Pergamon

0016-7037(95)00385-1

Effects of simple organic acids on sorption of Cu^{2+} and Ca^{2+} on goethite

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Abstract—Effects of phthalic acid and chelidamic acid on sorption of Cu^{2+} and Ca^{2+} were examined in goethite (α-FeOOH)/water suspensions. Single-sorbate sorption of Cu^{2+} and Ca^{2+} on goethite over a wide range of conditions (pH, I, sorbate/sorbent ratio) was described reasonably well by the Generalized Two Layer Model (GTLM). In the presence of the organic acids, particularly chelidamic acid, sorption of Cu^{2+} was significantly enhanced at low pH values. Sorption of Cu^{2+} in Cu^{2+}-phthalic acid and Cu^{2+}-chelidamic acid binary systems was quantitatively reproduced over a wide range of conditions (pH, Cu/organic acid concentration ratio) with the GTLM by using a unique set of Cu^{2+}-organic acid ternary surface complexes for each binary system. Sorption of Ca^{2+} remained unaffected in the presence of phthalic acid, but decreased in the presence of chelidamic acid due to the formation of nonsorbing Ca^{2+}-chelidamic acid solution complexes. These effects were predicted reasonably well by the GTLM. Although the exact sorption mechanisms are unconfirmed, available data suggest that enhanced sorption of Cu^{2+} resulted from sorption of Cu^{2+}-organic acid complexes in a ligand-like manner, i.e., involving oxide surface sites and carboxyl groups of the organic acids not participating in Cu^{2+} complexation. Results from this work suggest that the reported mineral-humate-cation interactions are consistent with the formation of cation-humate ternary surface complexes.

1. INTRODUCTION

Sorption onto mineral surfaces often controls the fate and transport of trace metals in natural aquatic systems. Both organic and inorganic complexing ligands are present in natural aquatic systems and numerous investigations have revealed that complexation of metal ions by ligands can dramatically increase or decrease metal ion sorption compared to ligand-free systems (Huang et al., 1977; Bolland et al., 1977; Bloesch et al., 1977; Davis and Leckie, 1978; Bourg and Schindler, 1978; Bourg et al., 1979; Elliott and Huang, 1979; Theis and Richter, 1980; Benjamin and Bloom, 1981; Balistrieri and Murray, 1981; Benjamin and Leckie, 1982; Theis and West, 1986).

Natural organic matter (NOM), derived from degradation of plant and animal matter, is an important metal complexing ligand in many natural aquatic systems (Thurman, 1985), and can significantly influence the fate and transport of chemical constituents, particularly metal ions. In laboratory batch sorption experiments, sorption of NOM, particularly humic substances, onto minerals has been found to be modified in the presence of Ca^{2+} and Mg^{2+} (Tipping, 1981a,b). Sorption of the metal ion Cu^{2+} has been found to be significantly influenced in the presence of humic substances (Tipping et al., 1983; Davis, 1984). These mineral-humate-ion interactions are not well understood and there has been limited success in applying surface complexation models (SCMs) to describe them, primarily because of the complex nature of humic substance and our weak understanding of their behavior (Dzombak et al., 1986; Fish et al., 1986).

Sorption characteristics of many simple organic acids having —COOH and —OH functional groups, the predominant functional groups in humic substances, have been found to be similar to those of humic substances (Davis, 1982; Gu et al., 1994; Ali and Dzombak, 1994; Ochs et al., 1994). Although humate molecules are much more complex than simple organic acids (e.g., they are polydisperse and multifunctional), experimentation with simple organic acids promises to provide a basis for better understanding of mineral-humate-ion interactions and their possible impact on fate and transport of contaminants in aquatic systems.

Only limited sorption data are available for systems containing cations and simple organic acids (e.g., Balistrieri and Murray, 1987; Davis and Leckie, 1978; Elliott and Huang, 1979; Theis and Richter, 1980), and efforts to describe these data with SCMs have been only partially successful. More systematic studies are needed to elucidate mineral-organic acid-ion interactions, the understanding of which is critical to accurate modeling of solute behavior in natural aquatic systems.

In the presence of a sorbent surface, metal ions and complexing ligands (e.g., an organic acid) can interact in a number of ways: (1) metal ions and ligands may compete directly for surface sites; (2) metal ions and ligands may influence sorption of each other indirectly by altering the electrostatic properties at the oxide/water interface; (3) nonsorbing or weakly sorbing metal-ligand complexes may form in solution, thereby reducing sorption of the metal ion compared to ligand-free systems; and (4) metal-ligand complexes may sorb strongly at the surface, thereby enhancing sorption of metal, ligand, or both compared to single-sorbate systems. It should be noted that metal-ligand surface complexes or ternary surface complexes may form by sequential bonding of the ions or by sorption of the solution complex. Thermodynamically, these mechanisms are equivalent and equilibrium sorption data provide no information by which to distinguish between them (Benjamin and Leckie, 1982).

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SCMs have been applied successfully to describe single-sorbate sorption of inorganic ions as well as simple organic acids onto oxide particles (Dzombak and Morel, 1990; Davis and Kent, 1990; Mesuere and Fish, 1992a; Ali and Dzombak, 1995). In recent applications, SCMs were successful in predicting anion sorption in binary systems over a wide range of conditions based on single-sorbate data fits (Mesuere and Fish, 1992b; Ali and Dzombak, 1995). However, there have been limited applications of SCMs to describe metal-ligand interactions (Bourg and Schindler, 1978; Balistrieri and Murray, 1981; Benjamin and Leckie, 1982; Hsi and Langmuir, 1985; Theis and West, 1986; Balistrieri and Murray, 1987; Schindler, 1990). In most cases, these applications were over limited ranges of conditions, and with only partial success. Formation of ternary surface complexes, which has been widely proposed as being responsible for enhanced sorption of metal ions in the presence of complexing ligands (Huang et al., 1977; Davis and Leckie, 1978; Bourg and Schindler, 1978; Bourg et al., 1979; Benjamin and Bloom, 1981; Benjamin and Leckie, 1982; Zelewsky and Bemtgen, 1982; Rudin and Motschi, 1984; McBride, 1985), has been considered only in few applications (e.g., Bourg and Schindler, 1978; Schindler, 1990). A primary reason for limited applications of SCMs to metal-ligand systems is lack of data over a wide range of conditions. For insightful and accurate modeling, sorption data spanning a range of conditions are essential.

In the present work, mineral-organic acid-ion interactions have been investigated in goethite (α-FeOOH) suspensions, using two simple organic acids—phthalic acid (benzene, 1,2-dicarboxylic acid) and chelidamic acid (4-hydroxypyridine, 2,6-dicarboxylic acid)—the metal ion Cu^{2+}, and the electrolyte ion Ca^{2+}. Phthalic acid possesses —COOH, and chelidamic acid possesses both —COOH and —OH functional groups, the predominant functional groups present in humic substances. Simple organic acids such as these are important constituents of NOM and, as a group, may account for approximately 5–8% of dissolved organic carbon (DOC) of natural waters (Thurman, 1985). These two organic acids differ significantly in their affinities for Cu^{2+} and Ca^{2+}. Compared to phthalic acid, chelidamic acid forms significantly stronger solution complexes with both Cu^{2+} and Ca^{2+}. Goethite (α-FeOOH), an iron oxide, occurs in almost all soils and in many lakes and streams, and is widely used as a model colloid in geochemical studies.

The specific objectives were to determine the effects of two simple organic acids on sorption of Cu^{2+} and Ca^{2+} onto goethite over a wide range of conditions, to assess the role of metal-organic acid ternary surface complexes and nonsorbing solution complexes in such systems, and to investigate the ability of surface complexation models to describe metal-organic acid-goethite interactions. Surface complexation modeling was performed using the Generalized Two Layer Model of Dzombak and Morel (1990).

2. MATERIALS AND METHODS

2.1. Synthesis and Characterization of Goethite

Goethite (α-FeOOH) was prepared according to the method outlined by Atkinson et al. (1968) and dried after preparation according to the procedure described in Schwertmann and Cornell (1991). De-

tails of goethite synthesis and characterization are provided in Ali (1994). With dried, powdered solids, goethite concentrations in the experimental suspensions could be controlled accurately and potential problems with extended storage in aqueous suspension were avoided. The crystal structure of the powdered goethite samples was verified by x-ray diffraction analysis. The specific surface area of goethite samples was determined by the N_2/BET method to be 79.4 $\pm$ 1 m^2/g. The pristine point of zero charge (PPZC) defined by the common intersection point of titration curves at three different ionic strengths was 8.0 $\pm$ 0.1. The powdered solid was used to make one liter stock suspension batches containing 12 g/L of goethite in deionized water. Goethite stock solutions were kept under N_2(g) atmosphere for at least two weeks before using in batch sorption experiments.

2.2. Sorption Experiments

Single-sorbate sorption of Cu^{2+} and Ca^{2+} was examined in goethite suspensions (1.6 g/L) as a function of pH, ionic strength (0.01 and 0.10 M), and sorbate to sorbent ratio (mol sorbate/mol surface sites). Sorption of Cu^{2+} and Ca^{2+} in the presence of either phthalic acid or chelidamic acid was investigated in binary-sorbate systems in 1.6 g/L goethite suspensions, at 0.01 M ionic strength. For each pair of sorbates (cation-organic acid), a range of combinations of total sorbate concentrations were examined (Cu: 0.0023–0.098 mM; Ca: 0.001–0.20 mM; phthalic acid: 0.25–1.0 mM; chelidamic acid: 0.04–0.20 mM). Sorption experiments with Ca^{2+} (both single- and binary-sorbate) were conducted with NaCl as background electrolyte, while those with Cu^{2+} were performed with $NaNO_3$ as background electrolyte. NaCl was not used in experiments with Cu^{2+} because Cl^- forms complexes with Cu^{2+} and interferes with the cupric ion-sensitive electrode that was used to measure Cu^{2+} concentration in the single-sorbate systems. Sorption of phthalic acid, chelidamic acid, and Ca^{2+} was investigated in a limited number of single-sorbate systems with $NaNO_3$ as background electrolyte, to study the effect of electrolyte type. Sorption of phthalic acid and chelidamic acid onto goethite (with NaCl as background electrolyte) was studied in complementary work (Ali and Dzombak, 1995).

