

Water Structure at Air–Aqueous Salt and Lipid Interfaces

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Water is essential for life. At surfaces and interfaces, water structure is elusive, reorganizing with addition of solute, ions and soluble or slightly soluble neutral molecules. Surface and interfacial water structure will be discussed for aqueous solutions of mono and divalent salts and the corresponding acids. At the water surface, prior to addition of solute, dangling OH bonds are detected as are the vibrational modes of surface and interfacial hydrogen bonded water species. Large polarizable anions significantly perturb both the bulk and surface water organization. At the surface, bromide and iodide anions are shown to create an increase in the depth of the interfacial region via concentration changes that give rise to macroscopic noncentrosymmetry. For the corresponding acids, bromide and iodide continue to perturb the surface. However, the proton causes additional changes to the interface that are different from the bulk behavior of solvated protons. That is, we observe an intensity enhancement above what one predicts from the bulk solvation experiments. Ammonium and sulfate salts at the air-aqueous interface are additionally interesting. Sulfate dianions order the water in the interface more effectively due to their divalency. This -2 charge has a significant effect on the orientation of the interfacial water molecules.

In addition to understanding water structure at the air-aqueous interface after addition of simple ions, we are beginning studies on water organization about the polar moieties of lipids. Lipids such as dipalmitoyl phosphatidylcholine (DPPC) and dimpalmitoyl phosphatidylethanolamine (DPPE) are different only in the substitution of the choline ($-N(CH_3)_3$) with ammonia ($-NH_3$) termination of the head group. Our initial studies suggest that this small difference causes significant differences in the organization of the surrounding water layers, extending beyond the first solvation shell. We have additionally focused on the dangling OH vibrational region when solvating the DPPC choline group. Using a Langmuir film balance, we have explored the dangling OH vibration as a function of changing surface pressure, while also obtaining surface vibrational spectra. In the more highly compressed region of the isotherm, the number of dangling OH bonds increases, counter to what one might expect. The spectra also reveal that the dangling OH very weakly interacts with the head group. We are continuing in our efforts to explore interfacial water structure about the head groups of lipid monolayer systems and additionally complex lung surfactant systems.