Competitive Sorption of Simple Organic Acids and Sulfate on Goethite

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Sorption of phthalic acid, chelidamic acid, and sulfate onto goethite (α-FeOOH) was examined in single-sorbate and in sulfate−organic acid binary-sorbate systems to determine the extent of competition between the simple organic acids and sulfate. Sorption characteristics of sulfate and the organic acids were similar and resembled those reported for humic substances onto oxides. Sorption data for all three sorbates over a wide range of conditions (pH, *I*, sorbate/sorbent ratio) were described quantitatively by the generalized two-layer model with a unique set of surface reactions and equilibrium constants for each sorbate. Sorption affinities of sulfate and the organic acids were comparable, and sulfate effectively competed with the organic acids for surface sites on goethite, particularly at low pH. These results suggest that sulfate can significantly influence the sorption of simple organic acids and humic substances in natural aquatic systems. Predictions of sorption in binary-sorbate systems based on single-sorbate data fits represented competitive sorption data reasonably well over a wide range of conditions. However, there were underpredictions of minor-component sorption in the presence of a major component, which may be explained by sorbate-specific surface site heterogeneity and/or by inaccurate representation of Coulombic effects in the model.

Introduction

Sorbed natural organic matter (NOM), particularly humic substances, can significantly alter the characteristics of mineral particle surfaces that often control the fate and transport of trace contaminants in natural aquatic systems. Mineral particles in many surface and subsurface aquatic systems exhibit negative surface charge as a result of the sorption of humic substances. Carboxylic and phenolic groups are the primary ionizable functional groups associated with humic substances, and it is these acidic functional groups that make the sorption behavior of humic substances similar to that of inorganic anions, that is, maximum sorption at low pH and decreasing sorption with increasing pH (*1*−*9*).

Interactions among particle surfaces, humic substances, and inorganic ions in solution have been studied in batch sorption experiments involving model mineral phases, chiefly iron and aluminum oxides. Humic substances and inorganic anions (e.g., SO_4^{2-}, PO_4^{3-}) have been found to compete with each other for sorption sites on metal oxides (*4, 8, 10*). Major electrolyte cations (e.g., Ca^{2+} and Mg^{2+}) have also been found to influence the sorption of humic substances (*2*−*4*). In the presence of NOM, sorption of Cu^{2+} onto alumina and goethite has been found to be enhanced at low pH and suppressed at high pH (*11, 12*).

Detailed quantitative interpretation of mineral−humate−ion interactions has been difficult because the current understanding of the structure and chemical behavior of humic substances is quite limited. Current models for these large molecular weight aromatic organic acids (*11*−*15*) are not sufficient for useful incorporation in surface complexation models.

Experimentation with simple organic acids having functional groups similar to those found in humic substances promises to provide a basis for a better understanding of mineral−organic acid−ion interactions and their possible impact on the fate and transport of contaminants in aquatic systems. There are some important similarities in sorption mechanisms of humic substances and simple organic acids, i.e., ligand exchange involving carboxylic/phenolic groups and oxide surface sites (*8*), which suggests that studying the sorption of simple organic acids can provide valuable insights into mineral−humate−ion interactions. Only limited data are available on competitive sorption of simple organic acids and inorganic ions (*16*−*18*) and on sorption of metal ions in the presence of organic acids (*19*−*21*). Efforts to describe these data using surface complexation modeling have been only partially successful.

Surface complexation models (SCMs) have been applied successfully to describe the sorption of single inorganic ions as well as simple organic acids onto oxide surfaces (*22*−*24*). However, the ultimate goal for the application of such models is to predict sorption in multicomponent, natural aquatic systems. Limited application of SCMs to predict sorption in multi-sorbate systems has yielded some promising results (*18, 25*−*28*), but often has been quantitatively unsuccessful (*17, 29*−*31*). It has been suggested that the accuracy of model predictions in multi-sorbate systems is influenced by the relative sorption densities of the sorbates (*18, 25*) and may

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0013-936X/96/0930-1061$12.00/0

also be affected by the heterogeneity of surface sites (*18, 29, 31*). From these limited applications, it is apparent that in order to test the ability of SCMs to describe sorption in multicomponent systems, it is essential to investigate sorption in single- and multi-sorbate systems over a wide range of conditions.

In this work, mineral−organic acid−ion interactions were investigated in goethite (α-FeOOH) suspensions using sulfate and two simple organic acids: phthalic acid (benzene-1,2-dicarboxylic acid) and chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid). Sulfate is a major electrolyte ion in many surface and subsurface aquatic systems (*32, 33*). It can compete directly with humic substances and inorganic ions for mineral surface sites and can influence the sorption of other ions indirectly by regulating the partitioning of humic substances. Phthalic acid possesses -COOH, and chelidamic acid possesses both -COOH and −OH groups. In addition, 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 (*34*). Goethite (α-FeOOH) 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 extent of competitive sorption between sulfate and the organic acids on goethite over a wide range of conditions (pH, ionic strength, and relative sorbate concentrations) and to test the ability of surface complexation models to predict sorption in binary systems over the wide range of conditions represented in the data, based on single-sorbate data fits. Surface complexation modeling was performed using the generalized two-layer model of Dzombak and Morel (*22*).

Materials and Methods

Synthesis and Characterization of Goethite. Powdered goethite (α-FeOOH) was prepared according to the method outlined by Atkinson et al. (*35*). The crystal structure of the powdered goethite samples was verified by X-ray diffraction analysis (*36*). The specific surface area of the goethite samples was determined by the N_2/BET method to be 79.4 ± 1 m^2/g. The powdered solid was used to make 1-L stock suspension batches containing 12 g/L goethite in deionized water. The pristine point of zero charge (PPZC) defined by the common intersection point of acid−base titration curves at three different ionic strengths was 8.0 ± 0.1. Goethite stock suspensions were purged with N_2(g) to remove any surface-bound carbonate and kept under N_2(g) atmosphere for at least 2 weeks before use in batch sorption experiments.