Enhancement of goethite dissolution by the organic acids used in this study was expected to be very small based on available data on ligand-promoted dissolution of iron oxides. Dissolution of goethite can be increased by large concentrations of some bidentate organic acids such as oxalic acid, but the dissolution rate is low and total dissolution over 24 hours is small (Zinder et al., 1986; Mesuere, 1991; Mesuere and Fish, 1992a,b). The assumption of negligible dissolution enhancement was supported by the observation that there was no shift in peak wavelength values for the UV measurements of organic acid concentrations in supernatant samples from the sorption experiments.

All experiments were conducted in batch in 40 mL polyethylene centrifuge tubes at a constant temperature of 20 $\pm$ 2°C. Experiments were set up by adding fixed amounts of N_2(g)-purged deionized water, goethite stock solution, electrolyte stock solution (1 M, CO_2-free), and sorbate spike(s) to each tube. Different (small) amounts of CO_2-free strong acid or base (0.10 M) were added to yield a range of pH values in the tubes. The tubes were capped after purging the headspace with nitrogen, placed on an end-over-end rotator and agitated for 24 hours. After the equilibration period, the tubes were removed from the rotator and centrifuged for about 15 minutes. The pH of the supernatant in each tube was then measured with a microelectrode probe and a sample of the supernatant was withdrawn with a 5 mL plastic syringe. This sample was expressed through a 0.2 μm membrane filter (in a filter holder attached to the syringe) and after discarding the first one milliliter, the filtrate was stored in a polyethylene sample vial for analysis. Losses due to filtration were found to be negligible when the first one mL of filtrate was discarded.

Sorbed concentrations of sorbates were calculated as the difference between total and solution concentrations. No corrections were made for possible adsorptive losses of the sorbates to tube walls under the assumption that goethite coatings on tube walls would outcompete any exposed polyethylene surface.

The purging with N_2(g) of the goethite stock solutions and the use of CO_2-free electrolyte solutions in the experiments was done to elim-

Table 1 Equilibrium expressions for solution reactions used in modeling

Equilibrium Expression[a]	log K[b]
$(OH^-) = (H^+)^{-1} (\gamma)^{-2} K$	-14.0
$(HSO_4^-) = (H^+)(SO_4^{2-}) \gamma_2 K$	1.99
$(H_2L_p) = (H^+)^2 (L_p^{2-}) (\gamma_1)^2 \gamma_2 K$	8.36
$(HL_p^-) = (H^+) (L_p^{2-}) \gamma_2 K$	5.41
$(NaL_p^-) = (Na^+)(L_p^{2-}) \gamma_2 K$	0.90
$(CaL_p^0) = (Ca^{2+})(L_p^{2-}) (\gamma_2)^2 K$	2.40
$(CaHL_p^+) = (H^+)(Ca^{2+})(L_p^{2-}) (\gamma_2)^2 K$	6.45
$(CuL_p^0) = (Cu^{2+})(L_p^{2-}) (\gamma_2)^2 K$	4.00
$(CuHL_p^+) = (H^+)(Cu^{2+})(L_p^{2-}) (\gamma_2)^2 K$	7.10
$(CuL_{p\,2}^{2-}) = (Cu^{2+})(L_p^{2-})^2 (\gamma_2)^2 K$	5.30
$(H_3L_c) = (H^+)^2 (HL_c^{2-}) (\gamma_1)^2 \gamma_2 K$	5.17
$(H_2L_c^-) = (H^+) (HL_c^{2-}) \gamma_2 K$	3.55
$(L_c^{3-}) = (H^+)^{-1} (HL_c^{2-}) (\gamma_1)^{-1} \gamma_2 (\gamma_3)^{-1} K$	-11.54
$(CaL_c^-) = (H^+)^{-1}(Ca^{2+})(HL_c^{2-}) (\gamma_1)^{-1} (\gamma_2)^2 K$	-4.62
$(CaHL_c^0) = (Ca^{2+})(HL_c^{2-}) (\gamma_2)^2 K$	2.11
$(CuL_c^-) = (H^+)^{-1}(Cu^{2+})(HL_c^{2-}) (\gamma_1)^{-2} (\gamma_2)^2 K$	1.98
$(CuHL_c^0) = (Cu^{2+})(HL_c^{2-}) (\gamma_2)^2 K$	7.06
$(CuHL_{c\,2}^{3-}) = (H^+)^{-1}(Cu^{2+})(HL_c^{2-})^2 (\gamma_1)^{-1} (\gamma_2)^3(\gamma_3)^{-1} K$	6.11
$(CuL_{c\,2}^{4-}) = (H^+)^{-2}(Cu^{2+})(HL_c^{2-})^2 (\gamma_1)^{-2} (\gamma_2)^3(\gamma_4)^{-1} K$	-0.32

[a] H_2L_p and H_3L_c represent phthalic and chelidamic acid, respectively;
( ) = molar concentration; γ_i = aqueous phase activity coefficients.
[b] I=0 M; Source: Martell and Smith, 1974, 1978.

inate possible effects of CO_2 on solute sorption in the systems of interest. Some studies have indicated that CO_2 sorption can influence sorption of other solutes under certain conditions (e.g., van Geen et al., 1994).

2.3. Reagents

Phthalic acid (99%, Aldrich Chemical Co. Inc.) and chelidamic acid (95%, Sigma Chemical Co.) were used as obtained without any additional purification. All other chemicals used in this study (e.g., $NaCl$, $NaNO_3$, $CaCl_2$, $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$, $NaOH$, HCl, HNO_3) were reagent grade. Concentrations of the organic acid stock solutions were tested periodically using the analytical technique described below and no changes were observed. Based on available information, no photodegradation of the two organic acids was expected.

2.4. Analytical Techniques

Phthalic acid and chelidamic acid concentrations (in single-sorbate systems) were measured with ultraviolet (UV) spectroscopy using a Hewlett Packard 8451 Diode Array Spectrophotometer. For measurement of the organic acid concentrations, two wavelengths were used for phthalic acid and one for chelidamic acid. Details of the organic acid measurement techniques are provided in Ali and Dzombak (1995). Copper concentrations were measured either by cupric-ion-sensitive electrode (for single-sorbate systems) or by flame or flameless atomic absorption spectrophotometry (for binary-sorbate systems). Calcium concentrations were measured by spiking the solution with radiolabeled ^{45}Ca and counting the remaining activity in the filtered supernatant with a scintillation counter (Model 5000TD, Beckman). It should be noted that organic acid concentrations in binary-sorbate systems could not be determined in this study because of the formation of cation-organic acid solution complexes and the resulting changes in UV absorbance characteristics.

Estimated errors in sorption data (expressed as percent sorbate sorbed) of all sorbates used in this study were within ±4 percent (Ali, 1994). Estimated errors in pH measurements were within ±0.02 pH unit.

2.5. Modeling of Sorption Data

All sorption data were modeled using the Generalized Two Layer Model (Dzombak and Morel, 1990), the central component of which

is the Diffuse Layer Model (Stumm et al., 1970; Huang and Stumm, 1973). Detailed description of the Generalized Two Layer Model is provided in Dzombak and Morel (1990).

As discussed later, only a single surface site type was used to model the sorption of inorganic and organic ions on goethite. Optimization of model parameters (e.g., surface site density, equilibrium constants for surface reactions) was performed using the nonlinear least square optimization program FITEQL (Westall and Morel, 1977; Westall, 1982). In the output of FITEQL, the main indicator of goodness of fit is the overall variance V_y which is the weighted sum of squares of residuals divided by the degrees of freedom. Values of V_y between 0.1 and 20 generally indicate a reasonably good fit (Westall, 1982). Data points corresponding to sorption of 90% or higher were removed from FITEQL optimization. Such data points, corresponding to low aqueous concentration of sorbates, are generally weighted heavily in FITEQL because of the assignment of fixed relative error, resulting in calculation of low overall error. Thus, inclusion of high sorption data can result in log K values greatly biased toward fitting these data points.

A site density (N_s) of 1.4 sites/nm^2 (0.016 mol/mol Fe) was used in all model simulations. This value for N_s was optimized by fitting the goethite acid-base titration data (Ali, 1994) and by modeling sorption of the anionic sorbates sulfate, phthalic acid, and chelidamic acid (Ali and Dzombak, 1995). The solution complexation reactions used in model calculations are listed in Table 1. Solution activity coefficients for aqueous species were taken from Dzombak and Morel (1990). Table 2 lists the surface hydrolysis reactions and the intrinsic equilibrium constants used for modeling surface acid-base chemistry of goethite.

Single-sorbate sorption data for each sorbate were modeled by defining the minimum number of surface species that consistently yielded good fits to all datasets. Equilibrium constants for the selected surface reactions were optimized separately for each dataset using FITEQL, and the best estimate for each equilibrium constant, the overall equilibrium constant, was calculated according to the procedure described in Dzombak and Morel (1990). The overall equilibrium constants were used for predicting sorption in the binary-sorbate systems.

3. RESULTS AND DISCUSSION

3.1. Single-Sorbate Sorption

Like most cations, sorption of both Cu^{2+} and Ca^{2+} increased with increasing pH. Cu^{2+} sorbed much more strongly

Table 2 Equilibrium expressions for surface complexation reactions and overall equilibrium constants [a]

Surface Acid-Base Reactions:	log K[int]
$(\equiv FeOH_2^+) = (H^+)(\equiv FeOH^0) \exp(-F\Psi/RT) \gamma_1 (K_{a1}^{int})^{-1}$	-7.68±1.01
$(\equiv FeO^-) = (H^+)^{-1}(\equiv FeOH^0) \exp(F\Psi/RT) (\gamma_1)^{-1} (K_{a2}^{int})$	-8.32±1.55
Calcium (Ca^{2+}) Sorption:	
$(\equiv FeOH)_2Ca^{2+} = (Ca^{2+})(\equiv FeOH^0)^2 \exp(-2F\Psi/RT) \gamma_2 K_1^{int}$	6.78±0.23
$(\equiv FeOCa^+) = (H^+)^{-1}(Ca^{2+})(\equiv FeOH^0) \exp(-F\Psi/RT) (\gamma_1)^{-1} \gamma_2 K_2^{int}$	-6.97±0.47
$(\equiv FeOCaOH^0) = (H^+)^{-2}(Ca^{2+})(\equiv FeOH^0) (\gamma_1)^{-2} \gamma_2 K_3^{int}$	-16.96±2.94
Copper (Cu^{2+}) Sorption:	
$(\equiv FeOCu^+) = (H^+)^{-1}(Cu^{2+})(\equiv FeOH^0) \exp(-F\Psi/RT) (\gamma_1)^{-1} \gamma_2 K_2^{int}$	2.21±0.24
Phthalic Acid (H_2L_p) Sorption[b]:	
$(\equiv FeHL_p^0) = (H^+)^2(L_p^{2-})(\equiv FeOH^0)(\gamma_1)^2 \gamma_2 K_1^{int}$	15.74±0.33
$(\equiv FeOHL_p^{2-}) = (L_p^{2-})(\equiv FeOH^0) \exp(2F\Psi/RT) \gamma_2 K_3^{int}$	2.17±0.33
Chelidamic Acid (H_3L_c) Sorption[b]:	
$(\equiv FeH_2L_c^0) = (H^+)^2(HL_c^{2-})(\equiv FeOH^0)(\gamma_1)^2 \gamma_2 K_1^{int}$	14.05±0.36
$(\equiv FeHL_c^-) = (H^+)(HL_c^{2-})(\equiv FeOH^0) \exp(F\Psi/RT) \gamma_1 \gamma_2 K_2^{int}$	7.92±0.63
$(\equiv FeOHL_c^{3-}) = (H^+)^{-1}(HL_c^{2-})(\equiv FeOH^0) \exp(3F\Psi/RT) (\gamma_1)^{-1} \gamma_2 K_4^{int}$	-6.24±0.41

