

Effects of pH and ionic strength on the surface charge density of self assembled monolayers (SAM)

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The properties of a surface depend very much on its surface charge density and polarity. Charged or highly polar surfaces are usually water wet and interact strongly with polar molecules. In some cases, such surface-organic affinities enhance organic compound adsorption. Surface charge density is therefore also important in making our society more sustainable through, for example, designing new material properties, filtering drinking water, ensuring safe CO₂ storage and enhancing oil recovery. We used ionizable COOH-terminated self assembled monolayers (SAM) to investigate the effect of solvent pH and ionic strength on surface charge density. We set up three different models for the effective charge-charge interaction between neighboring COO⁻ groups and calculated the fraction of deprotonated SAMs for various ionic strengths (figure).

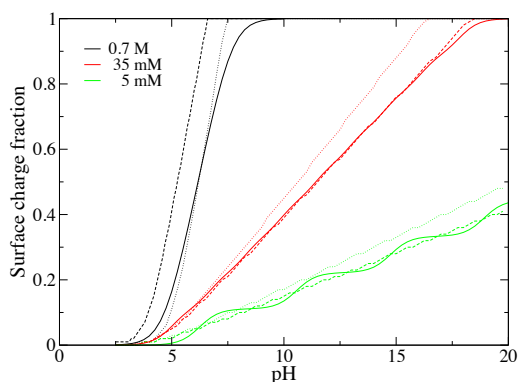


Figure: Titration curves predicted using the three models for three values of ionic strength.

The effective pK_a value of the SAM increases substantially from the monomer value at low salinity because of the increased charge-charge interaction between neighbors. As ionic strength decreases, the titration curves become flatter and deviate significantly from the standard Henderson-Hasselbalch expression. With these simulations, we obtain contour plots of the surface charge density at any pH and ionic strength. The simulations are nicely consistent with data from atomic force microscopy (AFM) chemical mapping.

Biogeochemistry of Acidic lakes in the Iberian Pyritic Belt

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The Iberian Pyritic Belt is one of the largest pyrite deposits on Earth. The exposure and subsequent oxidation of sulfide containing ores, resulting from mining activities, has led to the formation of acid mine drainage (AMD) in this region. Acidic, metal contaminated lakes, which often form as result of the inundation of mine pits are a substantial hazard in this region. For this reason the hydrochemistry of these systems has been the subject of several studies. However, there is very little known about the sediments in these lakes and the role of benthic-pelagic coupling for these systems. We conducted an interdisciplinary study that combined geochemical, stable isotope (H, O, C, S), and microbiological tools to develop a biogeochemical model for three pit lakes: Concepción, Nuestra Señora del Carmen, and Tharsis Filón Centro.

Consistent with the oxidation of sulfide minerals, monolimnion pH of these lakes ranged between 2 and 3, with enhanced concentrations of dissolved elements, such as SO₄²⁻, As, Fe, Al, Mn, and Zn. ORP ranged from +600 to +400 mV and Fe(III) dominated iron speciation within these zones. In general, Fe(II), CO₂, CH₄ and pH increased in the monolimnion of all lakes. Additionally, Eh decreased in these zones. In the sediments, pH ranged from 4 to 6 and ORP from -200 to +100 mV. Moderate sulfate reduction rates of up to 60 nmoles SO₄²⁻cm⁻³d⁻¹ were measured in the sediments. CO₂ and CH₄ concentrations were enhanced compared to the water column. 16S rRNA gene analysis revealed the presence of sulfate reducing bacteria as well as a broad spectrum of other bacteria, and archaea commonly associated with acidic sedimentary environments. Our results indicate that the sediments act as concentrators for organic material, resulting in microbial activity that enables the increase in pH of the sediments and bottoms waters of the lakes.