



Water in Confinement

Nancy E. Levinger

Water is the most ubiquitous bulk liquid on Earth's surface. Yet in biology as well as in natural and synthetic materials, it often is tucked away in tiny crevices inside proteins or in porous materials. What happens to water when it is confined to nanometer-scale cavities?

Recent investigations have increased our understanding of confined water, showing that in nanoscopic proportions, many water properties differ drastically from those of bulk water. Reverse micelles—isolated, surfactant-coated water droplets—have emerged as a tenable model for confined water in biological systems (1). The interior dimensions of reverse micelles are similar to confined spaces found in cavities in biological systems. These pockets of water are thought to be involved with folding and relaxation in proteins. Moreover, reverse micelles exist in membrane lipid bilayers during endosome formation. Reverse micelles have also been used as templates for nanoparticle synthesis (2).

Reverse micelles form when mixtures of water, surfactants, and nonpolar solvents are combined at the appropriate concentrations. The surfactant AOT (aerosol OT, sodium dioctyl sulfosuccinate) offers one of the easiest routes to creating these “nanopools” (3). AOT reverse micelles form in a wide range of solvents, including unusual ones such as supercritical ethane and propane. Because they appear to retain a spherical form over a wide hydration range, the simple relation

$$w_0 = [\text{water}]/[\text{surfactant}]$$

yields information about the sizes of the structures. AOT reverse micelles can solubilize substantial amounts of water; w_0 ranges from 0 to 70 for many systems.

From ultraviolet (UV)–visible absorption and fluorescence spectroscopy of probe molecules in reverse micelles to infrared (IR) absorption and nuclear magnetic resonance (NMR), spectroscopy has been a primary tool for investigating the structures of reverse micelles. Combined with time-resolved methods, the spectroscopic methods can also yield dynamical information.

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IR spectroscopy can be used to track subtle changes in intramolecular vibrations in samples containing reverse micelles. The water OH stretch near 3500 cm^{-1} has received particular attention. On the basis of multipeak deconvolution of the broad, relatively featureless IR peaks, different “types” of water have been identified, including water trapped between surfactant head groups, water bound to the interface, and relatively unperturbed, bulk-like water.

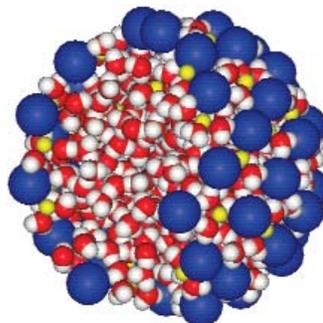
Venables *et al.* (4) have recently provided direct evidence for these different types of water. They have probed the far-IR spectrum of water encapsulated in AOT reverse micelles. This part of the spectrum reflects librational (hindered-rotational) motion of water molecules forming hydrogen bonds; the stronger the hydrogen bond, the higher the frequency. Spectra measured as a function of w_0 strongly suggest an equilibrium between two different forms of water. Of course, isolated water molecules that do not form hydrogen bonds, suggested to comprise some of the water in reverse micelles, would be transparent to these experiments.

In another recent study, Boyd *et al.* used terahertz time-domain spectroscopy to explore very low frequency modes of reverse micelles (5, 6). Dramatic resonances in the far-IR ($3\text{ to }33\text{ cm}^{-1}$) absorption, which they observed for various different reverse micellar solutions, shifted with w_0 . Because these resonances appeared only in the reverse micellar solutions and not in bulk water, the authors concluded that they reflect the confined structures and indicate substantial changes in the water vibrational modes inside the reverse micelles.

These studies reveal a strong dependence of the water collective motion on the reverse micellar confinement. Some of the water can remain relatively unaffected; for example, Venables *et al.* (4) provide

evidence for bulk-like character for water in large reverse micelles. But Boyd *et al.* (5, 6) show that the reverse micellar environment always has some impact on the micellar interior.

Probe molecules, especially fluorescent probes, have been introduced to investigate the interior of reverse micelles (7). One of



Model confinement. Modeled reverse micelle ($w_0 = 7.5$), showing the surfactant head groups and a slice of the interior. The micelle contains 70 AOT surfactant molecules, 70 Na^+ counterions, and 525 water molecules. Nearly all counterions (yellow spheres) reside at the interface. The surfactant head groups (blue spheres) do not completely shield the aqueous core from the nonpolar exterior, and some water molecules are trapped between head groups in contact with the nonpolar phase. The model suggests that it should be possible to catalyze a reaction of an insoluble probe at the micellar interface.

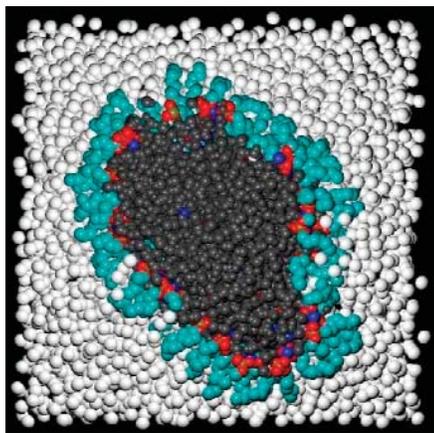
the problems with using a molecular probe is uncertainty about the probe's location in the solution. Amphiphilic probes, which contain long alkyl chains, can tether the probe to the micellar interface. But few molecular probes migrate to the micellar core, making it difficult to obtain detailed information about the interior of the micelles.