[a] log K and 99% confidence intervals obtained from FITEQL (Westall, 1982) optimization of sorption data according to the procedure described in Dzombak and Morel (1990).
[b] from Ali and Dzombak (1994).
( ) = molar concentration; γ_i = aqueous phase activity coefficients.

than Ca^{2+}. Under the experimental conditions, sorption of Cu^{2+} increased from zero (at pH $\sim$ 3.5) to about 100% (at pH $\sim$ 6) within a narrow pH range (Fig. 1). Relative to those for Cu^{2+}, sorption edges for Ca^{2+} (Fig. 2) were shifted to higher pH and covered a wider pH range (pH = 7–11.5). No significant sorption of Ca^{2+} was observed below pH 7. Similar results have been reported in the literature for Ca^{2+} and Cu^{2+} sorption on goethite (Balistrieri and Murray, 1981, 1982).

For all sorption experiments, the goethite concentration was 1.6 g/L and the corresponding sorption site concentration was $TOT(\equiv FeOH) = 0.295$ mM, based on the site density of 1.4 sites/nm^2 and the specific surface area of 79.4 m^2/g. As sorbate to sorbent ratio (i.e., mol sorbate/$TOT(\equiv FeOH)$) increased, sorption edges of both Cu^{2+} and Ca^{2+} were shifted to higher pH values (Figs. 1a, 2a), a feature commonly observed for cation sorption on metal oxides (Benjamin and Leckie, 1981; Dzombak and Morel, 1990). With increasing total sorbate concentrations, fractional sorption at a particular pH of both Cu^{2+} and Ca^{2+} decreased while sorption density increased.

An increase in ionic strength from 0.01–0.10 M had no noticeable effect on Cu^{2+} sorption (Fig. 1b), a feature commonly observed for metal ion sorption onto oxides (Hayes and Leckie, 1987; Dzombak and Morel, 1990). On the other hand, an increase in ionic strength from 0.01–0.10 M resulted in a small but detectable decrease in Ca^{2+} sorption (Fig. 2b). Similar effects of ionic strength on Ca^{2+} sorption onto hydrous ferric oxide have been reported by Cowan et al. (1991). Ionic strength effects are largely a measure of the relative contribution of coulombic forces to the overall change in free
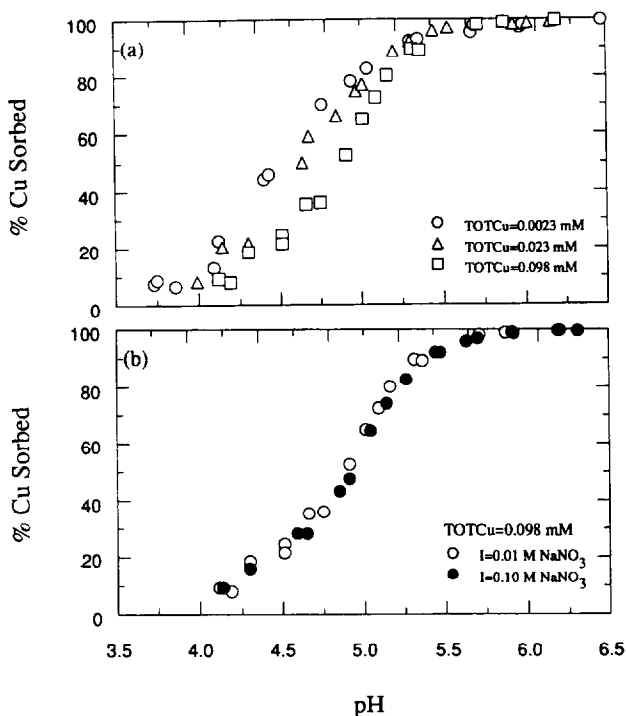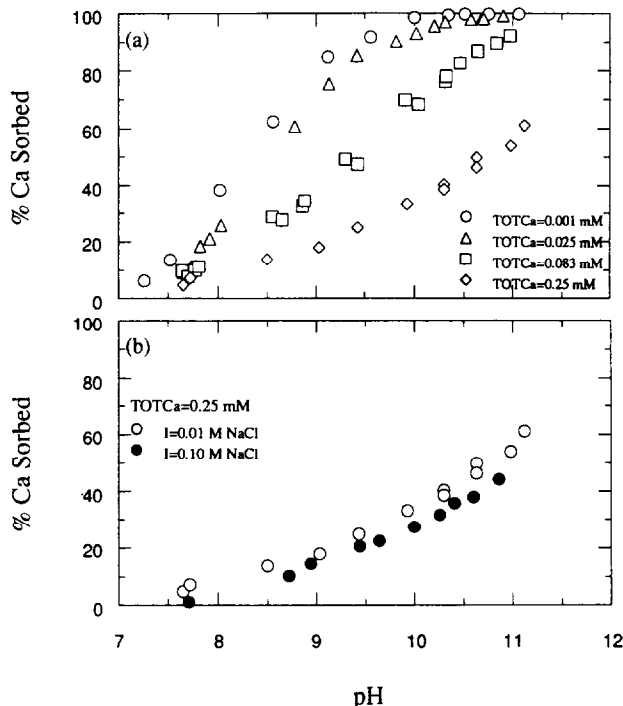

Fig. 2. Fractional sorption of Ca^{2+} onto goethite (1.6 g/L) as a function of pH (a) for $I = 0.01$ M NaCl and varying levels of total Ca^{2+} concentration, and (b) for TOTCa $= 0.25$ M and varying ionic strength.

energy associated with the sorption process. Most metal cations (e.g., Cu^{2+}) sorb onto oxides much more strongly than the electrolyte ion Ca^{2+}. Unlike Ca^{2+}, sorption of most metal ions occurs over a pH range where the surface is positively charged (i.e., pH < PPZC) and where coulombic forces are repulsive. As hypothesized by Dzombak and Morel (1990), lack of significant effect of ionic strength on metal ion sorption may result from a balance between a decrease in the positive surface potential at pH < PPZC (i.e., a decrease in repulsive coulombic forces) and a decrease in solution activity of metal ions (unfavorable for sorption) with increasing ionic strength. In the case of Ca^{2+}, sorption on goethite occurs principally over a pH range where the goethite surface is negatively charged (i.e., pH > PPZC) and where coulombic forces are attractive rather than repulsive. Therefore, the decrease in Ca^{2+} sorption with increasing ionic strength may be attributed to a decrease in the solution activity of Ca^{2+} and a simultaneous decrease in the negative surface potential (at pH > PPZC), i.e., a decrease in attractive coulombic forces.

Like most anions, sorption of phthalic acid and chelidamic acid decreased with increasing pH; no significant sorption was observed beyond the PPZC (Ali and Dzombak, 1995). The limited sorption data obtained for Ca^{2+}, phthalic acid, and chelidamic acid with NaNO$_3$ as background electrolyte were indistinguishable from the corresponding data with NaCl as background electrolyte (Ali, 1994).

3.2. Modeling of Single-Sorbate Sorption Data

Most reported surface complexation modeling of ion sorption data onto metal oxides has been performed by adopting

Fig. 1. Fractional sorption of Cu^{2+} onto goethite (1.6 g/L) as a function of pH (a) for $I = 0.01$ M NaNO$_3$ and varying levels of total Cu^{2+} concentration, and (b) for TOTCu $= 0.098$ M and varying ionic strength.

Table 3 Optimal equilibrium constants (log K)[a], goodness of fit (V$_Y$), and standard deviation of log K ($\sigma_{\log k}$) from fitting of single-sorbate data sets using FITEQL[b]

Sorbate	TOTC (mM)	I (M)	V$_Y$	log K$_1$	σ_1	log K$_2$	σ_2	log K$_3$	σ_3
Copper	0.0023	0.01	6.56			2.42	0.024		
	0.023	0.01	2.27			2.27	0.021		
	0.098	0.01	2.61			2.12	0.019		
	0.098	0.10	1.04			2.05	0.022		
Calcium	0.001	0.01	9.38	7.10	0.049	c	-	c	-
	0.025	0.01	11.2	6.65	0.034	c	-	c	-
	0.083	0.01	1.66	6.58	0.073	-7.04	0.029	c	-
	0.25	0.01	0.37	7.04	0.398	-6.76	0.187	-17.00	0.153
	0.25	0.10	0.03	6.60	0.391	-6.78	0.182	-16.86	0.323

[a] Reactions correspond to those given in Table 2 for particular K values. The K values reported in Table 3 include aqueous phase activity coefficients and thus are not listed as intrinsic constants.
[b] FITEQL (Westall, 1982).
[c] This surface reaction was not needed to fit the experimental data.

surface species with simple 1:1 stoichiometry. However, there is some evidence from spectroscopic studies of the presence of bidentate/binuclear (one sorbate molecule bound to two oxide surface metal atoms) surface species for sorbed cations as well as anions (Parfitt et al., 1977; Parfitt and Smart, 1978; Brown, 1990; Tejedor-Tejedor et al., 1992). For modeling of sorption data in this study, monodentate as well as bidentate/binuclear surface species were investigated. A bidentate/binuclear surface species was considered acceptable only if it produced fits significantly better than those obtained with monodentate surface species.

