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Adsorption of alpha amino acids at the water/goethite interface

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Abstract

The adsorption of amino acids onto mineral surfaces plays an important role in a wide range of areas, e.g., low-temperature aqueous geochemistry, bone formation and protein–bone interactions. In this work, the adsorption of three alpha aminoacids (sarcosine, MIDA and EDDA) onto goethite (α-FeOOH) was studied as a function of pH and background electrolyte concentration at 25.0 °C, and the molecular structures of the surface complexes formed were analyzed by means of ATR-FTIR spectroscopy. The results showed that adsorption of alpha amino acids were strongly dependent on the functionality and structure of the ligands. No adsorption was detected for the zwitterionic sarcosine indicating that simple alpha amino acids without other ionizable and/or functional groups display insignificant affinity for mineral surfaces such as goethite. With respect to the more complex amino acids, which are surface reactive, the number and relative positions of carboxylate and amine groups determine the types of surface interactions. These interactions range from non-specific outer-sphere to specific inner-sphere interactions as shown by the MIDA and EDDA results, respectively. The results presented herein suggest that isomerically-selective adsorption might only occur for amino acids that are capable of specific surface interactions, either through site-specific hydrogen bonding or inner-sphere complexation.

Keywords: Adsorption; Amino acids; Water/mineral interface; Goethite; ATR-FTIR spectroscopy

1. Introduction

The adsorption of amino acids onto mineral surfaces plays a key role in a wide range of areas such as low-temperature aqueous geochemistry, bone formation, protein–bone interactions, biochemical homochirality, and even the origin of life, and therefore has been the topic of a large number of studies [1–8]. The importance in geochemistry is a direct consequence of the prevalence of amino acids in soils and aquifers [9–11], as well as their significance as a nutrient source [12]. Much attention has been paid to the involvement of amino acids in geochemical processes at water/mineral interfaces since these processes have the potential to alter mobility and bioavailability of the acids and metal ions.

Torres et al. employed adsorption and electrophoretic measurements to develop an adsorption-isotherm-based model that describes the adsorption of iminodiacetic acid (IDA) to the surface of hematite (α-Fe_2O_3) [13]. They reported a specific surface interaction between the negatively charged IDA and hematite, but they did not elaborate on the structure of the surface complex. In another study aspartic acid was suggested to adsorb onto TiO_2 through the formation of covalent bonds to surface titanium metals, i.e. adsorption by inner-sphere surface complexation [14]. On kaolinite, however, aspartic acid was suggested to form outer-sphere surface complexes [15]; i.e. surface complexes where there is no direct bond between the donor atoms of the ligand and the metal ions at the surface. The simple amino acid serine did not adsorb at the surface of TiO_2, while glutamic acid and lysine were suggested to adsorb through hydrogen-bonding interactions [16].

Infrared spectroscopy was used to study the adsorption of glycine and alanine onto the surface of boehmite [17,18], as well as in a study of glycine adsorption onto silica [19]. As there were no significant changes observed in the infrared spectra of these amino acids upon adsorption, their interaction with the minerals was assumed to be through the formation of interfacial hydrogen bonds. Accordingly, the structure of the solution species, which involves intramolecular hydrogen-bonding between the protonated amines and the carboxylate groups, was

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assumed to be retained at the surface. The formation of interfacial hydrogen bonds has also been used to explain adsorption of larger amino acids IDA (iminodiacetic acid), NTA (nitrilotriacetic acid) and EDTA (ethylenediamine-N,N'- tetraacetic acid) onto γ-Al_2O_3 [20]. In these studies, the samples were dried prior to collecting their infrared spectra. As drying could significantly change the structures of amino acid–mineral surface complexes, these results may not be directly applicable to processes occurring at the water/mineral interface.

The examples above indicate that adsorption and the surface-bonding modes of amino acids on mineral surfaces is dependent both on the molecular properties of the acids, and on the structure and composition of the mineral surface. The objective of the present work was to study how variations in the number of carboxylate and amine groups and their structural positions influence the adsorption of alpha amino acids to the surface of goethite (α-FeOOH). We employed *in situ* ATR-FTIR spectroscopy and adsorption measurements to determine the manner in which sarcosine, MIDA (methyliminodiacetic acid) and EDDA (ethylenediamine-N,N'-diacetic acid) bind to the surface of goethite as a function of pH and ionic strength. The compounds were chosen because they represent amino acids that vary in the number of carboxylate and amine groups, as well as the relative position and ratio of these groups. Goethite is a well-characterized, commonly occurring, and frequently studied iron-bearing mineral. In this study, ATR-FTIR spectra have been collected in both H_2O and D_2O suspensions and the spectra have been analyzed with a 2-dimensional correlation method in order to better differentiate between the various surface complexes.

