Glutamate Surface Speciation on Amorphous Titanium Dioxide and Hydrous Ferric Oxide

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Hydrous ferric oxide (HFO) and titanium dioxide exhibit similar strong attachment of many adsorbates including biomolecules. Using surface complexation modeling, we have integrated published adsorption data for glutamate on HFO over a range of pH and surface coverage with published in situ ATR-FTIR studies of glutamate speciation on amorphous titanium dioxide. The results indicate that glutamate adsorbs on HFO as a deprotonated divalent anion at pH 3–5 and 0.2 μmol·m⁻² in the form of chelating-monodentate and bridging-bidentate species attached to the surface through three or four of the carboxylate oxygens, respectively. The amine group may interact weakly with the surface. However, at similar pH values and higher surface coverages, glutamate adsorbs mainly as a monoanion or divalent anion chelated to the surface by the γ-carboxylate group. In this configuration the α-carboxylate and amine groups might be free to interact above the surface with the free ends of adjacent glutamates, suggesting a possible mechanism for chiral self-organization and peptide bond formation.

Introduction

The attachment of aqueous amino acids to mineral surfaces is of fundamental interest in a variety of natural and artificial processes ranging from biominalization (1, 2) to the viability of implants of metallic titanium in the human body (3). Amino acid–mineral surface interactions may also have played a central role in life’s origins, either in determining chiral selection of left-handed amino acids in proteins or in facilitating the formation of peptide bonds (4). However, very little is known about the way amino acids attach to even the simplest mineral surfaces in water. The adsorption behavior as a function of environmental parameters such as pH, ionic strength, type of electrolyte, and surface coverage is poorly known, because few adsorption studies carried out under well-defined conditions exist (5–10). In addition, very few in situ ATR-FTIR spectroscopic studies have been carried out (10–13). Given this lack of data, there have been only a handful of surface complexation models of amino acid adsorption (7–9).

In contrast to the lack of information about the amino acid–mineral–water interface, considerable progress has been made in applying in situ ATR-FTIR spectroscopic and X-ray studies to investigate the way oxyanions attach to oxide surfaces. Results are available for the inorganic species sulfate, selenate, arsenite, arsenate, phosphate, and borate (14–22), the monocarboxylates acetate and benzoate (23), and the dicarboxylates oxalate, succinate, maleate, and phthalate (24–27). One unambiguous result of these studies is that there are generally two or more surface-bound oxyanion species whose proportions vary systematically with changes in environmental parameters. Another interesting result is that oxyanions often adsorb as partially or completely deprotonated species at pH values where the aqueous oxyanion is protonated. Integration of the spectroscopic results with the results of adsorption and proton surface titration experiments, along with the results of molecular calculations has recently become possible with surface complexation models (28–30). Equilibrium binding constants based on internally consistent standard states has enabled direct comparison of the binding strength of a given oxyanion on different oxides (31–33). Such comparisons suggest that oxyanions bind equally strongly to freshly precipitated hydrous ferric oxide (HFO) and titanium dioxide. Therefore it should be possible to apply the same speciation information to both oxides.

The amino acids most similar to dicarboxylate oxyanions are aspartate and glutamate. For these ions, an in situ ATR-FTIR spectroscopic study (13) inferred at least three modes of surface attachment of glutamate on amorphous titanium dioxide (Figure 1). In the present study, we use these ATR-FTIR results as a guide to interpret published glutamate adsorption experiments for HFO (5). We do this by developing a quantitative surface complexation model of the chemical reactions at the iron oxide–water–electrolyte interface using the approach developed in ref (30). We find that the same three surface species of glutamate can describe adsorption on titanium dioxide and HFO. The proportions of these species vary according to the pH and the amount of glutamate, but are predicted to show little variation with ionic strength. Interestingly, at high concentrations of glutamate, our model predicts that the elongate glutamate molecules attach by the γ-carboxylate end only and “stand up” on the surface. The other ends of the glutamate molecules, containing the α-carboxylate and amine groups, point away from the surface and are potentially able to interact with the free ends of adjacent glutamates. This alignment could provide a mechanism for chiral self-organization and peptide bond formation.