Table 2 lists equilibrium expressions and overall equilibrium constants for the surface complexation reactions that

yielded best fits to the single-sorbate sorption datasets. Table 3 contains detailed results (V$_y$, log K, $\sigma_{\log K}$) from FITEQL optimization. Modeling of single-sorbate sorption data of phthalic acid and chelidamic acid is described in Ali and Dzombak (1995). One surface species, $\equiv$FeOCu$^+$ was sufficient for fitting Cu^{2+} sorption data over the range of sorbate concentrations and over the pH range studied (Fig. 3). The same kind of surface species was used by Dzombak and Morel (1990) for modeling sorption of a number of divalent metal cations, including Cu^{2+}, onto hydrous ferric oxide. Three surface species, ($\equiv$FeOH)$_2$Ca^{2+}, $\equiv$FeOCa$^+$, and $\equiv$FeOCaOH^0 were required to fit Ca^{2+} sorption data. The monodentate surface species $\equiv$FeOCa$^+$ and $\equiv$FeOHCa^{2+}
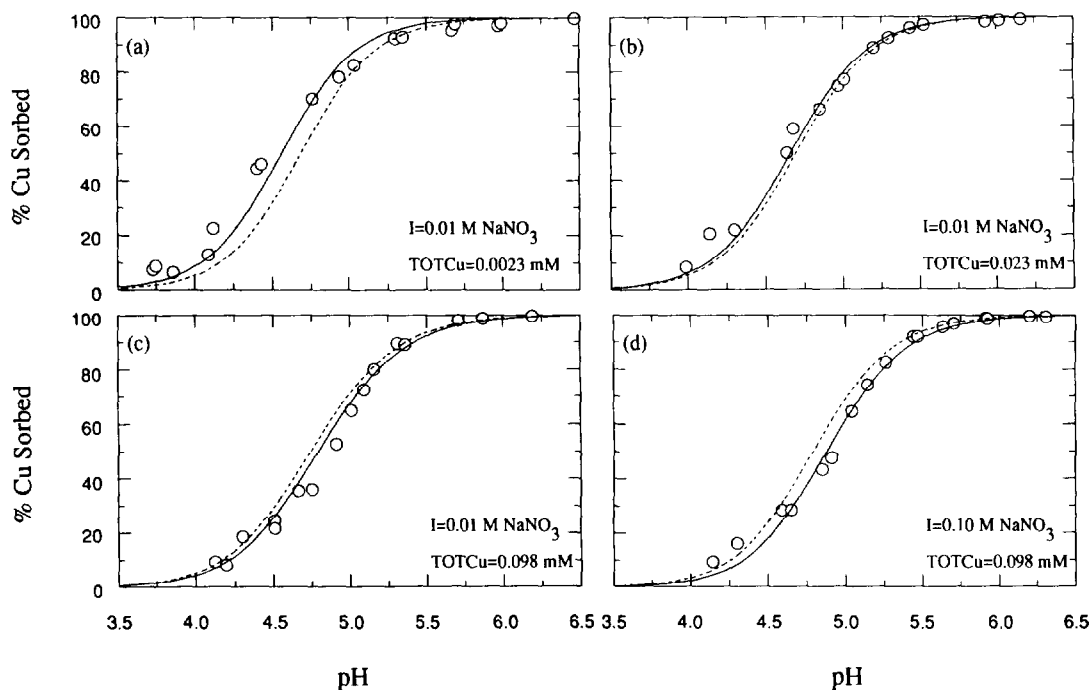

FIG. 3. Fractional sorption of Cu^{2+} on goethite (1.6 g/L) as a function of pH and model fits to sorption data. Solid lines represent individual fits and dotted lines represent overall fits. (a) TOTCu = 0.0023 mM, I = 0.01 M; (b) TOTCu = 0.023 mM, I = 0.01 M; (c) TOTCu = 0.098 mM, I = 0.01 M; (d) TOTCu = 0.098 mM, I = 0.10 M.

were used by Dzombak and Morel (1990) for modeling Ca^{2+} sorption on hydrous ferric oxide. The bidentate species ($\equiv$FeOH)$_2$Ca^{2+} was used in fitting the goethite data because it significantly improved fits in the low pH region, especially for the data at high sorbate concentrations (TOTCa = 0.083, 0.25 mM).

The optimum log K values for the Cu^{2+} surface species ($\equiv$FeOCu$^+$) differed by up to 0.4 log unit for the individual datasets. However, model fits based on overall (weighted average) log K values reproduced effects of sorbate concentration and ionic strength on Cu^{2+} sorption reasonably well (Fig. 3).

The optimum log K values for the various Ca^{2+} surface species also differed by up to 0.5 log unit for the individual datasets. Model fits based on overall log K values reproduced effects of sorbate concentration and ionic strength on Ca^{2+} sorption reasonably well for systems with high sorbate concentrations (TOTCa = 0.083, 0.25 mM; Fig. 4c,d). However, model fits were less successful in describing Ca^{2+} sorption at low sorbate concentrations (TOTCa = 0.001, 0.025 mM, Fig. 4a,b); Ca^{2+} sorption below pH 9 was significantly higher than that represented by the model fits.

Model fits to Cu^{2+} and Ca^{2+} sorption data at low sorbate-to-sorbent ratios could potentially be improved by postulating two binding site types (a smaller concentration of a stronger site type and a larger concentration of a weaker site type), an approach adopted by Dzombak and Morel (1990) for modeling of cation sorption on hydrous ferric oxide. Two site types were not employed in this work, however, because a single site type for goethite was adequate for fitting nearly all sorption data, and fits were not improved dramatically with two site types. The need for only a single site type for fitting goethite sorption data has been confirmed by Mathur (1995) who applied the GTLM to describe a wide range of data in order to extend the GTLM database (Dzombak and Morel, 1990) to goethite.

Figure 5 shows the calculated distributions of Ca^{2+} surface species at two system conditions. At low sorbate concentration (TOTCa = 0.025 mM, Fig. 5a), ($\equiv$FeOH)$_2$Ca^{2+} was the dominant surface species over the entire pH range. At high sorbate concentration (TOTCa = 0.25 mM), $\equiv$FeOCa$^+$ was also important at higher pH values and became the dominant surface species at pH > 10. $\equiv$FeOCaOH^0 also became important at pH > 10. These observations are also evident from Table 3 which shows that one surface species ($\equiv$FeOH)$_2$Ca^{2-} was needed to fit individual Ca^{2+} sorption data at low sorbate concentrations (TOTCa = 0.001, 0.025 mM), whereas $\equiv$FeOCaOH^0 was needed only for datasets at high sorbate concentrations (TOTCa = 0.25 mM).

3.3. Sorption in Binary-Sorbate Systems, Cu^{2+}-Organic Acids

Both phthalic acid and chelidamic acid form solution complexes with Cu^{2+}. The dominant solution complex between Cu^{2+} and phthalic acid is CuL$_p^0$; CuHL$_p^+$ is a minor species in the pH range of interest. Compared to phthalic acid, chelidamic acid forms stronger solution complexes with Cu^{2+}. The relative abundance of the four Cu^{2+}-chelidamic acid solution complexes (see Table 1) depends on pH and cheli-

damic acid/Cu concentration ratio. When Cu^{2+} is present in excess of chelidamic acid, CuHL$_c^0$ and CuL$_c^-$ are the principal solution complexes; whereas, when chelidamic acid is present in excess of Cu^{2+}, CuHL$_{c2}^{3-}$ and CuL$_{c2}^{4-}$ also become important.

Compared to single-sorbate systems, sorption of Cu^{2+} significantly increased in the presence of either phthalic acid or chelidamic acid in the low pH (pH < 5) region (Figs. 6, 7). As shown in Fig. 6, sorption of Cu^{2+} (TOTCu = 0.023, 0.098 mM) in the presence of phthalic acid was enhanced compared to single sorbate systems. In all cases, sorption edges for Cu^{2+} were shifted to lower pH values by about 0.5 pH unit. Chelidamic acid, even at relatively small concentrations, had a dramatic effect on Cu^{2+} sorption. In the presence of 0.04 mM chelidamic acid, sorption of Cu^{2+} at low sorbate concentration (TOTCu = 0.023 mM) was greatly enhanced in the low pH region (Fig. 7a). Sorption was further enhanced when chelidamic acid concentration was raised to 0.20 mM (Fig. 7b). In the presence of 0.04 mM chelidamic acid, sorption of Cu^{2+} at relatively high sorbate concentration (TOTCu = 0.098 mM) increased in the low pH region (Fig. 7c). However, when chelidamic acid concentration was raised to 0.20 mM, sorption increased at pH < 5 but decreased at pH > 5 (Fig. 7d). Very similar effects of humic substances on sorption of Cu^{2+} onto goethite and alumina were observed by Tipping et al. (1983) and Davis (1984), respectively (see Fig. 8), indicating similarities between humic substances and simple organic acids with respect to their interactions in mineral-ion systems. While humate molecules are much more complex than chelidamic acid, the similarities between Figs. 7c and 8a, and between Figs. 7d and 8b are remarkable.

An increase in Cu^{2+} sorption in the low pH region in the presence of an organic acid may result either (1) from a reduction in positive surface charge in the low pH region due to sorption of an organic acid anion, resulting in a more favorable electrostatic environment for Cu^{2+} sorption or (2) through sorption of Cu-organic acid complexes, i.e., the formation of Cu-organic acid-mineral ternary surface complexes. Decreased Cu^{2+} sorption in the presence of chelidamic acid at high pH may result from strong solution complexation between Cu^{2+} and chelidamic acid. These possibilities were investigated through surface complexation modeling.

3.4. Modeling of Cu^{2+}-Organic Acid Binary-Sorbate Sorption Data

Predictions of Cu^{2+} sorption, in the presence of either phthalic acid or chelidamic acid, based on single-sorbate sorption data fits and known Cu^{2+}-organic acid solution complexation constants are shown in Figs. 6 and 7 (in dotted lines). In the presence of 0.25 mM phthalic acid (Fig. 6a,c), Cu^{2+} sorption was predicted to be virtually unchanged (compared to single sorbate systems), while in the presence of 1.0 mM phthalic acid (Fig. 6b,d) Cu^{2+} sorption was predicted to go down (pH edges shifted to higher pH values by about 0.5 pH unit). Modeling results indicated that the predicted decline in sorption was due to a combination of Cu^{2+}-phthalic acid solution complexation and competition for surface sites between Cu^{2+} and phthalic acid.

