



A double-layer model of the surface electrochemical properties of the air/water interface

Philippe Leroy, Arnault Lassin, and Mohamed Azaroual

BRGM – Water Division, 3 av. C. Guillemin, BP 36009, 45060 France (p.leroy@brgm.fr)

The surface electrical potential of the air/water interface is a phenomenon of particular interest in the water unsaturated zone of porous media because it influences the air/water surface tension, the contact angle and then the capillary water volume. Moreover, this potential also influences the reactive transport of ionic species, nanoparticles, and colloids.

It's well known that, due probably to the hydrogen bonding network of the surface water molecules and the possible presence of hydroxide ions, air bubbles are negatively charged in pure water and solutions containing 1:1 salts at low ionic strength, i.e. inferior to 1 M. The resulting surface charge density is negative but has a very low amplitude compared to that of oxide minerals like silica. In addition, the amplitude of the corresponding zeta potential determined experimentally from electrophoresis decreases with the salinity and increases with the pH of the solution. To explain such phenomena, an electrostatic surface complexation model is used. The double layer is constituted of a negatively charged plane and of a diffuse layer. Zeta potential values of air bubbles in NaCl solution at different pH and ionic strengths taken from the literature are utilized to validate the model.

By considering negative surface sites which react with protons at the air/water surface, the electrical potential at the head-end of the diffuse layer is calculated using the geochemical software PHREEQC and model parameters are optimized by the software PEST. To diminish the number of adjustable parameters, only the capacitance of the inner part of the double layer is optimized for a given value of the total surface site density. The equilibrium constants of the surface complexation reactions are estimated using the apparent acidity quotients calculated from the electrokinetic data.

The predicted zeta potential values are in very good agreement with the experimental data for the whole range of pH and salinity. We find a very low capacitance value corresponding to an interfacial region possessing a very low relative dielectric constant. This is in accordance with the fact that surface water molecules have a low density, and are strongly oriented and structured, and with the fact that the electrical field is strong close to the air/water surface. In addition, in the physico-chemical conditions of our study and because of the weak surface charge density, only an ion depleted layer is considered close to the air/water surface. Its thickness corresponds to the diameter of hydrated cation. Our surface complexation model also predicts successfully the Jones-Ray effect associated with a minimum of the surface tension at 10⁻³ M of KCl solution. At very low ionic strength, the absence of ion in the first layer and the low counterion concentration in the diffuse layer lead to a slightly decreasing surface tension when salinity increases, but the counterion concentration increases with the ionic strength, and the excess of surface ionic species at 10⁻³ M creates an increasing surface tension. To conclude, our surface complexation model is able to predict successfully the zeta potential and the surface tension for the air/water interface of 1:1 electrolyte using an approach traditionally employed for characterizing the electrochemical properties of solid/water interface.