Experimental Section

Spectroscopic Evidence of Glutamate Surface Speciation. The in situ ATR-FTIR spectroscopic study of glutamate on amorphous titanium dioxide (13) emphasized surface speciation changes as functions of pH and glutamate concentration. No changes as a function of ionic strength were reported. Bulk adsorption data for aspartate on titanium dioxide showed no dependence on ionic strength (7). We have summarized the principle changes inferred in the ATR-FTIR study in Figure 2. We used pH and aqueous glutamate concentration as the axis variables in Figure 2 because these were the experimental parameters. Conversion of the aqueous glutamate concentration to surface coverages is not possible except in a qualitative sense, because the surface area of the
Glutamate surface species on amorphous TiO₂

a. CHELATING-MONODENTATE
b. BRIDGING-BIDENTATE
c. CHELATING

FIGURE 1. Surface species inferred from ATR-FTIR study of glutamate attached to the surface titanium ions of amorphous TiO₂ (13). These surface species are also consistent with the surface complexation calculations reported in the present study. Large spheres refer to oxygen, small filled spheres refer to carbon, small pale spheres refer to hydrogen or nitrogen, and the lowermost spheres refer to titanium. (a) Chelating-monomodentate species with three points of attachment involving two inner-sphere Ti—O—C bonds and one Ti—OH...O—C hydrogen bond. One O—C group of the α-carboxylate is free. (b) Bridging-bidentate species with four points of attachment involving two inner-sphere Ti—O—C bonds and two Ti—OH...O—C hydrogen bonds. (c) Chelating species with two points of attachment involving two inner-sphere Ti—O—C bonds to a single titanium ion.

FIGURE 2. Summary of the glutamate surface speciation inferred from ATR-FTIR spectroscopic results.

amorphous titanium dioxide is not known and the solid concentration is only known approximately.

It is important to emphasize that Figures 1 and 2 illustrate our interpretation of the discussion in the ATR-FTIR study. Additional modes of surface attachment were also mentioned as possibilities. Our representation in Figure 2 is an attempt to summarize the speciation inferred in the ATR-FTIR study in terms of the smallest set of species consistent with their discussion and the surface complexation calculations discussed below. For example, we infer a combination of inner-sphere (Ti—O—C) bonds and hydrogen bonds (TiOH...O—C) in Figure 1a and b, whereas only species involving inner-sphere bonds were depicted in the ATR-FTIR study. Such differences may be difficult to determine from either FTIR spectroscopic experiments or molecular calculations (24). Consequently, we relied on the surface complexation modeling to make a choice. Figures 1 and 2 do, however, preserve the major features of the glutamate attachment modes inferred previously (13).

Figure 2 illustrates the two principle changes in glutamate surface speciation inferred in the ATR-FTIR study. The first is a speciation change as a function of total glutamate concentration at pH = 3. At the lowest glutamate concentrations (1 × 10⁻⁴ M), a chelating-monomodentate species was inferred by the latter authors. Here there are three points of attachment of the glutamate to the surface (Figure 1a), i.e., the glutamate molecule can be thought of as “lying down” on the surface. The γ-carboxylate is chelated to a single Ti by a hydrogen bond (TiOH...O—C) and a Ti—O—C bond. The α-carboxylate is monodentate, with only one O attached to a Ti through a Ti—O—C bond while the other oxygen forms a C=O entity. The state of protonation of this species in Figure 1a represents our best estimate for a species of this type based on the surface complexation calculations. At the highest glutamate concentrations in Figure 2 (1 × 10⁻³ M), a chelating species was inferred (Figure 1c). Here the γ-carboxylate chelates to a single Ti either with two Ti—O—C bonds (as shown in the figure) or with one Ti—O—C bond and one TiOH...O—C hydrogen bond. We could not distinguish between these two possibilities in our surface complexation calculations. In both possibilities, the α-carboxylate and amine groups are pointing away from the surface, i.e., the glutamate molecule is “standing up” on the surface. However, in the species shown in Figure 1c the amine group is deprotonated, whereas in the other possible mode it is protonated. Interaction of the γ-carboxylate with an alumina surface, also at high surface coverage, has previously been suggested (10) although only a single surface coverage was reported. It should also be noted that no definitive information on the state of protonation of the amine group in the adsorbed glutamate was reported in ref (13) because the adsorption bands are so weak.