In the presence of chelidamic acid, Cu^{2+} sorption was predicted to decrease significantly, primarily due to the formation
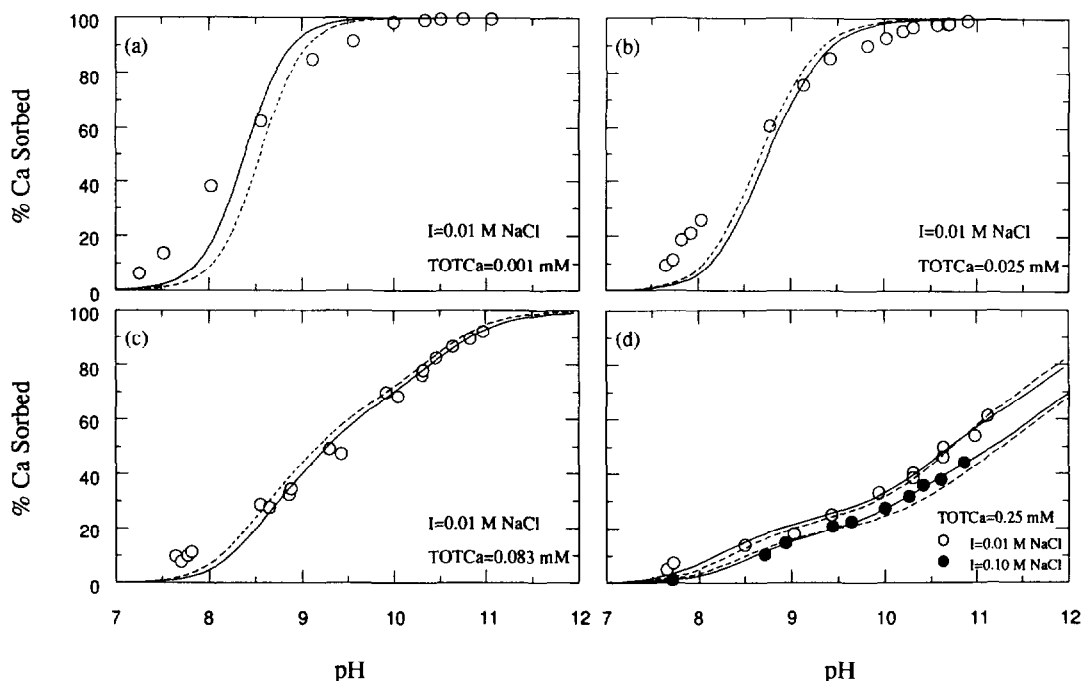
Fig. 4. Fractional sorption of Ca^{2+} on goethite (1.6 g/L) as a function of pH and model fits to sorption data. Solid lines represent individual fits and dotted lines represent overall fits. (a) TOTCa = 0.001 mM, I = 0.01 M; (b) TOTCa = 0.025 mM, I = 0.01 M; (c) TOTCa = 0.083 mM, I = 0.01 M; (d) TOTCa = 0.25 mM, I = 0.01 M and 0.10 M.

of strong Cu^{2+}-chelidamic acid solution complexes. According to the model, a substantial increase in Cu^{2+} sorption in the low pH region could not be explained by favorable electrostatic interactions. The same conclusion was also reached in a number of other studies (Davis and Leckie, 1978; Benjamin and Bloom, 1981; Benjamin and Leckie, 1982) in describing increased metal ion sorption onto oxides in the presence of strongly sorbing anionic complexing ligands.

Formation of Cu^{2+}-organic acid ternary complexes, therefore, appeared to be the most likely reason for increased Cu^{2+} sorption in the presence of the organic acids. Possible ternary surface complexes were investigated through modeling of sorption data from binary systems. Modeling was done by proposing the minimum number of ternary surface complexes that consistently yielded good fits to all datasets for a particular pair of sorbates. Optimization of equilibrium constants for the ternary surface complexes was performed by fitting experimental data via trial and error method. FITEQL (Westall, 1982) could not be used for optimization because concentrations of the organic acids in binary systems could not be measured with the analytical technique employed.

Cu^{2+} sorption data in the presence of phthalic acid were modeled successfully by using only one ternary surface complex, $\equiv FeOHCuL_p^0$ (see Table 4). Model fits with $\equiv FeOHCuL_p^0$ (in addition to the surface species needed to describe single-sorbate sorption) were in good agreement with data (Fig. 6) and successfully described Cu^{2+} sorption over a wide range of Cu/phthalic acid concentration ratios. The calculated distributions of Cu^{2+} surface species, shown for two system conditions in Fig. 9, show that the ternary complex $\equiv FeOHCuL_p^0$ was, in fact, the dominant surface species over most of the pH range of interest. The pH region

of dominance of $\equiv FeOHCuL_p^0$ increased with increasing phthalic acid concentration. An increase in phthalic acid concentration favors formation of the solution complex CuL_p^0
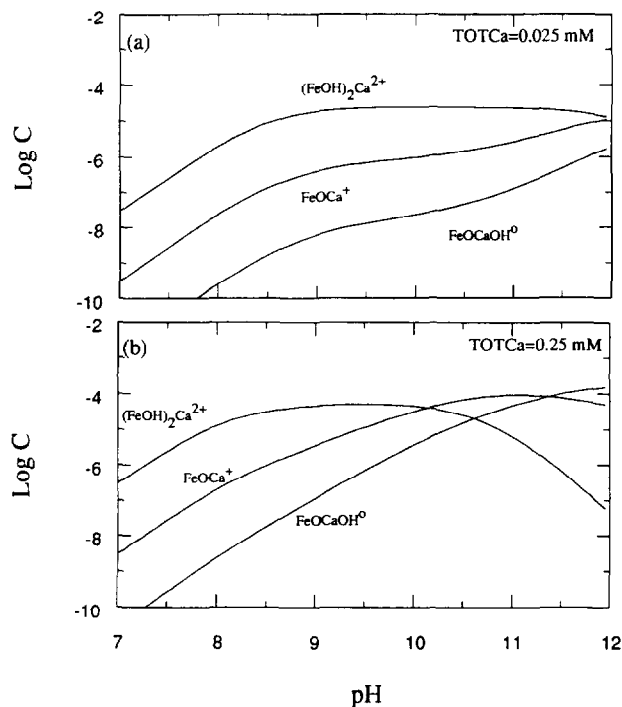

Fig. 5. Calculated distribution of Ca^{2+} surface species on goethite (1.6 g/L) at I = 0.01 M and system conditions: (a) TOTCa = 0.025 mM; (b) TOTCa = 0.25 mM.

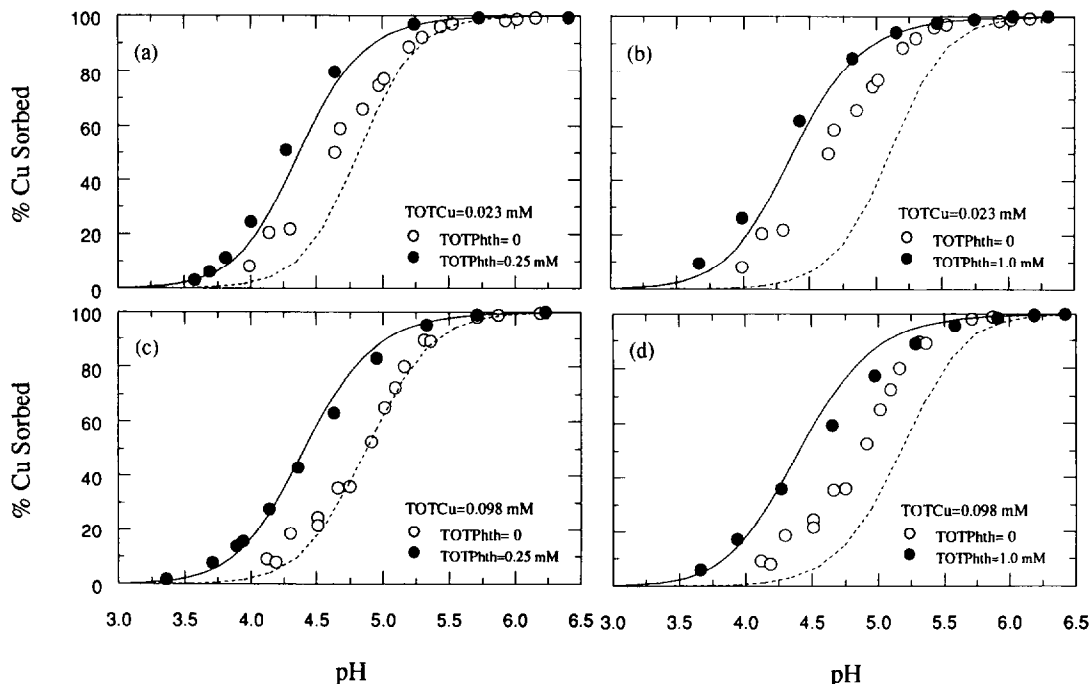FIG. 6. Fractional sorption of Cu^{2+} onto goethite (1.6 g/L) in the presence of phthalic acid at I = 0.01 M $NaNO_3$. Dotted lines represent simulated sorption of Cu^{2+} in the binary systems without consideration of ternary surface complexes. Solid lines represent model fits with the Cu^{2+}-phthalic acid ternary surface complex shown in Table 4. (a) TOTCu = 0.023 mM, TOTPhth = 0.25 mM; (b) TOTCu = 0.023 mM, TOTPhth = 1.0 mM; (c) TOTCu = 0.098 mM, TOTPhth = 0.25 mM; (d) TOTCu = 0.023 mM, TOTPhth = 1.0 mM.

and, therefore, one could expect increased sorption of Cu^{2+} with increasing phthalic acid concentration. However, increased phthalic acid concentration also results in increased competition for surface sites among the different surface species. As a result of these competing effects, the concentration of $\equiv FeOHCuL_p^0$ was predicted to increase only slightly (at pH > 5), and the concentration of $\equiv FeOCu^+$ decreased as phthalic acid concentration increased from 0.25 mM to 1.0 mM. The overall effect was that sorption of Cu^{2+} remained virtually the same in the presence of 0.25 mM and 1.0 mM phthalic acid.

