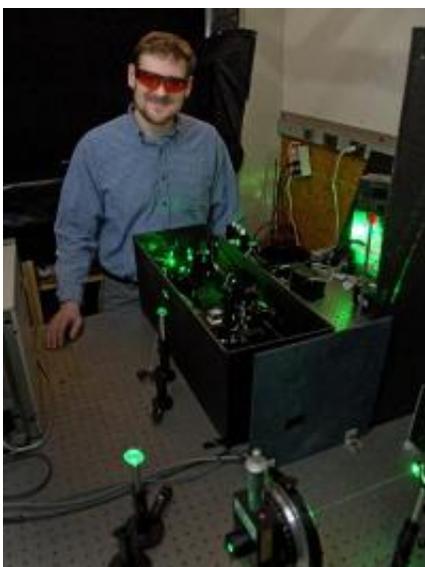


Oil and water: An icy interaction when oil chains are short, but steamy when chains are long

December 3 2012, by Elizabeth K. Gardner



Purdue graduate student Joel Davis stands with equipment used to identify a new structure water molecules assume when interacting with oil. Credit: Purdue University photo/Mark Simons

(Phys.org)—Water transforms into a previously unknown structure in between a liquid and a vapor when in contact with alcohol molecules containing long oily chains, according to Purdue University researchers. However, around short oily chains water is more icelike.

Water plays a huge role in [biological processes](#), from [protein](#) folding to

membrane formation, and it could be that this transformation is useful in a way not yet understood, said Dor Ben-Amotz, the professor of [chemistry](#) who led the research.

Ben-Amotz's research team found that as they examined alcohols with increasingly long carbon chains, the transformation occurred at lower and lower temperatures.

When in contact with a chain seven [carbon atoms](#) long, the [water molecules](#) became much looser and more vaporlike at a [temperature](#) of 140 degrees [Fahrenheit](#), which is about halfway between the melting and boiling points.

"For oils with chains longer than four carbons, or about one nanometer in length, we saw the water transform into a completely new structure as the temperature rose," Ben-Amotz said. "If the trend we saw holds true, then this transformation could be happening at body temperature around important physiological molecules like proteins and phospholipids. Water responds very sensitively in its structure to small changes, he said.

"Water's versatility is what makes it so special," he said. "For instance, the surfaces of proteins have both oily and charged regions; and water changes itself to accommodate these very different components and everything in between. We are learning more about exactly how it does this."

The researchers found that water molecules interacting with the oil always formed a more ordered, icelike structure at lower temperatures, while the bulk of the water remained liquid. This ice-like structure would melt away as the temperatures increased and in longer molecules a new structure would appear, he said.

A paper detailing the National Science Foundation-funded work is

published in the current issue of *Nature* and is also highlighted in a news and views article in the same issue. In addition to Ben-Amotz, co-authors include Purdue graduate student Joel Davis and postdoctoral fellows Kamil Gierszal and Ping Wang.

The team's observations add to a more than 70-year debate over the interaction of oil and water, with some studies suggesting that water forms little icebergs around the oil molecules, while others point to a more disordered, vaporlike water structure.

"This question was really up for grabs until we introduced an experimental method that could see these subtle changes in water structure," Ben-Amotz said. "Surprisingly, we found that both sides are right, and it depends on the size of the oil."

The challenge of the experiment was that the team needed to see the very small number of water molecules that are in contact with the oil chains in the presence of a very large number of other water molecules.

The team combined Raman scattering and multivariate curve resolution to create an analysis method capable of managing an unprecedented signal-to-noise ratio of 10,000-to-1.

"Most people never take a spectrum with a signal-to-noise ratio greater than 100-to-1, but if we performed this experiment that way we wouldn't see anything," Ben-Amotz said. "We needed to have a higher signal-to-noise ratio because we were looking for a needle in a mountain-sized haystack."

Raman scattering involves shooting a beam of light containing photons into a sample. As the photons hit molecules within the sample, they lose or gain energy. Such measurements create a spectrum of peaks that reveal the vibrational motions of the molecules present in the sample.

Shifts in the peaks' shapes can show changes in the strength of bonds between water molecules and whether the molecules are becoming more or less ordered.

"With Raman scattering the bulk of the water creates a mountainous peak in the spectrum that buries everything else," Ben-Amotz said.

"Multivariate curve resolution lets us see small changes in water structure under that mountain. As is often the case in science, the key was combining two already established techniques in a new way."

Davis said the team next plans to explore the effects of changes in pH and ionic charges on this transformation with the goal of making the experiments more relevant to proteins and biological systems.

"We are trying to better understand the driving forces of the behavior of proteins and cell membranes that are critical to our health," he said. "The role of [water](#) is an important piece of the puzzle."

More information: Water structural transformation at molecular hydrophobic interfaces, Joel G. Davis, Kamil P. Gierzal, Ping Wang & Dor Ben-Amotz, *Nature*, 2012.

ABSTRACT

Hydrophobic hydration is considered to have a key role in biological processes ranging from membrane formation to protein folding and ligand bonding. Historically, hydrophobic hydration shells were thought to resemble solid clathrate hydrates, with solutes surrounded by polyhedral cages composed of tetrahedrally hydrogen bonded water molecules. But more recent experimental and theoretical studies have challenged this view and emphasized the importance of the length scales involved. Here, we report combined polarized, isotopic and temperature-dependent Raman scattering measurements with multivariate curve resolution (Raman-MCR) that explore hydrophobic hydration by

mapping the vibrational spectroscopic features arising from the hydrophobic hydration shells of linear alcohols ranging from methanol to heptanol. Our data, covering the entire 0-100 degrees Celsius temperature range, show clear evidence that at low temperatures the hydration shells have a hydrophobically enhanced water structure with greater tetrahedral order and fewer weak hydrogen bonds than the surrounding bulk water. This structure disappears with increasing temperature and is then, for hydrophobic chains longer than ~1nm, replaced by a more disordered structure with weaker hydrogen bonds than bulk water. These observations support our current understanding of hydrophobic hydration, including the thermally induced water structural transformation that is suggestive of the hydrophobic crossover predicted to occur at lengths of ~1nm.

Provided by Purdue University

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