Sorption Experiments. Single-sorbate sorption of sulfate, phthalic acid, and chelidamic acid was examined in goethite suspensions (1.6 g/L) as a function of pH, ionic strength (0.01 and 0.10 M NaCl), and sorbate/sorbent ratio (mol of sorbate/mol of surface sites). Competitive sorption of the organic acids and sulfate was investigated in binary-sorbate systems (in 1.6 g/L goethite suspensions) at 0.01 M (NaCl) ionic strength. For each pair of sorbates, a range of combinations of total sorbate concentrations was examined. 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 (*18, 24, 37, 38*).

All experiments were conducted in batch in 40-mL polypropylene centrifuge tubes with screw-on caps at a constant temperature of 20 ± 2 °C. Experiments were set up by adding fixed amounts of goethite stock suspension, electrolyte stock solution (1 M NaCl, CO_2 free), and sorbate spike(s) to each tube. 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 N_2(g), placed on an end-over-end rotator, and agitated for 24 h. After the equilibration period, the tubes were centrifuged for about 15 min. 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. The sample was then expressed through a 0.2-μm membrane filter (Millipore Corp.) in a filter holder attached to the syringe. After discarding the first 1 mL to minimize the loss of sorbate due to sorption onto the filter and filter holder, the filtrate was stored in a polyethylene sample vial for analysis.

In all cases, sorbed concentrations were calculated as the difference between total and solution concentrations. No corrections were made for possible sorptive losses of the sorbates to tube walls under the assumption that goethite coatings on tube walls would outcompete any exposed polyethylene surface. Losses due to filtration were found to be negligible when the first 1 mL of the filtrate was discarded.

Preliminary experiments showed that sorption equilibrium in single-sorbate experiments was established within 24 h. Additional binary-sorbate experiments with longer (>24 h) equilibration times were performed to examine if true equilibrium was established for these systems within 24 h. Some additional experiments were performed to examine the effect of the order of sorbate addition on sorption in binary-sorbate systems.

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 (e.g., NaCl, Na_2SO_4, NaOH, and HCl) used were of reagent grade.

Analytical Techniques. Aqueous-phase concentrations of phthalic acid and chelidamic acid were quantified with ultraviolet (UV) spectroscopy using a 8451A diode array spectrophotometer (Hewlett Packard). For phthalic acid, absorbances were measured at 282 (for samples with pH < 5) and 274 nm (for samples with pH > 5) wavelengths. These wavelengths are in agreement with those reported as optimal for phthalic acid (*39*). In samples with low concentrations of phthalic acid, measurements were performed at a wavelength of 200 nm. For chelidamic acid, absorbance was measured at 282 nm wavelength. Below a pH of about 4, a shift in the peak wavelength (from 282 nm to lower wavelengths) was observed for chelidamic acid, and therefore, all sample pH values were raised above 4 before taking UV absorbance measurements. UV spectroscopy has been used in a number of studies for quantifying organic acids, including humic substances (*2, 40, 41*). Sulfate was analyzed by spiking the solution with radiolabeled $[^{35}S]Na_2SO_4$ and counting the remaining activity in the filtered supernatant with a scintillation counter (Model 5000 TD, Beckman).

Estimated errors in sorption data (expressed as “percent sorbate sorbed”) of sulfate, phthalic acid, and chelidamic acid were within ±4% (*36*). Estimated errors in pH measurements were within ±0.02 pH unit.

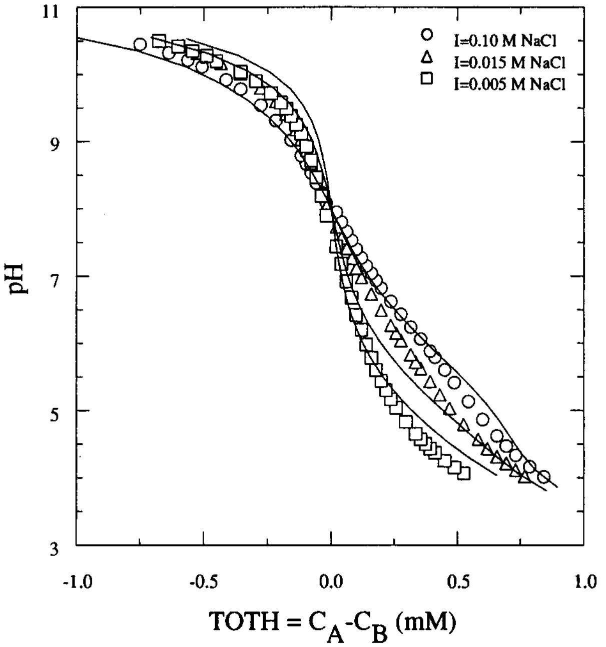

FIGURE 1. Titration data of goethite suspension (4.25 g/L) at three different ionic strengths and model fits to titration data (solid lines).

Modeling of Sorption Data. All data were modeled using the generalized two layer model (*22*), the central component of which is the diffuse layer model (*42, 43*). A detailed description of the generalized two-layer model is provided in Dzombak and Morel (*22*).

Only a single surface site type was needed 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 (*44, 45*). In the output of FITEQL, the main indicator of the 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 (*45*). Data points corresponding to a sorption of 85% of total sorbate or higher were removed from FITEQL optimization. Such data points, corresponding to low aqueous-phase concentrations of sorbates, are weighted heavily in FITEQL and can result in log K values greatly biased toward fitting them.

Because model fits of acid–base titration data were found to be sensitive to changes in the surface site density parameter N_s, a detailed sensitivity analysis was performed with respect to this parameter (*36*). The approach was similar to those used in Hayes et al. (*46*) and Mesuere (*37*). Contrary to the suggestion by Hayes et al. (*46*) and in agreement with Mesuere (*37*), model fits of goethite titration data were found to be sensitive to changes in the parameter N_s (site density), especially at high ionic strengths (e.g., 0.10 M) and at lower pH values (pH < 6), where the sorption of H^+ was significant (*36*). From titration data fits (Figure 1), a site density of 1.4 sites/nm^2 (0.016 mol/mol of Fe) was found to be optimum. This value of N_s was greater than the Γ_{max} values observed for the anionic sorbates used in this study (described later), a condition that must be met in order to model the sorption data. In all model simulations, a site density (homogeneous and amphoteric) of 1.4 sites/nm^2 (0.016 mol/mol of Fe) was used.