Three ternary surface complexes, $\equiv FeOHCuHL_c^0$, $\equiv FeOCuL_c^{2-}$, and $\equiv FeOHCuHL_{c2}^{3-}$ (see Table 4) were postulated to describe Cu^{2+} sorption in the presence of chelidamic acid. Model fits with the ternary surface complexes were in reasonable agreement with Cu^{2+} sorption data in the presence of 0.04 mM chelidamic acid (Fig. 7a,c). However, model fits were less successful in describing Cu^{2+} sorption data in the presence of 0.20 mM chelidamic acid (Fig. 7b,d), although the general trend of sorption was captured reasonably well. For example, diminished sorption of Cu^{2+} at TOTCu = 0.098 mM in the presence of 0.20 mM chelidamic acid at high pH was reproduced fairly well (Fig. 7d). Considering the complexity of the system (with a number of Cu-chelidamic acid solution complexes) and the lack of chelidamic acid concentration data to constrain modeling, the model fits were reasonable and could fairly describe Cu^{2+} sorption over a wide range of Cu/chelidamic acid concentration ratios. The calculated distributions of Cu^{2+} surface spe-

cies, presented for two system conditions in Fig. 10, show that when total chelidamic acid was present in excess of total Cu^{2+} (Fig. 10a), $\equiv FeOCu^+$ was predicted to become a minor surface species and Cu^{2+}-chelidamic acid ternary complexes accounted almost entirely for Cu^{2+} sorption. In this case $\equiv FeOHCuHL_{c2}^{3-}$ was predicted to be the most dominant ternary complex. On the other hand, when total Cu^{2+} was present in excess of chelidamic acid (Fig. 10b), $\equiv FeOCu^+$ was predicted to become a dominant surface species at pH > 4 along with $\equiv FeOCuL_c^{2-}$, while $\equiv FeOHCuHL_c^0$ and $\equiv FeOHCuHL_{c2}^{3-}$ were predicted to be dominant below pH 4.

Thus, sorption of Cu^{2+} in the presence of the two simple organic acids was successfully modeled with surface complexation modeling using Cu^{2+}-organic acid ternary surface complexes. Similarities in sorption behavior of Cu^{2+} observed here and those reported in the presence of humic substances (Tipping et al., 1983; Davis, 1984) strongly suggest formation of Cu^{2+}-humate ternary surface complexes in mineral-humate-Cu^{2+} systems.

3.5. Sorption in Binary-Sorbate Systems, Ca^{2+}-Organic Acids

Sorption of Ca^{2+} (TOTCa = 0.25 mM) remained virtually unaffected in the presence of 0.25 mM phthalic acid (Fig. 11). The absence of effects of phthalic acid on Ca^{2+} sorption is consistent with the fact that no significant sorption of phthalic acid was observed beyond pH 8 in single-sorbate systems (Ali and Dzombak, 1995). Thus, there was little opportunity for
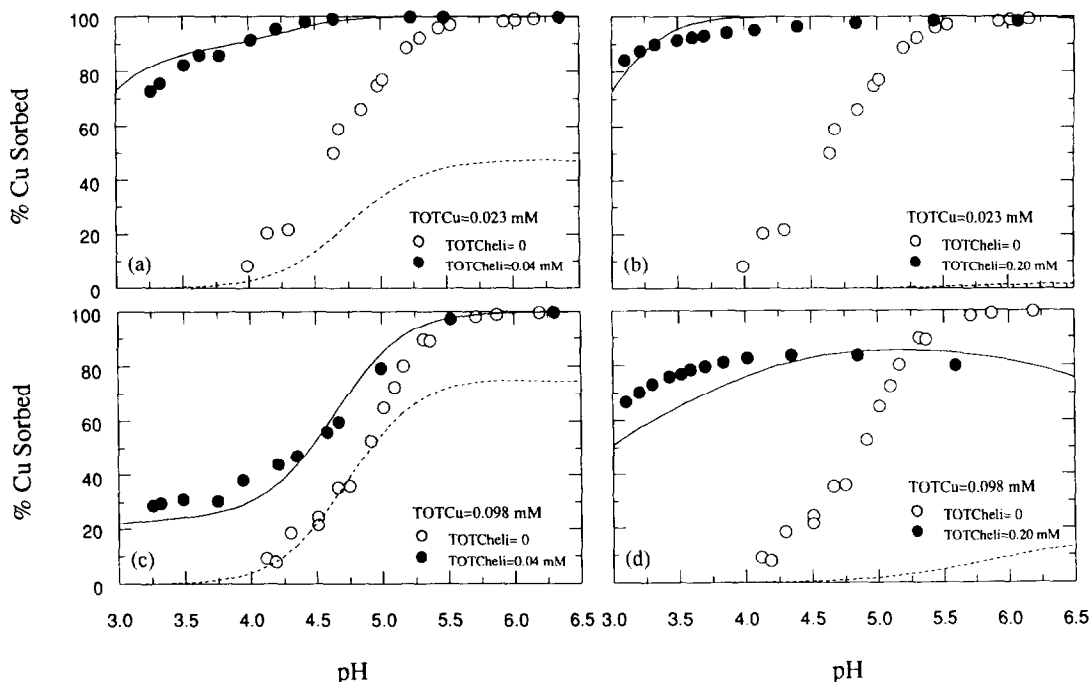
Fig. 7. Fractional sorption of Cu^{2+} onto goethite (1.6 g/L) in the presence of chelidamic acid at $I = 0.01$ M $NaNO_3$. Dotted lines represent simulated sorption of Cu^{2+} in the binary systems without consideration of ternary surface complexes. Solid lines represent model fits with the Cu^{2+}-chelidamic acid ternary surface complexes shown in Table 4. (a) TOTCu = 0.023 mM, TOTCheli = 0.04 mM; (b) TOTCu = 0.023 mM, TOTCheli = 0.20 mM; (c) TOTCu = 0.098 mM, TOTCheli = 0.04 mM; (d) TOTCu = 0.098 mM, TOTCheli = 0.20 mM.

competition with Ca^{2+} for goethite surface sites. Also, since phthalic acid forms only weak solution complexes with Ca^{2+} (see Table 1), it had no significant effect on Ca^{2+} sorption. Model prediction of Ca^{2+} sorption based on single-sorbate sorption data fits and known solution complexation constants was in good agreement with data (Fig. 11).

In the presence of chelidamic acid, however, sorption of Ca^{2+} significantly decreased, especially at high pH (Fig. 12). Unlike phthalic acid, chelidamic acid forms relatively strong solution complexes with Ca^{2+}, especially at high pH values. CaL_c^- is the dominant solution complex as may be seen from the constants in Table 1. As a result Ca^{2+} was held in solution as CaL_c^- and Ca^{2+} sorption decreased. Prediction of Ca^{2+} sorption based on single-sorbate data fits and known solution complexation constants between Ca^{2+} and chelidamic acid reproduced the general effect of solution complexation, although there were some significant overpredictions of Ca sorption (Fig. 12a,b). It should be noted, however, that the model predictions were very sensitive to changes in the complexation constant for the solution species CuL_c^-. As shown in Fig. 12 (dotted lines), a small change of 0.20 log unit in this constant (uncertainty reported for this constant in Martell and Smith, 1974) had a significant effect on model predictions. Considering these uncertainties, model predictions of Ca^{2+} sorption in the presence of chelidamic acid were reasonable. These results indicate that formation of nonsorbing, cation-organic acid complexes can significantly reduce cation sorption onto minerals and that SCMs can describe such interaction reasonably well.

3.6. Predictions of Organic Acid Sorption in the Presence of a Cation

Although sorption of the organic acids in the binary-sorbate systems was not measured, predictions of organic acid sorption in the presence of Cu^{2+} and Ca^{2+} were made to examine possible effects of cations on organic acid sorption. Since at the lower pH values, where organic acid sorption is greatest, Ca^{2+} does not sorb and forms only weak solution complexes with the organic acids, Ca^{2+} had virtually no effect on simulated sorption of either phthalic acid or chelidamic acid. Slightly enhanced sorption of phthalic acid was predicted in the presence of Cu^{2+}, as a result of ternary complex formation (Ali, 1994).

The predicted effect of Cu^{2+} on chelidamic acid sorption was as dramatic as the observed effect of chelidamic acid on Cu^{2+} sorption. Simulated sorption of chelidamic acid at low concentration (TOTCheli = 0.04 mM) was significantly enhanced in the presence of Cu^{2+} (Fig. 13a) over almost the entire pH range (except for a slight decline between pH 3 and 4). Also, chelidamic acid sorption was predicted to increase with increasing Cu^{2+} concentration. Sorption of chelidamic acid at TOTCheli = 0.20 mM, on the other hand, was predicted to decrease below pH 4 and increase above pH 4 in the presence of Cu^{2+} (Fig. 13b). The extent of this effect increased with increasing Cu^{2+} concentration.

Tipping (1981a,b) reported enhanced sorption of humic substances onto goethite over a wide pH range in the presence of Ca^{2+} and Mg^{2+}, while Davis (1982) reported reduced sorption of humic substances at low pH and enhanced sorp-
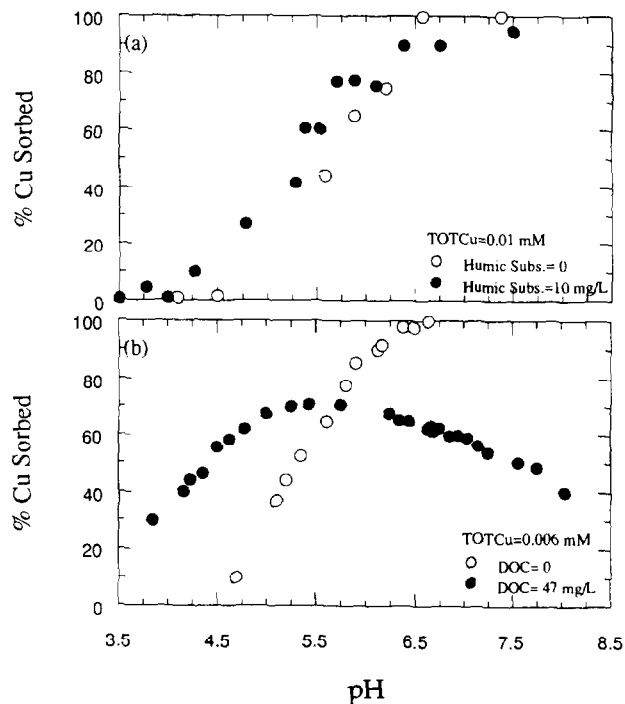
FIG. 8. (a) Sorption of Cu^{2+} onto goethite (0.1 g/L) in the presence of humic substances at $I = 0.01$ M NaCl (from Tipping et al., 1983); (b) Sorption of Cu^{2+} onto alumina in the presence of natural organic matter (NOM) at $I = 0.01$ M NaCl (from Davis, 1984).

