Cryogenic X-ray photoelectron spectroscopy and electrochemical impedance study of electrolyte ion adsorption at the hematite/water interface

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The hematite/water interface was probed by cryogenic X-ray photoelectron spectroscopy (XPS), electrophoretic mobility, and various electrochemical techniques. Cryogenic XPS and electrophoretic mobility measurements were carried out on colloidal hematite particles (36 nm diameter) equilibrated in aqueous solutions of monovalent ions (Na+, K+, Rb+, Cs+, NH4+, F-, Cl-, Br-, I-) at pH 2-11. XPS measurements notably reveal coexisting cations and anions both below and above the point of zero charge of hematite. Surface loadings follow hydrous ionic radii in both alkali metal (Na+ > K+ > Rb+ ≈ Cs+) and halide (F- > Cl- ≈ I- > Br-) ions. Experiments on a suite of sodium halide electrolytes moreover point to a correlation between Na+ co-adsorption and the identity of the halide ion (Fig. 1).

Na+ surface loadings show an inverse relationship with hydrous ionic radii of halide ions, excluding fluoride which tends to form direct coordinative bonds to surface iron species. This suggests that Na+ co-adsorption may be responsible in stabilizing large halide ions by maintaining hydration of the interfacial region. Sorption of ammonium ion occurs, on the other hand, through the formation of NH3 (e.g. =Fe-OH⋯NH3), a mechanism shifting the pKs of NH4+ from 9.3 in water to 8.4 at the interface. These findings are further discussed in terms of basic electrochemical properties of hematite single crystal electrodes. Measurements on electrodes with various polished crystallographic orientations produce surface potentials from controlled combinations of amphoteric surface hydroxyl functional groups. Electrochemical impedance spectroscopic measurements of these electrodes are also discussed in the context of double layer capacitance.