TABLE 1

Equilibrium Expressions for Solution Reactions Used in Modeling

equilibrium expression[a]	log K[b]
$[OH^-] = [H^+]^{-1}(\gamma_1)^{-2}K$	−14.0
$[HSO_4^-] = [H^+][SO_4^{2-}]\gamma_2K$	1.99
$[H_2L_p] = [H^+]^2[L_p^{2-}](\gamma_1)^2\gamma_2K$	8.36
$[HL_p^-] = [H^+][L_p^{2-}]\gamma_2K$	5.41
$[NaL_p^-] = [Na^+][L_p^{2-}]\gamma_2K$	0.90
$[H_3L_c] = [H^+]^2[HL_c^{2-}](\gamma_1)^2\gamma_2K$	5.17
$[H_2L_c^-] = [H^+][HL_c^{2-}]\gamma_2K$	3.55
$[L_c^{3-}] = [H^+]^{-1}[HL_c^{2-}](\gamma_1)^{-1}\gamma_2(\gamma_3)^{-1}K$	−11.54

[a] H_2L_p and H_3L_c represent phthalic acid and chelidamic acid, respectively. Molar concentrations given in brackets. γ_i, aqueous-phase activity coefficients. [b] $I = 0$ M. Source: Martell and Smith (*47, 48*).

TABLE 2

Equilibrium Expressions for Surface Complexation Reactions and Overall Equilibrium Constants[a]

	log K^{int}
Surface Acid–Base Reactions	
$[\equiv FeOH_2^+] = [H^+][FeOH^0]\exp[-F\Psi/RT]\gamma_1(K_{a1}^{int})^{-1}$	−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
Sulfate [SO_4^{2-}] Sorption	
$[\equiv FeHSO_4^0] = [H^+]^2[SO_4^{2-}][\equiv FeOH^0](\gamma_1)^2\gamma_2K_1^{int}$	13.83 ± 0.14
$[\equiv FeSO_4^-] = [H^+][SO_4^{2-}][\equiv FeOH^0]\exp[F\Psi/RT]\gamma_1\gamma_2K_2^{int}$	8.41 ± 1.22
$[\equiv FeOSO_4^{3-}] = [H^+]^{-1}[SO_4^{2-}][\equiv FeOH^0]\exp[3F\Psi/RT](\gamma_1)^{-1}\gamma_2K_4^{int}$	−6.04 ± 0.40
Phthalic Acid [H_2L_p] Sorption	
$[\equiv FeHL_p^0] = [H^+]^2[L_c^{2-}][\equiv FeOH^0](\gamma_1)^2\gamma_2K_1^{int}$	15.74 ± 0.33
$[\equiv FeOHL_p^{2-}] = [L_p^{2-}][\equiv FeOH^0]\exp[2F\Psi/RT]\gamma_2K_3^{int}$	2.17 ± 0.33
Chelidamic Acid [H_3L_c] Sorption	
$[\equiv FeH_2L_c^0] = [H^+]^2[HL_c^{2-}][\equiv FeOH^0](\gamma_1)^2\gamma_2K_1^{int}$	14.05 ± 0.36
$[\equiv FeHL_c^-] = [H^+][HL_c^{2-}][\equiv FeOH^0]\exp[F\Psi/RT]\gamma_1\gamma_2K_2^{int}$	7.92 ± 0.63
$[\equiv FeOHL_c^{3-}] = [H^+]^{-1}[HL_c^{2-}][\equiv FeOH^0]\exp[3F\Psi/RT](\gamma_1)^{-1}\gamma_2K_4^{int}$	−6.24 ± 0.41

[a] Log K and 99% confidence intervals obtained from FITEQL (*45*) optimization of sorption data according to the procedure described in Dzombak and Morel (*22*). Molar concentrations given in brackets. γ_i, aqueous-phase activity coefficients.

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 (*22*). Table 2 lists surface hydrolysis reactions and the intrinsic equilibrium constants used for modeling the surface acid–base chemistry of goethite.

Single-sorbate sorption data for each sorbate were modeled by identifying the minimum number of surface species that consistently yielded good fits to all data sets. Equilibrium constants for the selected surface reactions were optimized separately for each data set using FITEQL, and the best estimate for each equilibrium constant, the overall equilibrium constant, was calculated for all the data obtained for each sorbate according to the procedure described in Dzombak and Morel (*22*). The overall equilibrium constants were then used for predicting sorption in binary-sorbate systems.

Results and Discussion

Single-Sorbate Sorption. Sorption of the organic acids (phthalic acid and chelidamic acid) and sulfate, like most

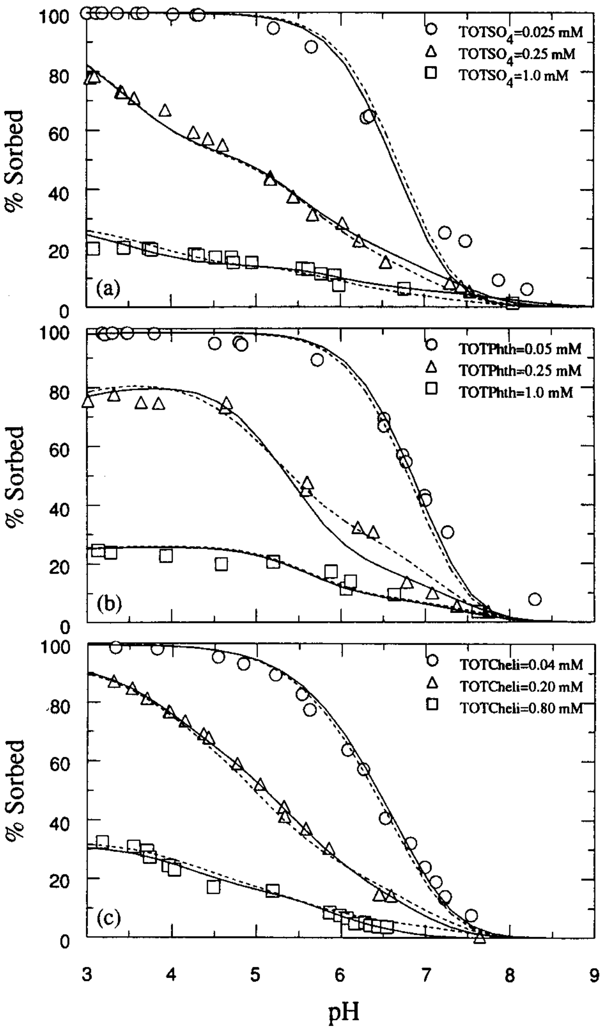

FIGURE 2. Fractional sorption of sulfate (a), phthalic acid (b), and chelidamic acid (c) onto goethite (1.6 g/L) at *I* = 0.01 M NaCl as a function of pH and varying levels of total sorbate concentrations. Solid lines represent overall fits (log *K* values listed in Table 2); dashed lines represent individual fits (log *K* values listed in Table 3).