To address this problem, Zhong *et al.* (8) recently used a tiny molecular ion, the azide ion $\text{N}=\text{N}=\text{N}^-$, to probe reverse micelles. Because of its small size and high charge, this molecule is likely to dive to the core of the reverse micelles. Confirming this hypothesis, spectra of the azide ion in reverse micelles with large w_0 approached the spectrum in bulk water. The researchers intend to use the azide ion

in time-resolved studies to explore the dynamics of the surrounding solution, as they have for bulk solution (9).

Time-resolved spectroscopy, especially time-resolved fluorescence spectroscopy, is widely used to explore reverse micelles. New time-resolved spectroscopies, such as photon echoes and vibrational echoes, promise to expand our understanding of these systems. Bursing *et al.* have performed three-pulse photon echo peak shift experiments to measure the solvation response in lecithin vesicles (10). An intermediate-time scale process that dominated the response for bulk water was completely absent for water at a lipid bilayer. Instead, the response included only a large, ultrafast (14 fs) component and a slow, diffusive component. The authors attribute these observations to a perturbed water structure with reduced hydrogen bonding arising from interactions with the interface.

Spurred by these experimental advances, several groups have begun to develop effective models for reverse micelles and processes occurring therein (11–14).



For example, Salaniwal *et al.* (13, 14) have followed the molecular motions leading to the formation of reverse micelles from ternary mixtures of water, nonpolar molecules or CO₂, and surfactant.

In contrast, Faeder and Ladanyi (11, 12) use a model for an isolated reverse micelle and focus on the structure and dynamics of the micellar interior. The nonpolar phase is treated as a dielectric continuum, and surfactant head groups are confined to a spherical interface (see the first figure). The authors found reasonable agreement with IR spectroscopy measurements of solvation dynamics in reverse micelles.

Beyond the sphere. Computer simulation of a reverse micelle ($w_0 = 10$) formed from a novel double-chained phosphate surfactant in CO₂. The system includes 1616 water molecules, 160 surfactant molecules, 160 counterions, and 6991 CO₂ molecules in a cubic box. Unlike the micelle in the first figure, this micelle is not restricted to a spherical shape. However, as in the other model, a large fraction (~90%) of the counterions are in contact with the interface. A big challenge of this simulation is to determine how many surfactant molecules are necessary for a given w_0 ratio.

Senapati *et al.* (15) have developed a third model that explicitly includes molecular components of the solution while focusing on the molecular properties of the reverse micellar interior. Molecular interactions drive the formation of the reverse micelles, leading to a range of shapes (see the second figure). A major advantage of molecular simulations over experiments is the ability to visualize the system and explore it layer by layer.

The advent of new experimental tools and faster computers promises to divulge more details about water in nanoscopic volumes. Starting with these simplified reverse micellar systems, we can begin to understand how differently water behaves when it is confined in biological cavities

and how these pools affect biological function. As our understanding advances, we should be able to capitalize on the unusual properties of water in these confined spaces for applications such as the controlled formation of nanoparticles or the “fixing” of broken proteins.

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PERSPECTIVES: SOLID STATE CHEMISTRY

Porous Materials with a Difference

Mark M. Turnbull and Christopher P. Landee

The design and preparation of porous molecular solids has been pursued for decades, inspired by the success of natural and synthetic zeolites in catalysis (1). Modern porous materials include metal oxides and salts (2), metal-organic coordination polymers (3, 4), and organic networks (5). They have been used in separation (6), ion-exchange (7), and sensor applications (8). The introduction of compounds with specific magnetic, optical, or electrical properties into such microporous solids should yield materials with unique responses to the adsorption of small molecules, interaction with radiation, or temperature changes.

On page 1762 of this issue, Halder *et al.* (9) report the synthesis and properties of a microporous material with such un-

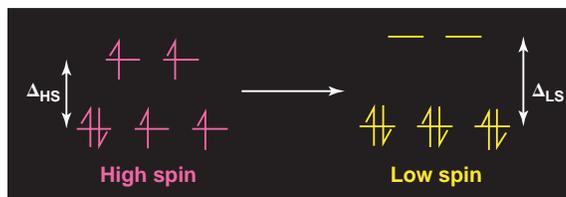
usual properties. The symmetry, pore size, and thermal behavior of the material depend on the presence of small molecules (low molecular weight alcohols) in the lattice. Such complexes are referred to as host-guest complexes, where the lattice provides the “host” and the small, sorbed molecules are the “guests.”

The most striking feature of the material is the change in the magnetic and optical properties that occurs when the guest molecules are gained or lost. In a process known as “spin crossover,” some of the iron(II) atoms change their electronic configuration. This phenomenon can occur in octahedral metal complexes (with six ligands bound to the central metal ion) in which the metal ions contain four to seven electrons in their *d*-orbitals. The *d*-electron orbitals in a transition metal ion complex are split into

different energy levels depending on the geometry of the complex. In the octahedral geometry, the splitting of the orbitals gives a pattern of two higher energy and three lower energy levels (see the figure).

These orbitals are usually occupied by the highest energy electrons in the compound, with a maximum of two electrons per orbital. Depending on the relative size of the orbital splitting energy (Δ) and the electron pairing energy (P , the energy introduced by the repulsion of two electrons in the same orbital), the compound can exist in the high-spin state ($\Delta < P$) or the low-spin state ($\Delta > P$). The most important difference between the two states is the number of unpaired electrons.

When Δ and P are of similar energy, the



Spin crossover in an iron(II) complex. Horizontal lines represent electron energy levels (orbitals); up and down arrows denote the electrons in these orbitals. Δ is the energy difference between the high- and low-energy orbitals. The ratio of Δ to the pairing energy, P , determines whether the complex is high spin or low spin.



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