At pH = 3 and intermediate glutamate concentrations (1 × 10⁻³ M) in Figure 2 the chelating attachment mode is accompanied by at least one other surface species, possibly a bridging-bidentate species. Here there are four points of attachment of the glutamate to the surface (Figure 1b). The glutamate molecule can again be thought of as “lying down” on the surface. Both carboxylate groups are bound to the surface in the same way: one oxygen is coordinated directly to a Ti and the other is coordinated through a hydrogen bond to a different Ti. The state of protonation of this species in Figure 1b represents our best estimate for a species of this type based on the surface complexation calculations. For example, a species in which all four oxygens of the carboxylate groups were directly coordinated to four different Ti atoms could not fit the adsorption data satisfactorily. Overall, the major glutamate surface speciation change at pH = 3 as a function of increasing glutamate concentration is a transition from glutamate “lying down” at the lowest concentration to “standing up” at the highest concentration. This change may be attributable to surface crowding at progressively higher glutamate concentrations (13). The second principle change in speciation emphasized by the latter authors is a change as a function of pH. At the intermediate glutamate concentration and pH = 3 in Figure 2, the bridging-bidentate species is just one of at least two surface glutamate species. However, at higher pH values approaching neutrality, it was reported to be the predominant species.

The existence of multiple surface species of glutamate on amorphous titanium dioxide and the systematic changes as a function of environmental parameters are both features of the amino acid—mineral—water interface that are similar to the more extensive results obtained for both inorganic and organic oxyanions. Integration of these features into a surface complexation model permits application of the spectroscopic results to the adsorption of glutamate on other similar solids over a wide range of environmental conditions.

**Surface Complexation Model of Glutamate on HFO.** The approach used in the present study builds on the predictive single-site triple-layer model and associated crystal chemical and Born solvation theory referred to as the extended triple-layer model or ETLM (34–36). Recent theoretical advances in the application of the ETLM to oxyanion adsorption on...
TABLE 1. Aqueous Glutamate Properties, HFO Characteristics, and Extended Triple-Layer Model Parameters for Proton, Electrolyte, and Glutamate Adsorption on Hydrous Ferric Oxide

| Name                  | Reaction                                  | log K
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<tr>
<td></td>
<td>FeOH + H⁺ + Glu ↔ Fe(OH)₂ + H⁺ + 2H₂O</td>
<td>4.07</td>
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<tr>
<td></td>
<td>&gt;FeOH + &gt;Fe(OH)₂ + 2H⁺ + HGlu ↔ &gt;Fe &gt;Fe(OH)₂ Glu + 2H₂O</td>
<td>2.303 RT</td>
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<tr>
<td></td>
<td>&gt;Fe(OH)₂ + H⁺ + HGlu ↔ &gt;FeGlut + 2H₂O</td>
<td>2.303 RT</td>
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<tr>
<td></td>
<td>&gt;FeOH + &gt;Fe(OH)₂ + H⁺ + H₂O</td>
<td>2.303 RT</td>
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<tr>
<td></td>
<td>4 &gt;FeOH + H⁺ + HGlut → (&gt;FeOH)₂ &gt;FeGlut + 2H₂O</td>
<td>2.303 RT</td>
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<td>&gt;Fe(OH)₂ + H⁺ + HGlut → &gt;FeGlut + 2H₂O</td>
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<td>&gt;FeOH + H⁺ + HGlut → &gt;FeGlut + 2H₂O</td>
<td>2.303 RT</td>
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References:

1. Protonation constants from ref (40); electrolyte pair constants assumed to be the same as for aspartate given by ref (41).
2. HFO properties are N₅ = 118 sites-nm⁻², Aₛ = 600 m²·g⁻¹, Cₒ = 100 µF·cm⁻², βₚZ = 7.9, ΔpKₒ = 5.6, log Kᵢ = 5.1, log Kᵢ₋ = 10.7, log Kᵢ₊ = 4.3, log Kᵢ₋₋ = 4.5 (32).
3. Equilibrium constants relative to site-occupancy standard states were also written relative to charged surface sites calculated using the following equations:

\[ \log K₀ⁿ_{Fe(II)-Fe(OH)₄}^{FeGlut} = \log K₀ⁿ_{Fe(II)-Fe(OH)₄}^{FeGlut} + \log \left( \frac{N₅A₄C₄}{100} \right) \]