anions, decreased with increasing pH (Figures 2 and 3). In all cases, no significant sorption was observed beyond the PPZC. Similar results have been reported in the literature for phthalic acid (*17*) and sulfate (*49*) sorption on goethite.

For all three sorbates, sorption was investigated at three different ratios (s/s ratio) of total sorbate concentration, TOTC (mol/L) to sorbent concentration, TOT(≡FeOH^0) (mol/L of sites): (i) low s/s ratio, when TOTC $\ll$ TOT(≡FeOH^0); (ii) intermediate s/s ratio, when TOTC and TOT(≡FeOH^0) are comparable; and (iii) high s/s ratio, when TOTC > TOT(≡FeOH^0). For all sorption experiments, the sorption site concentration was TOT(≡FeOH^0) = 0.295 mM based on the measured site density and specific surface area. At low s/s ratio, the sorption of all three sorbates increased from zero to about 100% as suspension pH decreased (Figure 2). As s/s ratio increased, fractional adsorption of all sorbates at a particular pH decreased, while sorption density of the sorbates increased. Maximum sorption density, Γ_{max}, was obtained at high s/s ratios. Γ_{max} values derived from sorption data for sulfate, phthalic acid, and chelidamic acid were 1.6, 1.94, and 2.03 μmol/m^2, respectively, which are relatively similar. Differences in Γ_{max} values may result from various degrees of steric hindrances or differences in surface reaction stoichiometries.

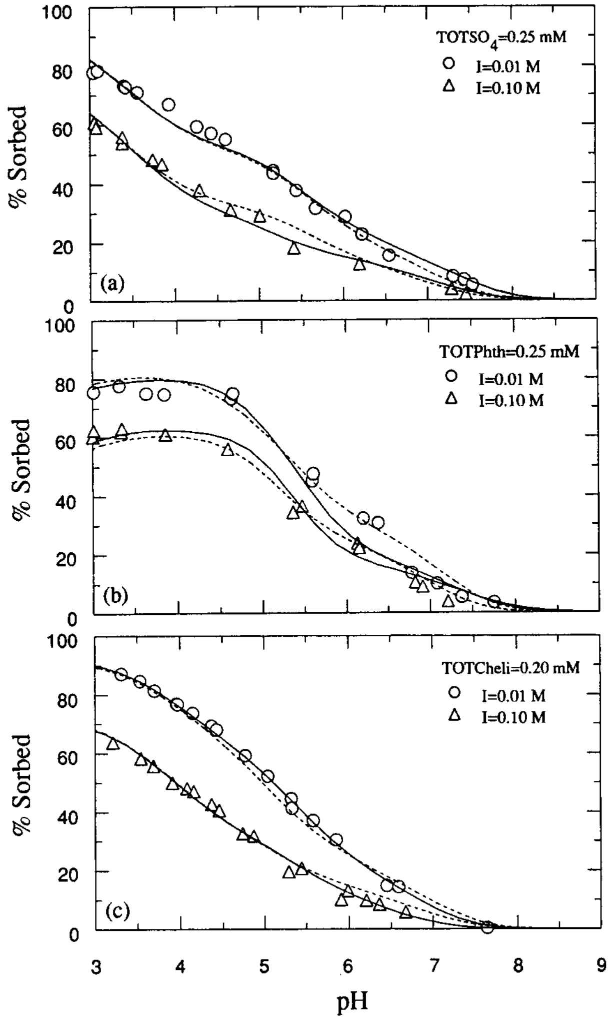

FIGURE 3. Fractional sorption of sulfate (a), phthalic acid (b), and chelidamic acid (c) onto goethite (1.6 g/L) as function of pH and ionic strength (NaCl). Solid lines represent overall fits (log *K* values listed in Table 2); dashed lines represent individual fits (log *K* values listed in Table 3).

As ionic strength increased from 0.01 to 0.10 M NaCl, sorption of all three sorbates decreased (Figure 3). Effects of ionic strength on the sorption of strongly sorbing anions such as phosphate, selenite, and molybdate have been found to be negligible (*30, 50, 51*), whereas increased ionic strength has been found to suppress the sorption of relatively weakly sorbing anions such as sulfate, selenate, oxalate, and chromate (*24, 51*–*53*). Ionic strength effects are largely a measure of the relative contribution of Coulombic forces to the overall change in free energy associated with the sorption process. Dzombak and Morel (*22*) have hypothesized that reduction in anion sorption with increasing ionic strength results from (i) a decrease in solution activity of anions (unfavorable for sorption) and (ii) a decrease in the positive surface potential at pH < PPZC (i.e., a decrease in attractive Coulombic force). While Davis (*4*) observed decreased sorption of humic substances onto alumina with increasing ionic strength, Jardine et al. (*5*) and Gu et al. (*8*) observed a negligible effect of ionic strength on the sorption of humic substances onto soil and goethite. Such differences in ionic strength effect possibly indicate differences in sorption affinities of NOM from various sources.

