Long-range ordering of water next to hydrophilic surfaces: Implications for energetics and phase changes

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Surfaces are thought to impact the contiguous aqueous phase to no more than a few water-molecule layers. We find, however, that colloidal and molecular solutes in water are profoundly excluded from the vicinity of hydrophilic surfaces, to distances typically several *hundred* micrometers. Such large "exclusion zones" (EZs) have been observed next to many different hydrophilic surfaces, and many solutes are excluded. Hence, the exclusion phenomenon appears to be general. Others have confirmed its existence.

To test whether the physical properties of the EZ differ from those of bulk water, a variety of spectroscopic, physical, and imaging methods have been applied. The results collectively reveal that this near-surface zone is a physically distinct, ordered phase of water that can co-exist essentially indefinitely with the contiguous solute-containing phase. This zone may be a candidate for water's long-postulated "fourth phase."

The energy responsible for building this low entropy EZ comes from light. We found that incident radiant energy including all visible and near-infrared wavelengths induce EZ growth in a spectrally sensitive manner. IR is particularly effective. Five-minute exposure to weak radiation at 3.1 μm (corresponding to OH stretch) causes EZ-width increase up to three times. Apparently, incident photons predispose constituent molecules to build the EZ. And, as the EZ is charged and the region beyond is oppositely charged, the photons effectively charge the battery.

It appears that sunlight charges the EZ battery. Such a light-driven charge separation bears resemblance to the first step of of photosynthesis. Indeed, this light-induced energy production seems relevant not only for photosynthesis-like actions, but also for many realms of nature involving water and interfaces. Some implications of this feature are discussed in a public lecture http://uwtv.org/programs/displayevent.aspx?rID=22222 and will be presented at the meeting.

Also to be presented are newer data showing surprising impact of these phenomena on evaporation and freezing. Evaporation is a discrete process intimately tied to the EZ; it involves massive numbers of molecules evaporating collectively in an on/off fashion. And regarding freezing, the EZ appears to be a spatial and temporal intermediate between bulk water and ice; bulk water apparently passes through the EZ phase as it crystallizes into ice.