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Exploring Specific Ion Effects on Ion Hydration at Aqueous Interfaces

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We used sum frequency generation vibrational spectroscopy to probe the interactions of ions with self-assembled monolayers and proteins at aqueous interfaces. I will discuss the behavior of cations and anions as they relate to the Hofmeister series, which is a rank ordering of the efficacy of these species to influence the physical behavior of colloidal and interfacial systems in solution. Ion specific effects at these interfaces were found to be determined by several factors. These include the sign and magnitude of the surface potential, ion pairing effects in the double layer, as well as the presence of polar and nonpolar interfacial moieties. At negatively charged, hydrophilic surfaces, we found that Na^+ adsorption and double layer formation were modulated by the type of the counterion in solution. The same ordering was observed for the anions whether this interface was relatively hydrophobic or hydrophilic. Changing the sign of the charge at the interface also led to a similar Hofmeister ordering. Moreover, at negatively charged hydrophilic surfaces, the smallest and best hydrated cations were mostly favored over more poorly hydrated cations. By contrast, well hydrated cations were repelled from more apolar surfaces.