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_4	σ_4
sulfate	0.025	0.01	6.24	c		c		−6.13	0.05
	0.25	0.01	1.01	13.87	0.05	8.58	0.14	−5.57	0.37
	0.25	0.10	0.68	13.80	0.04	8.08	0.17	−5.83	0.69
	1.0	0.01	0.17	13.81	0.49	9.07	1.05	−4.77	2.58
chelidamic acid	0.04	0.01	0.67	c		c		−6.16	0.03
	0.20	0.01	0.14	14.10	0.04	8.03	0.11	−6.51	0.40
	0.20	0.10	0.26	14.04	0.04	7.92	0.13	−6.76	0.45
	0.80	0.01	0.13	13.77	0.21	7.56	0.39	−7.71	2.11
sorbate	**TOTC, mM**	**I, M**	**V_y**	**log K_1**	**σ_1**			**log K_3**	**σ_3**
phthalic acid	0.05	0.01	1.40	c				2.26	0.03
	0.25	0.01	1.35	15.65	0.05			1.68	0.20
	0.25	0.10	0.56	15.81	0.04			2.03	0.23
	1.0	0.01	0.27	15.85	0.42			2.39	1.45

[a] Reactions correspond to those given in Table 2 for particular K values. The K values listed in this table include aqueous-phase activity coefficients and thus are not listed as intrinsic constants. [b] FITEQL (*45*). [c] This surface reaction was not needed to fit the experimental data.

Modeling of Single-Sorbate Sorption Data. Most reported surface complexation modeling of ion sorption onto metal oxides has been performed by adopting surface species with simple 1:1 stoichiometry. However, there is some spectroscopic evidence of the presence of binuclear/bidentate (one sorbate molecule bound to two oxide surface metal atoms) surface species for sorbed cations as well as anions (*41, 54−56*). Based on IR spectroscopic studies of sulfate sorption on a number of metal oxides including goethite, Parfitt and Smart (*55*) suggested that sulfate forms a binuclear bridging surface complex ($\equiv$Fe—O—SO_2—O—Fe$\equiv$) onto these oxides. Tejedor-Tejedor et al. (*41*) studied the bonding structure of a number of benzoic compounds, including phthalic acid, at the α-FeOOH−water interface and suggested that phthalate is bound to the goethite surface through one carboxyl group forming monodentate (one oxygen of carboxyl bound to one surface Fe atom) as well as bidentate/binuclear (involving both oxygens of the carboxyl bound to two surface Fe atoms) surface species.

For modeling of single-sorbate sorption data, monodentate (1:1 stoichiometry) as well as bidentate/binuclear surface species were proposed. However, with bidentate/binuclear surface species, FITEQL optimization either did not converge or produced fits not as good as 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 data sets. Table 3 contains a summary of the key results (V_y, log K, $\sigma_{\log K}$) from the FITEQL optimizations of the single-sorbate sorption data. As may be seen by comparing the log K values in Table 2 for similar reactions, phthalic acid was found to exhibit the greatest affinity for goethite surface sites, while affinities of sulfate and chelidamic acid were found to be similar but somewhat lower than that of phthalic acid.

In modeling the sorption of oxalate and chromate on goethite, Mesuere and Fish (*24*) invoked sorbate-specific subsets of surface sites by using the ratio N_s/Γ_{max} as the mass balance coefficient for the component $\equiv FeOH^o$ in all anion sorption reactions. They argued that failure to constrain the model in this way could lead to significant overprediction of sorption. Γ_{max} values for anions often depend on solution conditions, such as pH, and reported Γ_{max} values may differ depending on the experimental condition under which they were determined. The ratio N_s/Γ_{max}, therefore, can become not only sorbate-specific but also specific to particular experimental conditions. Hence, this approach is unwieldy and *ad hoc* in nature. In this study, the sorption of three sorbates with different (but close) Γ_{max} values was successfully modeled over a wide range of conditions without using any sorbate-specific mass balance coefficient, i.e., without invoking sorbate-specific sites.

Three surface species $\equiv FeHSO_4^0$, $\equiv FeSO4^-$, and $\equiv FeOSO_4^{3-}$ were required to fit sulfate sorption data over the ranges of total sorbate concentrations studied. A similar set of surface species was used by Mesuere and Fish (*24*) to fit data for oxalate sorption on goethite. For phthalic acid, two surface species ($\equiv FeHL_p^0$ and $\equiv FeOHL_p^{2-}$) and for chelidamic acid three surface species ($\equiv FeH_2L_c^0$, $\equiv FeHL_c^-$, and $\equiv FeOHL_c^{3-}$) were required to fit sorption data. Similar surface species have been used by Dzombak and Morel (*22*) for the modeling of anion sorption on hydrous ferric oxide. For all three anionic sorbates, the optimum log K values from the optimization of individual data sets differed substantially (by over one log unit) for some of the surface species (Table 3). Using the overall equilibrium constants, the effects of s/s ratio and ionic strength on sorption were reproduced reasonably well for all three sorbates (Figures 2 and 3).

Figure 4 shows the calculated distributions of surface species for sulfate and phthalic acid, respectively, for two system conditions. At an intermediate s/s ratio (Figure 4a,c), calculations indicate that the neutral surface species are dominant in the low pH region, and as pH increases, the negatively charged surface species become dominant. Similar distributions of surface species were obtained at high s/s ratio. However, at low s/s ratio (Figure 4b,d), calculations suggest that the negatively charged surface species dominate over a wider pH range. Calculated distributions of chelidamic acid surface species were similar to those for sulfate (*36*). The different surface species required to fit sorption data under different conditions highlights the need to obtain data over a wide range of pH and s/s ratios for accurate modeling of anion sorption.

