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Ordered water in surface complexation modeling

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Introduction

Mineral surfaces, particularly metal (hydr)oxides, often act as reservoirs for metals and oxyanions through both specific and non-specific adsorption processes because of their ubiquitous distribution and high specific surface area. Surface complexation models that describe the mineral-water interface in terms of one or more molecular capacitors arranged in series have not explicitly considered the effect of solvent ordering on ion adsorption.

Ordered Water Near the Mineral Interface

Water molecules at the aqueous-mineral interface display some degree of structural order, depending on the atomic structure and physical properties of the surface [1]. Surface complexation models have attempted to incorporate the ordered character of surface adsorbed water by treating the capacitance ($C = \varepsilon_0\varepsilon/d$) of the Inner Helmholz Layer (IHL – molecular capacitor adjacent to the surface) as an adjustable fitting parameter. However, given the constraint imposed on IHL thickness d by adsorbed ion size, C values that result from fitting SCMs to adsorption data often yield dielectric constant values ε for IHP adsorbed water of 60 or greater.

We have recently incorporated a three-state water model that describes the effects of oriented water dipoles on the electrostatic potential in the IHP into CD-MUSIC model descriptions of ion adsorption at the aqueous-mineral interface. Calculations were made over a wide range of phosphate surface coverage on goethite, using the CD-MUSIC model as formulated in FITEQL [2]. The resulting ε values for the IHP were in line with expectation for structured water, and varied in a systematic fashion with the density of solution oriented phosphate oxygen ligands. Experimental adsorption, surface charging, and ζ-potential data were well described by CD-MUSIC model results with the three-state water model incorporated, which allows the IHP C to be calculated based on physical interpretation of the aqueous-mineral interface rather than being treated as an adjustable fitting parameter.

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In situ identification of the surface functional species in sum frequency experiments

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The properties of mineral/electrolyte interfaces are controlled by the surface functional species. In order to model surface reactivity and adsorption/desorption processes a large number of functional groups has been postulated. In most cases, however, a direct proof for the existence of these species in real aquatic environment is lacking because it is difficult to obtain chemical in situ information with interface selectivity. Here we apply interface selective sum frequency (SF) vibrational spectroscopy to study the (001) and (110) surfaces of sapphire (α-Al_2O_3) under water between pH 4 and 12. We use sapphire as a simple model for natural clay minerals and related iron phases. The data are required in order to reliably predict the migration of actinide ions in the aquifer. These studies are an essential part of our research on the safety of repositories for nuclear waste.

In the O-H stretch region of the infrared spectrum between 2900 and 4000 cm^{-1}, we observe a surprisingly large number of 9 SF bands in total. Two of them are due to the polar ordered water film near the mineral surface which is well known from various aquatic interfaces. The other bands originate from up to 7 different aluminol species or from specifically[1] bound water molecules. The prominent peak of the (001) surface (SF intensity maximum at 3690 cm^{-1}), we attribute to an OH species bridging two[1-4] aluminium atoms. At the (110) surface, the concentration of this species is considerably smaller. Another aluminol species that can be detected at the (001) and the (110) surface (signal maximum between 3425 and 3475 cm^{-1} depending on the pH) exhibits O-H bonds which are almost parallel to the interface plane. This species is probably the in-plane aluminol group predicted in recent molecular dynamics calculations.[4]

The protonation and deprotonation of the aluminol species are the most basic reaction of the interfaces. We observe that the concentrations of the different groups depends differently on the pH. The measurement of the stability constants is in progress.

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