

How ion identity, ion concentration, and pH history affect the Silica/Water interface

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The silica/water interface is one of the most environmentally relevant interfaces. Processes at this interface are governed by the electrostatic interactions between the silica surface and the aqueous electrolyte. Thus, understanding how the composition of the aqueous phase affects the acid-base chemistry of the silica/water interface is important for understanding a range of phenomena like pollutant transport and mineral processing in mining and fuel extraction. Previous work utilizing nonlinear optical (NLO) methods by others has shown that the planar silica/water interface has two distinct pKa values of 4.5 and 8.5. This bimodal behavior has been attributed to two acidic silanol (SiOH) sites in different hydrogen bonding or solvation environments that strongly affect their resulting acidity.

Here we utilize the surface specific NLO method second harmonic generation to observe changes in the surface charge density of silica and the corresponding pKa values of the silanol sites in the presence of different electrolytes. Specifically, the effect of alkali chloride and alkaline earth chloride identity and concentration will be discussed [1] [2]. In addition to observing a significant influence of the alkali chloride on the relative distribution of the two acidic sites, we have recently found that the pH history also plays a role in the relative amount and type of silanol site. For example, exposure to pH 12 results in three apparent sites on the silica surface, with uniquely different acidities. In contrast exposure to pH 2 results in only two sites as the pH is increased. Finally, to understand the role of water in these interfacial processes the NLO method vibrational sum frequency generation was employed to determine how the alignment of water at the interface was impacted by the alkali and alkaline earth chlorides. Similar to the SHG results, ion identity strongly influenced the interfacial structure of the water as a function of pH.

[1] Azam, Weeraman & Gibbs-Daivs (2012) *J. Phys. Chem. Lett.* 3, 1269-1274. [2] Azam, Darlington & Gibbs-Davis (2014) *J. Phys.: Condens. Matter* 26, 244107-244117