Calculated surface charge on goethite particles (*36*) decreased with increasing sorbate concentrations, i.e., with

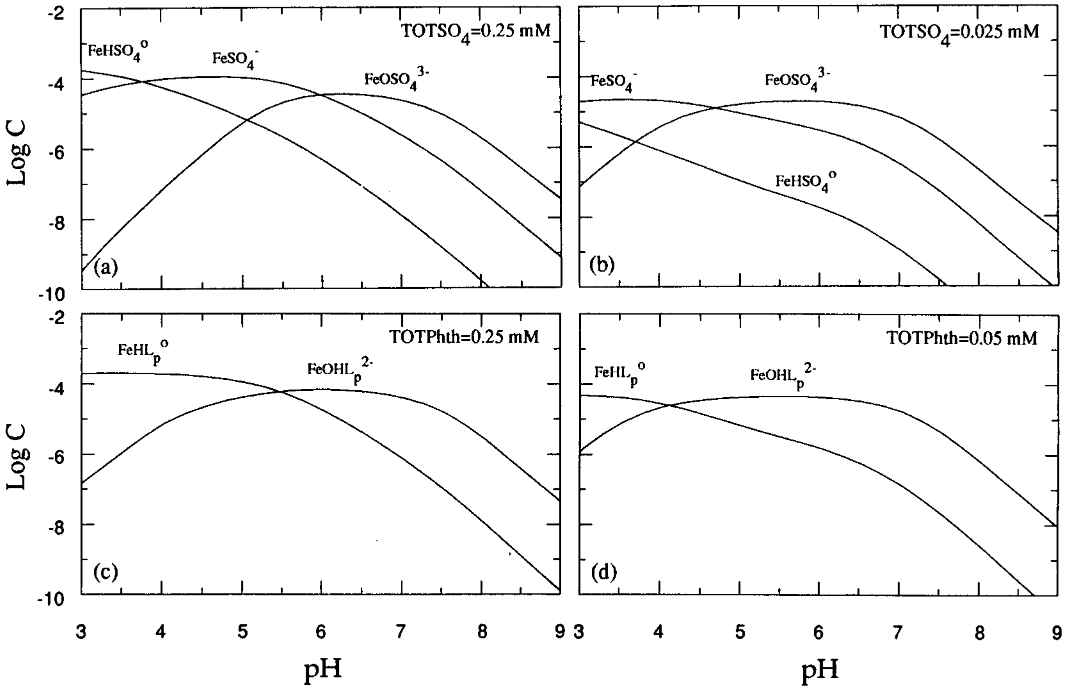

FIGURE 4. Calculated distributions of sulfate and phthalic acid surface species on goethite (1.6 g/L) at $I = 0.01$ M. (a) TOTSO$_4$ = 0.25 mM; (b) TOTSO$_4$ = 0.025 mM; (c) TOTPhth = 0.25 mM; (d) TOTPhth = 0.05 mM.

increasing sorption density of the sorbates. Calculated surface charge distributions were consistent with the observed reduction in electrophoretic mobility of goethite particles with increasing sorbate concentrations (*36*).

Sorption in Binary-Sorbate Systems. Based on relative sorbate concentrations, binary-sorbate systems examined in this work can be divided into three categories: (i) both sorbates at intermediate s/s ratio; (ii) one (minor) sorbate at low s/s ratio, the other (major) sorbate at intermediate s/s ratio; (iii) one (minor) sorbate at low s/s ratio, the other (major) sorbate at high s/s ratio. Experimentation with longer (>24 h) equilibration times indicated that, for the first two categories of binary systems, sorption equilibrium was established within 24 h. However, for systems in the third category, longer times were needed for sorption equilibrium to be established. As shown in Figure 5a, the sorption of chelidamic acid (low s/s ratio) in the presence of sulfate (high s/s ratio) increased with increasing equilibration time, especially at low pH. In the presence of a major component, surface saturation with the major component is approached and concentration of free surface sites is greatly reduced. This, in effect, increases the sorbate to (free) sorbent ratio for the minor component, resulting in slower sorption kinetics (*57*).

Effect of the order of sorbate addition was investigated for the chelidamic acid-sulfate system discussed above. Chelidamic acid (minor component) was added before and after sulfate (major component) in goethite suspensions with subsequent equilibration for 24 h. Figure 5b shows that when sulfate was added a few hours before the major component, the sorption of chelidamic acid (minor component) was slightly enhanced, especially at low pH. The sorption of chelidamic acid with an equilibration time of 135 h (and with the simultaneous addition of sulfate and chelidamic acid), shown in Figure 5a, closely matched the results obtained when chelidamic acid was added 1 or 6 h before sulfate and equilibrated for 24 h. This result is consistent with slower sorption kinetics of a minor component in the presence of a major component; when the minor component is added ahead of the major component, equilibrium with respect to the minor component is quickly attained, and final equilibrium in the presence of the major component is established within 24 h. On the other hand, when added simultaneously, the same amount of sorption of the minor component is attained after a much longer time. A significant effect of the order of sorbate addition on sorption was also reported in Davis (*12*) and Violante et al. (*58*).

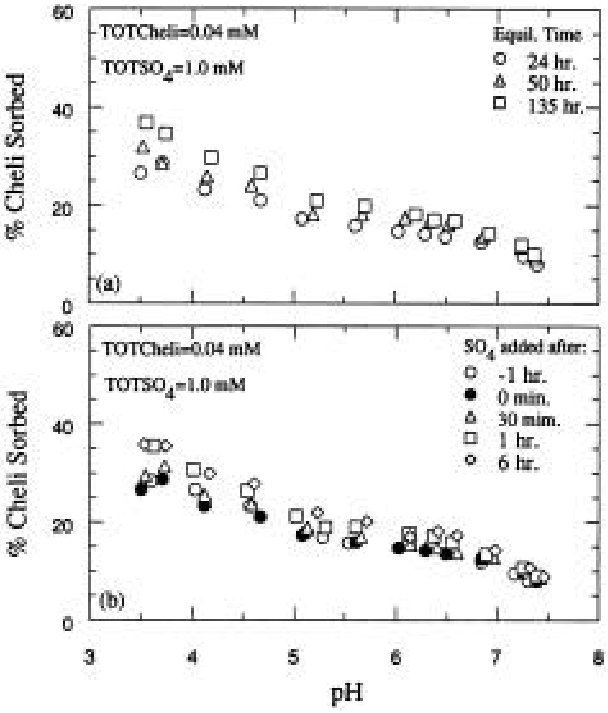

FIGURE 5. Fractional sorption of chelidamic acid (minor component) onto goethite (1.6 g/L) at $I = 0.01$ M NaCl in the presence of sulfate (major component). (a) Sorption as a function of equilibration time. (b) Sorption as function of the order of sorbate addition.