2. Experimental

2.1. Chemicals, solutions and suspensions

All aqueous solutions and suspensions were prepared using deionized water (Milli-Q Plus), boiled to remove dissolved CO_2. D_2O (Aldrich, 99.9 at%) and DCl (Aldrich, 35%) were used for experiments conducted in deuterated water. The ionic strength was adjusted to 0.01 M or 0.1 M (Na)Cl (the parentheses around Na indicate that the chloride concentration was held constant) using NaCl (Merck, p.a.) dried at 180 °C. pH adjustments were accomplished by means of standardized NaOH (0.2 M), HCl (0.1 M), and DCl (0.1 M in D_2O). Stock ligand solutions were prepared by dissolving weighed amounts of dried sarcosine, CH_3NHCH_2COOH (Fluka BioChemika, >99%), dried H_2MIDA, $CH_3NH(CH_2COOH)_2$ (Aldrich, 99%) and dried H_2EDDA, $HOOCCH_2NH(CH_2)_2NHCH_2COOH$ (Fluka Chemika, >98%). All experiments were conducted at 25 °C.

Goethite (α-FeOOH) was synthesized in polyethylene bottles by adding 2.5 M KOH (EKA, p.a.) to 10 L of 0.15 M $Fe(NO_3)_3$ (Merck, p.a.) at a rate of 10 mL/min [21]. The precipitates were aged for 96 h at 60 °C and dialyzed for three weeks. The resulting particles were identified to be goethite by X-ray powder diffraction and the surface area was determined to be 94 m^2/g using N_2 BET analysis (Micrometrics Flowsorb II 2300). The suspension was diluted, and batches with three different sodium chloride concentrations (0, 0.01, and 0.1 M NaCl) were prepared. Goethite suspensions in D_2O were obtained by resuspending goethite dried at 90 °C in D_2O and equilibrating for 24 h. Potentiometric titrations have shown that proton adsorption/desorption equilibria for goethite are reached within 24 h [21]. Hence, a 24 h pre-equilibration in D_2O is believed to be sufficient for the surface protons to exchange with deuterium.

2.2. Adsorption experiments

Adsorption experiments were carried out in batch mode in the pH range 3–10 and at background electrolyte concentrations of 0 M, 0.01 M and 0.1 M (Na)Cl. Both quantitative adsorption data and infrared spectra were collected for experiments in goethite suspensions in H_2O. Only infrared spectra were collected for experiments conducted in D_2O with MIDA in 0 M (Na)Cl and EDDA in 0 and 0.1 M (Na)Cl.

The stock suspensions of goethite that were used for batch-sample preparation were acidified to pH ∼5 and purged overnight with N_2(g) to desorb any carbonate contamination. Each batch sample was prepared by transferring an aliquot of a stock goethite suspension to a 15 mL polypropylene centrifuge tube wrapped in aluminum foil, adding a volume of freshly prepared stock ligand solution, and adjusting the pH to a value between 3 and 10 using standardized acid or base. All samples were diluted so that the total ligand concentration was 2.0 $\mu mol/m^2$ of goethite, corresponding to 1.9 mM, and the goethite concentration was 10 g/L. During batch sample preparation, the centrifuge tubes were continuously purged with N_2(g) to avoid carbonate contamination. After equilibrating at 25 °C on an end-over-end rotator for 24 h, the pH of each batch sample was measured with a combination electrode (Orion) that was calibrated with commercial buffers (Merck). The outer reference cell of this electrode was filled with 0.01 M NaCl for experiments in 0 M and 0.01 M ionic medium, and with 0.1 M NaCl for experiments in 0.1 M ionic medium. For measurements conducted in D_2O, pD was calculated by adding 0.4 to the reading from the pH meter [22]. Prior to infrared and quantitative adsorption measurements, the samples were centrifuged at a relative centrifugal force of 2880*g* for 20 min, and the supernatant was filtered through a 0.22 μm Millipore filter. As described below, the supernatant was analyzed to determine the concentration of adsorbed ligand and to check for dissolved iron. Small amounts of the supernatant and the wet mineral paste were also analyzed using infrared spectroscopy.

2.3. Analysis

The amount of aminocarboxylate adsorbed at the water/goethite interface was determined by measuring the concentration of ligand remaining in the supernatant with ion chromatography, as described below, and subtracting this value from the total ligand concentration. For sarcosine and MIDA, a custom-built ion chromatograph was used that was equipped with a HPLC pump (LKB 2150), an anion-exchange separation column (Ionpac AS11, 4 mm, 250 mm), and a UV detector