

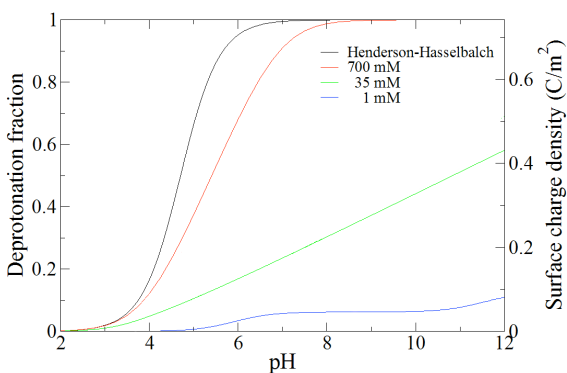
Surface charges of carboxyl self assembled monolayers – prediction and experiments

S. DOBBERSCHÜTZ, M.H.M. OLSSON, J. MATTHIESEN M.P. ANDERSSON, N.R. PEDERSEN, T. HASSENKAM, S.L.S. STIPP

Nano-Science Center, Department of Chemistry,
University of Copenhagen, Universitetsparken 5,
2100 Copenhagen Ø, Denmark,
sdobber@nano.ku.dk

The wettability of a mineral surface depends on its surface charge density. Charged and polar surfaces are water wet, while neutral and nonpolar surfaces are oil wet. These charges play a role in groundwater contamination and enhanced oil recovery, among others. For theoretical predictions of surface charge density the Henderson-Hasselbalch equation is often used for the pH dependence. We show that this approach is in many cases not adequate.

We used an atomic force microscope to perform titrations of COO(H) self assembled monolayers on gold surfaces. We used a tip functionalized with mercaptoundecanoic acid in solutions of KCl and NaCl with concentrations of 1, 35 and 700 mM and pH ranging from 3 to 9. The surface charge reconstructed from these measurements remains low, contrary to Henderson-Hasselbalch predictions. To explain the difference, we set up a mean field model that takes the interaction of neighboring molecules as well as the concentration explicitly into account. The model gives flattened titration curves, predicting significantly protonated surfaces in accordance with our experiments. This highlights the effect of ionic strength on the determination of $pK_{1/2}$ values.



Titration curves predicted by our model that takes neighbouring interactions into account, compared with results from the Henderson-Hasselbalch expression.