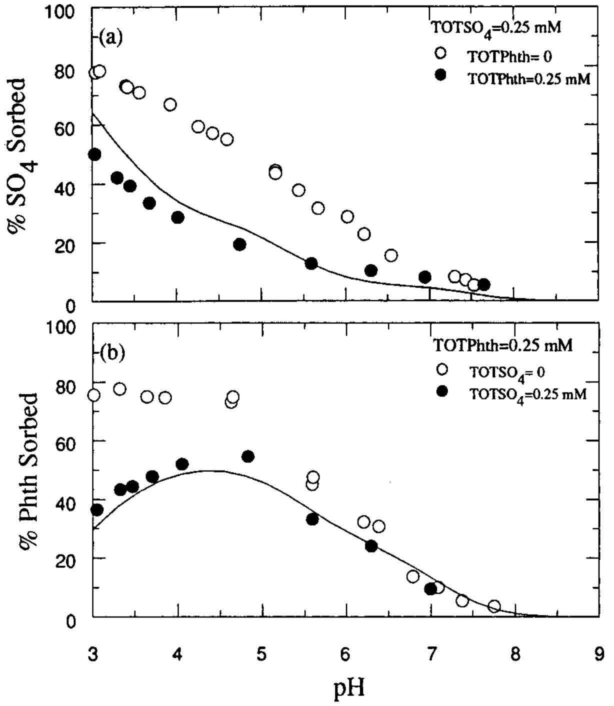

FIGURE 6. Fractional sorption of sulfate (a) and phthalic acid (b) on goethite (1.6 g/L) at *I* = 0.01 M NaCl from binary-sorbate systems where both sorbates are present at intermediate s/s ratios. Solid lines represent model predictions based on single-sorbate data fits.

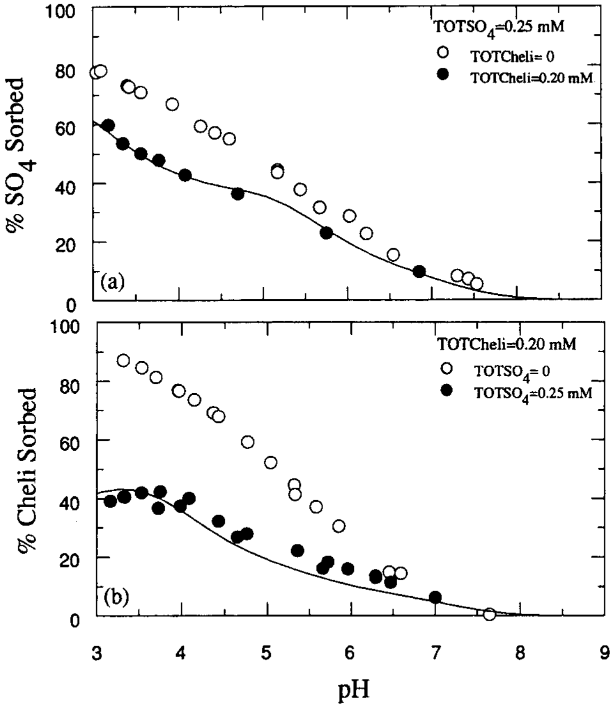

FIGURE 7. Fractional sorption of sulfate (a) and chelidamic acid (b) on goethite (1.6 g/L) at *I* = 0.01 M from binary-sorbate systems where both sorbates are present at intermediate s/s ratios. Solid lines represent model predictions based on single-sorbate data fits.

Results presented in Figure 5 emphasize the need for careful consideration of equilibration time and order of sorbate addition in binary-sorbate sorption experiments, especially under conditions when surface saturation with one or both sorbates is approached. In this study, the majority of the binary-sorbate experiments were conducted under conditions where sorption equilibrium was reached with 24 h. However, for four binary systems (Figures 9, 10b, and 11b) where the sorption of a minor component (low s/s ratio) was examined in the presence of a major component (high s/s ratio), complete sorption equilibrium was probably not established within the 24-h period allowed for equilibration. The data presented in Figure 5 indicate though that, for these systems, sorption at the end of 24 h was probably not greatly different than at longer equilibration times.

Figures 6 and 7 show the results from binary sorbate experiments where both sorbates were present at intermediate s/s ratio. Under these conditions, sulfate effectively competed with both phthalic acid and chelidamic acid for goethite surface sites. The competition was particularly pronounced at pH < 5, where sorption densities of both sorbates were high. Phthalic acid, with slightly higher affinity for goethite surface sites, suppressed sulfate sorption more than chelidamic acid did (Figures 6a and 7a). For the same reason, the reduction of chelidamic acid sorption by sulfate was more pronounced than was the case for phthalic acid.

Figures 8−11 show the sorption of a minor component (low s/s ratio) in the presence of a major component (intermediate or high s/s ratio). The sorption of sulfate present as a minor component was significantly suppressed over the entire pH range by both phthalic acid and chelidamic acid (Figures 8 and 9) present as major components. The effect of phthalic acid was, however, greater than that of chelidamic acid. On the other hand, the sorption of both the organic acids present as minor components was significantly suppressed by sulfate (major component) (Figures 10 and 11). Compared to phthalic acid, chelidamic acid sorption was suppressed to a greater extent by sulfate.

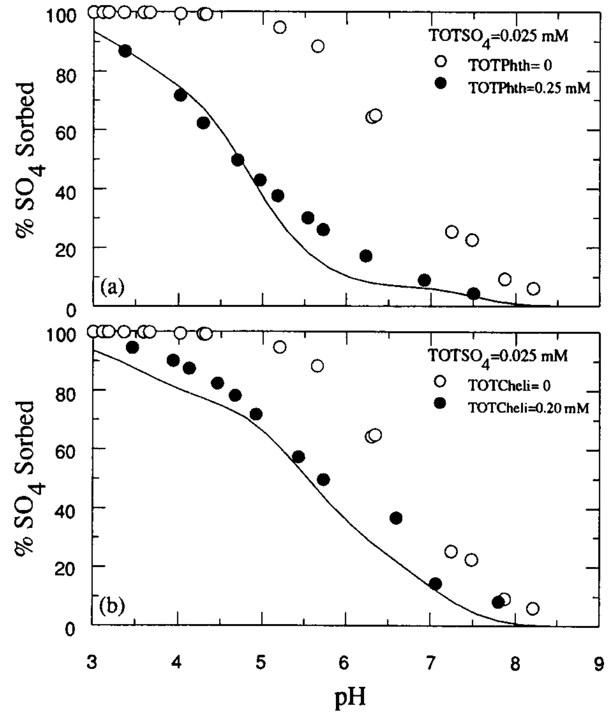

FIGURE 8. Fractional sorption of sulfate (minor component) in the presence of phthalic acid and chelidamic acid present at intermediate s/s ratios. Solid lines represent model predictions based on single-sorbate data fits. (a) TOTSO$_4$ = 0.025 mM, TOTPhth = 0.25 mM; (b) TOTSO$_4$ = 0.025 mM, TOTCheli = 0.20 mM.