\[ \log K₀ⁿ_{Fe(OH)₂-FeGlut} = \log K₀ⁿ_{Fe(OH)₂-FeGlut} + \log \left( \frac{N₅A₄C₄}{100} \right) \]

\[ \log K₀ⁿ_{Fe(OH)₂-FeGlut} = \log K₀ⁿ_{Fe(OH)₂-FeGlut} + \log \left( \frac{N₅A₄C₄}{100} \right) \]

oxides (30, 33) have emphasized the role of water dipoles during adsorption and indicated the magnitude of this effect. These advances have facilitated incorporation of the nature of surf ace species established by spectroscopic studies into surface complexation calculations. In turn this modeling has enabled prediction of surface speciation as a function of environmental parameters consistent with spectroscopically obtained results. We apply the ETLM here to the adsorption of glutamate on HFO (37). We investigate the applicability of the three surface species deduced above for glutamate on amorphous titanium dioxide to the adsorption of glutamate on HFO. In particular the level of protonation of the surface species are determined from the stoichiometry of the reactions formulated through iterative application of the surface complexation calculations to the bulk adsorption data for HFO.

Surface chemical studies of HFO (37, 38) established that freshly precipitated HFO aged for 4 h is a reliable solid for use in surface chemistry experiments. We have previously analyzed the proton surface charge and sulfite and selenite adsorption data measured by Davis and Leckie for this solid (32). The surface chemical characteristics of the HFO, i.e., the BET surface area and the surface protonation and electrolyte adsorption equilibrium constants, capacitance, and site density, are given in Table 1. X-ray diffraction studies of freshly precipitated HFO have established that it is the mineral ferrihydrite, whose crystal structure has recently been determined (39) yielding a formula of Fe₃O₄(OH)₂. The latter corresponds to 81.6 g·mole⁻¹ of Fe, which we have used in our surface complexation calculations to convert the 0.001 M concentration of Fe in the glutamate adsorption experiments to a solid concentration of HFO in g·L⁻¹. Aqueous protonation of glutamate was treated using equilibrium constants taken from the NIST compilation (40). Electrolyte ion-pairing with glutamate was approximated by assuming that it was the same as literature values for aspartate (41). The equilibrium constants for glutamate are summarized in Table 1. Aqueous activity coefficients were calculated using the extended Debye-Hückel equation (42), using previously described electrolyte characteristics (43).

Three surface complexation reactions, corresponding to the formation of the species depicted in Figure 1a, b, and c, were found to be consistent with the adsorption data plotted in Figure 3a. The reactions are represented as follows:

**Chelating-monodentate species (Figure 1a)**

\[ \text{FeOH} + \text{Fe(OH)₂} + 2H⁺ + HGlut \rightarrow \text{Fe} >\text{Fe(OH)₂} \text{Glu} + 2H₂O \]

**Bridging-bidentate species (Figure 1b)**

\[ 4 \text{FeOH} + H⁺ + HGlut \rightarrow (>\text{FeOH}₂) >\text{FeGlut} + 2H₂O \]

**Chelating species (Figure 1c)**

\[ >\text{Fe(OH)₂} + H⁺ + HGlut \rightarrow >\text{FeGlut} + 2H₂O \]

It should be noted that writing the species \( >\text{FeOH} \) and \( >\text{Fe(OH)₂} \) in eqs 1 and 3 implies a two-site model. However, eqs 1 and 3 are computationally almost identical to the reactions

\[ 2 >\text{FeOH} + 2H⁺ + HGlut \rightarrow >\text{Fe₂Glut} + 2H₂O \]

and

\[ >\text{FeOH} + H⁺ + HGlut \rightarrow >\text{FeH₂Glut} + H₂O \]

respectively, which are true one-site reactions. Similar representations of \( >\text{FeOH} \) and \( >\text{Fe(OH)₂} \) have been used previously (44). As noted above (see also Figure 1), eqs 1, 2, and 3 refer to the completely deprotonated form of glutamate. This is similar to results for many inorganic and organic oxynions which adsorb as partially or completely deprotonated species at pH values where the aqueous oxynion is protonated.