FIG. 9. Calculated distributions of Cu^{2+} sorption species on goethite (1.6 g/L) in Cu^{2+}-phthalic acid binary systems at $I = 0.01$ M $NaNO_3$ and two system conditions: TOTCu = 0.023 mM, TOTPhth = 0.25 mM (solid line); TOTCu = 0.023 mM, TOTPhth = 1.0 mM (dotted line).

tion at high pH onto alumina in the presence of Ca^{2+}. Such sorption behavior is consistent with the simulated sorption behavior of phthalic acid and chelidamic acid in the presence of Cu^{2+}, i.e., consistent with the formation of ternary surface complexes.

3.7. Sorption Mechanism

Sorption of simple organic acids usually is thought to be governed by ligand exchange involving carboxylic/phenolic functional groups on the organic molecules and oxide surface sites. Tejedor-Tejedor et al. (1992) studied bonding structure of a number of benzoic compounds, including phthalic acid, at the α-FeOOH/water interface using CIR-FTIR (cylindrical internal reflection—Fourier transform infrared) spectroscopy. Tejedor-Tejedor et al. (1992) concluded that phthalic acid was bound to the surface of α-FeOOH through one car-
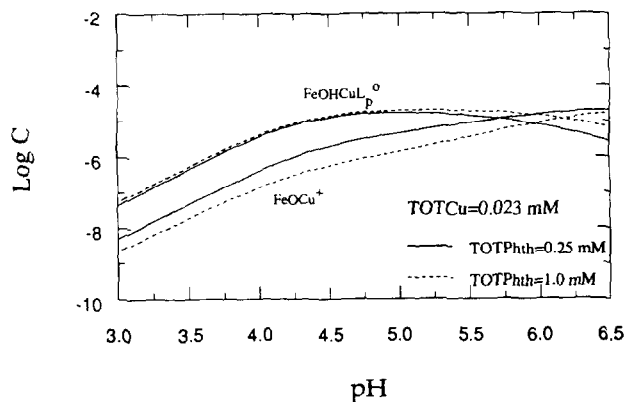
boxyl group, forming bidentate and monodentate surface complexes. The former involves both oxygens of the carboxyl, each bound to one surface Fe atom. Monodentate complexes involve one oxygen of carboxyl bound to one surface Fe atom.

Similarities in sorption characteristics of phthalic acid and chelidamic acid (Ali and Dzombak, 1995) suggest similar sorption mechanisms for these two organic acids. Since the phenolic group in chelidamic acid is not located in ortho or chelating position with respect to the carboxyl groups, formation of a chelate structure involving one carboxyl group and the phenolic group attached to one surface Fe atom, as has been suggested for salicylic acid in Yost et al. (1990) and Biber and Stumm (1994), does not appear likely. However, a chelate structure involving one carboxyl group and one nitrogen atom is possible, as has been suggested in Davis and Leckie (1978).

Consideration of the most likely organic acid surface complexation configurations can be used to explain sorption of Cu^{2+} in systems with phthalic acid and chelidamic acid. Solution complexation of Cu^{2+} by phthalic acid probably results in a monodentate complex (Fig. 14a). A seven-membered chelate structure, as shown in Fig. 14b, probably does not form because chelate rings containing more than six members have been found to be generally unstable (Chaberek and Martell, 1959). Chelidamic acid has a much stronger affinity for

Table 4 Equilibrium expressions for ternary surface complexes and corresponding equilibrium constants [a]

Cu-Phthalic acid ternary surface complex:	log K^{int}
$(\equiv FeOHCuL_p^0) = (\equiv FeOH^0)(Cu^{2+})(L_p^{2-})(\gamma_2)^2 K_1^{int}$	10.91
Cu-Chelidamic acid ternary surface complexes:	
$(\equiv FeOHCuHL_c^0) = (\equiv FeOH^0)(Cu^{2+})(HL_c^{2-})(\gamma_2)^2 K_1^{int}$	13.06
$(\equiv FeOCuL_c^{2-}) = (H^+)^{-2}(\equiv FeOH^0)(Cu^{2+})(HL_c^{2-}) exp(2F\Psi/RT)(\gamma_1)^{-2}(\gamma_2)^2 K_2^{int}$	-0.74
$(\equiv FeOHCuHL_{c2}^{2-}) = (H^+)^{-1}(\equiv FeOH^0)(Cu^{2+})(HL_c^{2-})^2 exp(3F\Psi/RT)(\gamma_1)^{-1}(\gamma_2)^3 K_3^{int}$	10.24

[a] Equilibrium constants were obtained by fitting experimental sorption data via trial and error method; H_2L_p and H_3L_c represents phthalic and chelidamic acid respectively;

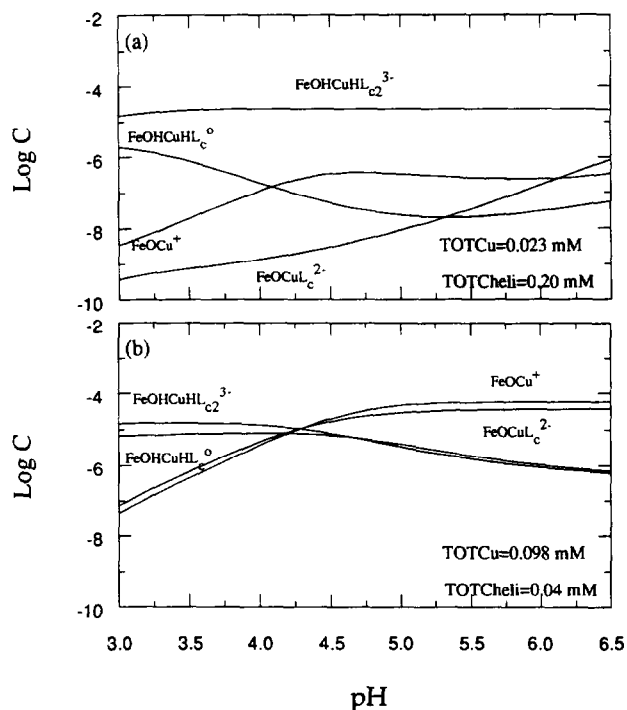( ) = molar concentration; γ_i = aqueous phase activity coefficients.

FIG. 10. Calculated distributions of Cu^{2+} sorption species on goethite (1.6 g/L) in Cu^{2+}-chelidamic acid binary systems at $I = 0.01$ M $NaNO_3$ and two system conditions: (a) TOTCu = 0.023 mM, TOTCheli = 0.20 mM; (b) TOTCu = 0.098 mM, TOTCheli = 0.04 mM.

Cu^{2+} and is likely to form five-membered chelate structures with Cu^{2+} as shown in Fig. 14c.

The Cu^{2+}-phthalic acid monodentate complex and the Cu^{2+}-chelidamic acid chelate complexes, shown in Fig. 14, have carboxyl groups available for complexation with goethite surface sites. Enhanced sorption of Cu^{2+} in the presence of the organic acids, therefore, may result from sorption of Cu^{2+}-organic acid complexes by ligand exchange similar to systems without metal ion, with Cu^{2+} complexation by the carboxyl group not involved in surface complexation. This
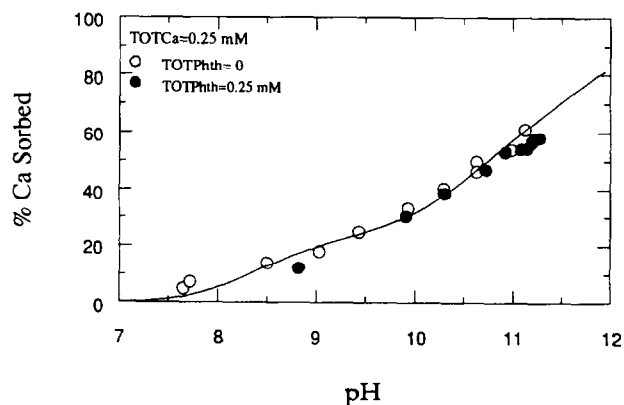

FIG. 11. Fractional sorption of Ca^{2+} onto goethite (1.6 g/L) in the presence of phthalic acid at $I = 0.01$ M NaCl. Solid line represents model prediction of Ca^{2+} sorption in Ca^{2+}-phthalic acid binary system.
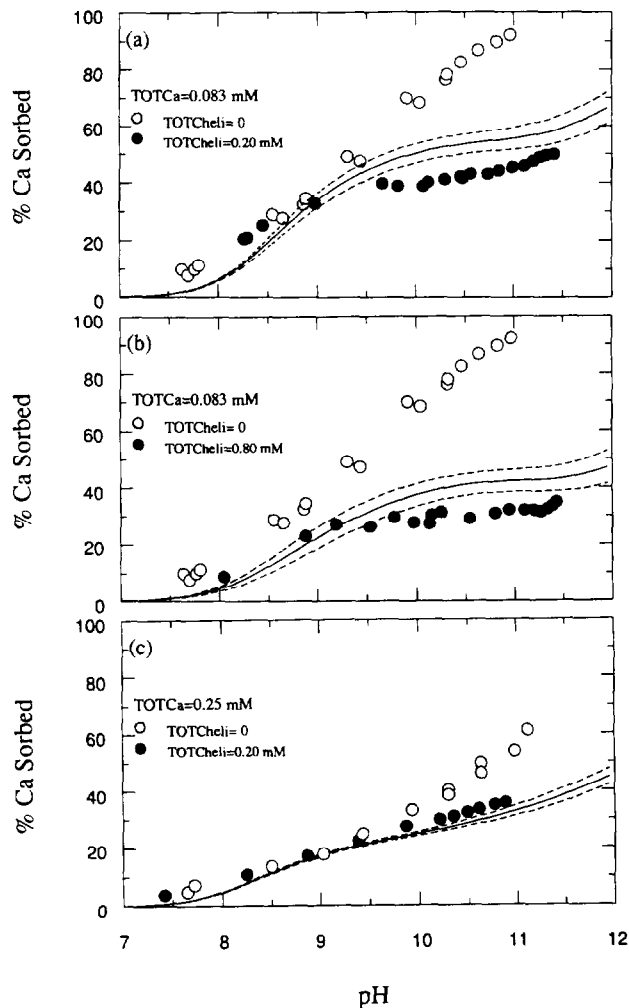

FIG. 12. Fractional sorption of Ca^{2+} onto goethite (1.6 g/L) in the presence of chelidamic acid at $I = 0.01$ M NaCl. Solid lines represent model predictions of Ca sorption in Ca-chelidamic acid ternary systems. Dotted lined show sensitivity of model predictions to changes in log K value (± 0.20 log unit) for the formation of the solution complex CaL_c^-. (a) TOTCa = 0.083 mM, TOTCheli = 0.20 mM; (b) TOTCa = 0.083 mM, TOTCheli = 0.80 mM; (c) TOTCa = 0.25 mM, TOTCheli = 0.20 mM.

mechanism will be most effective at low pH, where sorption of the organic acids is maximum, and will be more pronounced for chelidamic acid which forms stronger complexes with Cu^{2+}. Support for this mechanism is provided by the data for Cu^{2+} sorption onto hydrous ferric oxide in the presence of picolinic acid reported by Davis and Leckie (1978). Picolinic acid effectively prevented Cu^{2+} sorption onto the hydrous ferric oxide. As shown in Fig. 14d, picolinic acid is likely to form a chelate structure with Cu^{2+}, but this leaves the complex with no functional groups available for binding with oxide surface sites. Although surface-sensitive spectroscopic techniques have been used to characterize sorption mechanisms for some organic acids and metal ions on oxides, direct study of Cu^{2+}-organic acid ternary surface complexes with these techniques would be difficult (Ali, 1994).

