MOLECULAR MODELING STUDY OF SULFATE AND PHOSPHATE

ADSORPTION AT THE MINERAL-WATER INTERFACE

by

Kristian W. Paul

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ABSTRACT

The transport and bioavailability of sulfate and phosphate are significantly affected by adsorption reactions with soil minerals. Elucidating the adsorption mechanisms and kinetics is critical to improving surface complexation models, which are used to simulate the reactive transport of nutrients in soils. The objective of this investigation was to utilize computational DFT methods to improve our understanding of sulfate and phosphate adsorption at the mineral-H_2O interface.

The effect of dehydration on sulfate adsorption at the α-Fe_2O_3-H_2O interface was investigated, using ATR-FTIR spectroscopy and DFT calculations. The DFT calculations were performed with edge-sharing dioctahedral Fe^{3+} cluster models of sulfate and bisulfate complexes. The DFT calculations suggested that sulfate formed a monodentate or bidentate bridging complex under hydrated conditions, but that bisulfate formed under dehydrated conditions (i.e., speciation change). A QMD simulation of monodentate bisulfate at the (101) α-FeOOH-H_2O interface, however, suggested that a speciation change is probably reversible.

The energies of sulfate adsorption pathways on edge-sharing dioctahedral Al^{3+} and Fe^{3+} cluster models were estimated with DFT calculations. The DFT-calculated adsorption energies were directly related to the H^+/SO_4^{2-} stoichiometry and the overall charge of the Al^{3+} and Fe^{3+} clusters. DFT-calculated adsorption energies for bidentate

bridging and monodentate sulfate on a +1 charged Fe^{3+} cluster agreed reasonably well with experimental measurements of sulfate adsorption on α-FeOOH.

The binding geometries of bidentate bridging and monodentate sulfate complexes at the Fe-(hydr)oxide-H_2O interface were investigated, using cluster and periodic slab DFT calculations. The DFT cluster calculations were performed with edge-sharing dioctahedral Fe^{3+} models. The periodic DFT calculations were performed with a slab model of the (100) α-FeOOH surface. The cluster model predictions of the interatomic distances and angles of monodentate and bidentate bridging sulfate were in good agreement with the periodic slab model predictions.

QMD simulations were performed to better understand the dynamical behavior of sulfate and phosphate complexes at the (101) α-FeOOH-H_2O interface. The H-bonding interactions of sulfate and phosphate with α-FeOOH surface OH functional groups and with solvent H_2O molecules were investigated. To explain why phosphate is a stronger competitor than sulfate for α-FeOOH surface sites, a proton-assisted ligand exchange mechanism was proposed.