The reactions in eqs 1, 2, and 3 correspond to the equilibrium constants

\[ \log K^n_{>\text{Fe(OH)₂}-\text{Glut}} = \frac{a_{>\text{Fe(OH)₂}-\text{Glut}}a_{>\text{Fe(OH)₂}-\text{Glut}}}{a_{>\text{Fe(OH)₂}-\text{Glut}}a_{>\text{Fe(OH)₂}-\text{Glut}}} \]

\[ \log K^n_{>\text{Fe(OH)₂}-\text{Glut}} = \frac{a_{>\text{Fe(OH)₂}-\text{Glut}}a_{>\text{Fe(OH)₂}-\text{Glut}}}{a_{>\text{Fe(OH)₂}-\text{Glut}}a_{>\text{Fe(OH)₂}-\text{Glut}}} \]

\[ \log K^n_{>\text{Fe(OH)₂}-\text{Glut}} = \frac{a_{>\text{Fe(OH)₂}-\text{Glut}}a_{>\text{Fe(OH)₂}-\text{Glut}}}{a_{>\text{Fe(OH)₂}-\text{Glut}}a_{>\text{Fe(OH)₂}-\text{Glut}}} \]

where the superscripts "+" and "-" refer to reactions written relative to \( >\text{FeOH} \) and to site-occupancy standard states (34), respectively. The terms involving \( \DeltaΨ_{r₁}, \DeltaΨ_{r₂} \) and \( \DeltaΨ_{r₃} \) in eqs 6, 7, and 8 represent the electrical work involved in the reaction. In the ETLM, the electrical work includes contributions not only for the ions going on or off the surface, but also for the water dipoles coming off the surface in eqs 1, 2, and 3. The latter contribution to \( \DeltaΨ \) is \(-nH₂O(\Psi₁ - \Psi₂)\), where \( nH₂O \) represents the number of moles of water on the right side of the reaction. In eqs 1, 2, and 3, \( nH₂O = 2 \), which results in \( \DeltaΨ_{r₁} = \Psi₁ \) and \( \DeltaΨ_{r₂} = \DeltaΨ_{r₃} = 0 \).

The regression calculations discussed below generated values of the equilibrium constants for glutamate adsorption
for the jth surface species represented by $\log^* K^j_0$ in Table 1. The superscript "0" represents the hypothetical 1.0 M standard state (34). These values were converted to values of $\log K^j_\theta$ referring to site-occupancy standard states and referenced to $\sim SO^-$ using equations and the values of $N_s$ (site density), $A_s$ (BET surface area), pH<sub>ZPC</sub>, and $\Delta pK^s_n$ given in Table 1. The values of $\log K^j_\theta$ in Table 1 are independent of the individual sample characteristics. Consequently, values of $\log K^j_\theta$ are useful for comparing the binding of glutamate on different oxides.

Adsorption data for glutamate on HFO in 0.1 M NaNO<sub>3</sub> solutions at three total glutamate concentrations are represented by the symbols in Figure 3a. The solid curves in the figures represent regression calculations using the reactions in eqs 1, 2, and 3. The data sets are noteworthy for the strong adsorption at pH values less than about 7 and for the strong dependence on glutamate concentration (i.e., surface coverage). The assessment of uncertainties in experimental adsorption studies is often not provided. However, for anion uptake experiments, uncertainties are typically largest at the lowest percentages adsorbed and may be of the order of ±5–10% adsorbed (7). The calculated curves in Figure 3a show relatively small discrepancies with the experimental data within this uncertainty. Clearly, the surface species indicated by ATR-FTIR spectroscopy for glutamate on titanium dioxide can be applied to describe glutamate adsorption on HFO as a function of pH and surface coverage. Many other surface complexation reaction stoichiometries were tested, but did not satisfactorily account for the adsorption data and preserve consistency with the spectroscopic results. Our equilibrium constants for glutamate adsorption were also tested by predicting the ionic strength dependence of glutamate adsorption and the trends of surface speciation with pH and surface coverage.