The above mechanism is also consistent with the observed sorption of Ca^{2+} in the presence of phthalic acid and cheli-
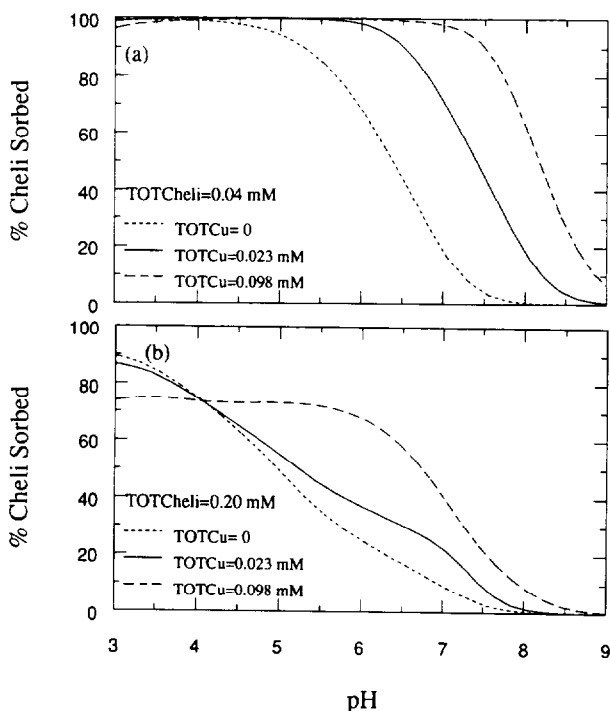
FIG. 13. Simulated sorption of chelidamic acid on goethite (1.6 g/L) at $I = 0.01$ M in the presence of Cu^{2+}. (a) TOTCheli = 0.04 mM, TOTCu = 0.023, 0.098 mM; (b) TOTCheli = 0.20 mM, TOTCu = 0.023, 0.098 mM.

Sorption of Cu^{2+} and Ca^{2+} onto goethite over a wide range of conditions, including variable pH, ionic strength, and sorbate to sorbent ratio, was reproduced reasonably well by the Generalized Two Layer Model with a unique set of surface complexation reactions and equilibrium constants for each sorbate. Consideration of bidentate/binuclear surface species improved model fits to Ca^{2+} sorption data compared to those obtained with only monodentate surface species. Calculated distributions of Ca^{2+} surface species indicated that different surface species were required to fit sorption data under different conditions of pH and sorbate to sorbent ratio. This illustrates the need for obtaining sorption data over wide range of conditions (pH, sorbate to sorbent ratio) for accurate modeling using SCMs.

Compared to results from the single-sorbate systems, sorption of Cu^{2+} was enhanced in the presence of phthalic acid. Sorption edges for Cu^{2+} were shifted to lower pH values by about 0.5 pH unit. Chelidamic acid, even at relatively small concentrations, dramatically enhanced Cu^{2+} sorption at lower pH values. At higher pH (>5), chelidamic acid reduced sorption of Cu^{2+}.

Understanding of solution complex formation is critical to interpretation of data for metal-organic acid sorption. Lack of significant effect of phthalic acid on Ca^{2+} sorption was due to weak solution complexation between Ca^{2+} and phthalic acid, and reduced sorption of Ca^{2+} in the presence of chelidamic acid was consistent with the formation of nonsorbing Ca^{2+}-chelidamic acid solution complexes. These effects were reproduced by the GTLM reasonably well.

damic acid. Solution complexes between Ca^{2+} and the organic acids are also likely to have carboxyl groups available for complexation with goethite surface sites. Ca^{2+}-phthalic acid solution complexes are very weak and, in the presence of phthalic acid, formation of Ca^{2+}-goethite surface complexes outcompetes formation of Ca^{2+}-phthalic acid solution complexes, thereby keeping Ca^{2+} sorption unaffected. Chelidamic acid forms relatively strong solution complexes with Ca^{2+}, but only at higher pH values where chelidamic acid does not sorb. Ca^{2+} sorption, therefore, decreases due to the formation of nonsorbing Ca^{2+}-chelidamic acid complexes at high pH.

Although the exact mechanism of metal-organic acid surface bonding remains unconfirmed, these results suggest that: (1) oxide surface sites compete with ligands for complexation of metal ions; (2) depending on the pH and the structure of a metal-organic acid complex, such a complex may be strongly sorbing, weakly sorbing or nonsorbing; and (3) if the structure of the metal-organic acid complex is known, some apriori judgment may be made as to how certain ligands would affect sorption of a metal ion.

4. CONCLUSIONS

Like most cations, sorption of both Cu^{2+} and Ca^{2+} increased with increasing pH. Cu^{2+} sorbed much more strongly than Ca^{2+}; compared to Cu^{2+}, sorption edges of Ca^{2+} were shifted to higher pH and covered a wider pH range. While ionic strength had little effect on Cu^{2+} sorption, increased ionic strength slightly reduced Ca^{2+} sorption.
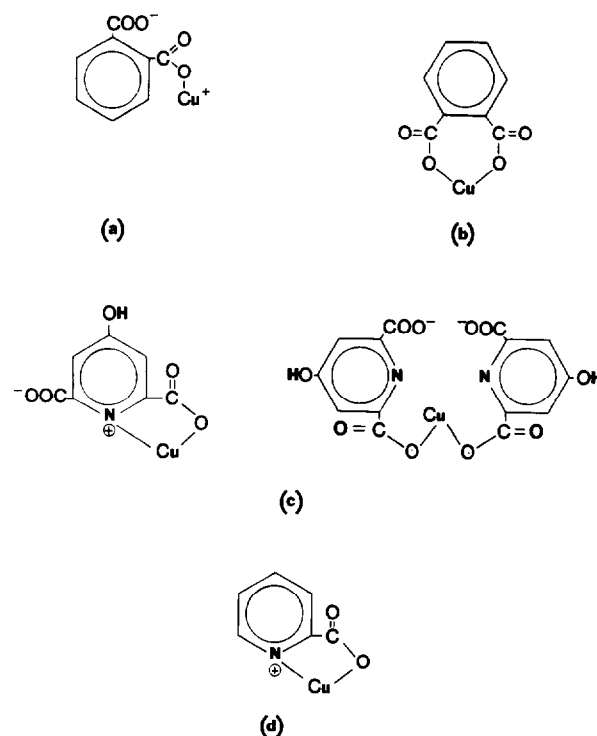

FIG. 14. Possible structures of Cu^{2+}-organic solution complexes. (a) Cu^{2+}-phthalic acid monodentate complex; (b) Cu^{2+}-phthalic acid chelate complex; (c) Cu^{2+}-chelidamic acid chelate complexes; (d) Cu^{2+}-picolinic acid chelate complex.

Sorption of Cu^{2+} in Cu^{2+}-phthalic acid and Cu^{2+}-chelidamic acid binary systems was quantitatively reproduced over a wide range of Cu/organic acid concentration ratios with a unique set of Cu-organic acid ternary surface complexes and equilibrium constants for each binary system. The ternary surface complexes and equilibrium constants accompanied those postulated on the basis of the single-sorbate data. Although formation of ternary surface complexes has been proposed for many metal-ligand systems, there has been very limited use of ternary surface complexes in surface complexation modeling. The modeling work presented here suggests that surface complexation models can be useful in describing sorption in complex metal-ligand systems.

Although the exact sorption mechanisms are unconfirmed, available data suggest that enhanced Cu^{2+} sorption in the presence of the carboxylic and phenolic organic acids resulted from sorption of Cu^{2+}-organic acid complexes in a ligand-like manner. Sorption of the complexes likely involved a carboxyl group not participating in complexation of Cu^{2+}. Reduced sorption of Cu^{2+} resulted from formation of Cu^{2+}-chelidamic acid solution complexes. The Generalized Two Layer Model, with the assumption of homogeneous surface sites, could describe metal-organic acid interactions in the presence of goethite reasonably well. However, work is needed to advance understanding of the effects of structure of organic acids (e.g., MW, number and location of functional groups, presence of aliphatic chains) and metal-organic acid complexes on sorption.

Results from this work provided useful insights into mineral-NOM-ion interactions. Sorption characteristics of Cu^{2+} in the presence of the two simple organic acids, particularly chelidamic acid, closely resembled those reported for Cu^{2+} sorption in the presence of humic substances by Tipping et al. (1983) and Davis (1984). Results obtained in this study indicate that similar mechanisms, i.e., formation of Cu^{2+}-humate ternary surface complexes are probably responsible for the observed sorption behavior of Cu^{2+} in the presence of humic substances. The simulated sorption of phthalic acid and chelidamic acid in the presence of cations closely resembled that reported for humic substances in the presence of Ca^{2+} and Mg^{2+} by Tipping (1981a,b) and Davis (1982). Therefore, the observed sorption behavior of Cu^{2+} in the presence of humic substances and observed sorption behavior of humic substances in the presence of Ca^{2+} and Mg^{2+} are both consistent with the formation of cation-humate ternary surface complexes.

Editorial handling: M. F. Hochella Jr.

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