Although the ionic strength dependence of glutamate adsorption on HFO was not reported, the adsorption of aspartate on titanium dioxide shows no ionic strength dependence (7). Assuming, as a first approximation, that aspartate and glutamate have similar behavior, we might expect that glutamate adsorption will also not show a significant ionic strength dependence. Predicted adsorption curves for glutamate in 0.005 M NaNO<sub>3</sub> solutions are shown in Figure 3b, where it can be seen that they are almost identical to the curves in Figure 3a.

Additional tests of the ETLM for glutamate adsorption on HFO can be made by predicting the surface speciation changes as functions of surface coverage and pH. Predicted model speciation curves for three surface coverages are shown in Figure 3c, d, and e. The curves in this figure can be compared to the trends in Figure 2. At pH = 3, it can be
seen in Figure 3c, d, and e that the predominant species is predicted to change with increasing surface coverage from the chelating-monodentate type to the chelating type. The same change is evident in Figure 2. At pH 3 and the intermediate surface coverage (Figure 3d), the two most abundant surface complexes are predicted to be the bridging-bidentate and the chelating types, which also agrees with the spectroscopic results. As pH increases to between 5 and 7 at the two highest surface coverages (Figures 3d and e), it can be seen that the bridging-bidentate complex is predicted to become more important, even dominant, which again agrees qualitatively with Figure 2. More detailed comparisons would be possible if the exact surface coverages for the spectroscopic data were known. However, the predicted speciation changes for glutamate on HFO are qualitatively consistent with the trends inferred in the spectroscopic study.

Discussion

The calculations described above provide a preliminary picture of the adsorption of glutamate on oxide surfaces by integrating in situ spectroscopic results with bulk adsorption data. We have established that the same three surface species of glutamate can describe adsorption on amorphous titanium dioxide and HFO. The surface speciation is predicted to vary according to the pH and the amount of glutamate in ways that are qualitatively consistent with trends inferred from the spectroscopic study. In addition, the bulk adsorption is predicted to show little variation with ionic strength, which is consistent with independent data for aspartate adsorption on titanium dioxide. Both of these results are of broader interest.

The changes in glutamate surface speciation described above may have implications for origin of life studies. At low pH and at low and intermediate surface coverages, the ATR-FTIR study (13) and our model indicate that, together, the chelating-monodentate and bridging-bidentate species (Figure 1a and b) are predominant. Both species can be thought of as glutamate molecules essentially “lying down” on the surface. However, at low pH and the highest surface coverages, the chelating species (Figure 1c) predominates. In this picture, the elongate glutamate molecules attach by the γ-carboxylate end only and “stand up” on the surface. The other ends of the glutamate molecules, containing the α-carboxylate and amine groups, point away from the surface and are potentially able to interact with the free ends of adjacent glutamates.

These interactions of adjacent amino acids are of potential interest to models of prebiotic chemistry for at least two reasons. First, such strong interactions could potentially lead to local surface-bound domains of chiral self-organization, as has been observed for clusters of molecules adsorbed to other crystalline surfaces (45-46). In addition, the proximity of the amine group from one glutamate to the α-carboxylate group of an adjacent amino acid might promote peptide bond formation. Thus adsorption of amino acids onto mineral surfaces could promote both the selection and synthesis of homochiral prebiotic oligomers (4).

The apparent lack of variation of adsorption with ionic strength for glutamate and aspartate on oxide minerals provides a contrast with results for oxygen ions in general, and dicarboxylate anions in particular. The latter typically show a significant dependence of adsorption on ionic strength. In our surface complexation model for glutamate, the predicted lack of ionic strength dependence is a consequence of the reactions used. Specifically, the three electrostatic factors in eqs 6, 7, and 8, i.e., ΔΨ_{α1} = Ψ_0 and ΔΨ_{α2} = ΔΨ_{α3} = 0, are either zero or only weakly dependent on ionic strength. In turn, this is a consequence of the number of water molecules desorbing from the surface in eqs 1, 2, and 3. In contrast, dicarboxylylate anions, such as succinate, fumarate, maleate on alumina, and phthalate on hematite (24-49), adsorb with a strong dependence on ionic strength which may result from a combination of a different number of water molecules desorbing and the existence of outer-sphere surface species. It therefore appears that there are significant differences in the behavior of the acidic amino acids and dicarboxylate anions on a variety of oxide surfaces.

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Literature Cited

(18) Peak, D.; Sparks, D. L. Mechanisms of selenite adsorption on


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