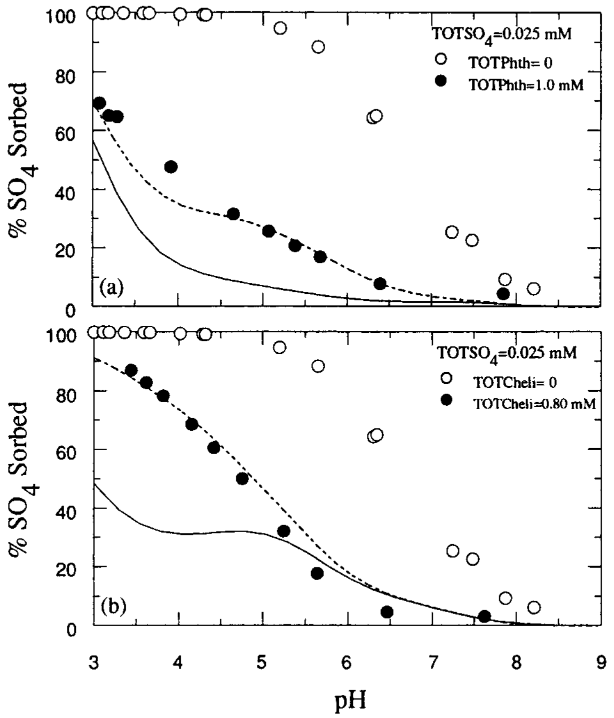

FIGURE 9. Fractional sorption of sulfate (minor component) in the presence of phthalic acid and chelidamic acid present at high s/s ratios. Solid lines represent model predictions based on single-sorbate data fits (log *K* values listed in Table 2). Dashed lines represent simulated sulfate sorption with the adjusted log *K* values listed in Table 4. (a) $TOTSO_4$ = 0.025 mM, TOTPhth = 1.0 mM; (b) $TOTSO_4$ = 0.025 mM, TOTCheli = 0.80 mM.

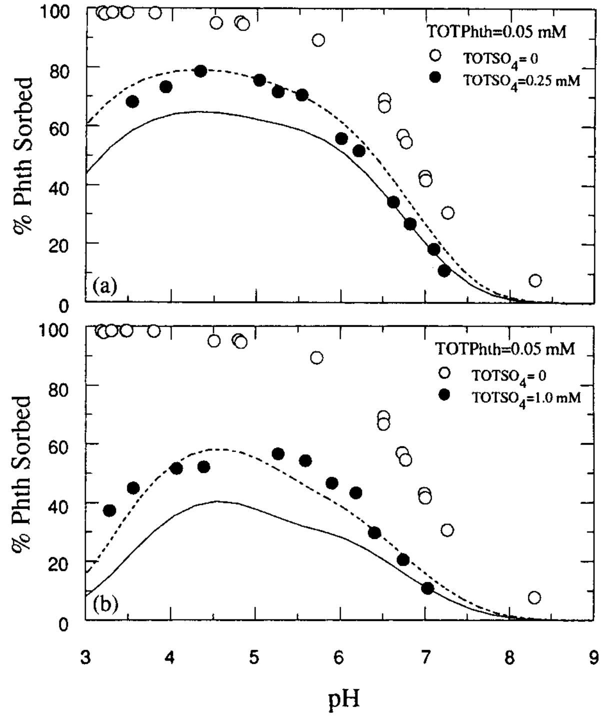

FIGURE 10. Fractional sorption of phthalic acid (minor component) in the presence of sulfate present at intermediate and at high s/s ratios. Solid lines represent model predictions based on single-sorbate data fits (log *K* values listed in Table 2). Dashed lines represent simulated phthalic acid sorption with the adjusted log *K* values listed in Table 4. (a) TOTPhth = 0.05 mM, $TOTSO_4$ = 0.25 mM; (b) TOTPhth = 0.05 mM, $TOTSO_4$ = 1.0 mM.

While sulfate is a weakly sorbing electrolyte ion, it is abundant in many natural aquatic systems. These results,

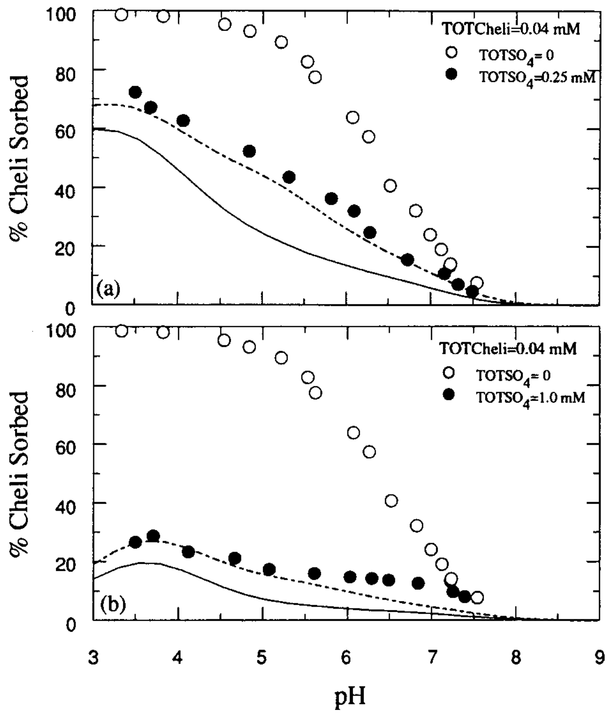

FIGURE 11. Fractional sorption of chelidamic acid (minor component) in the presence of sulfate present at intermediate and at high s/s ratios. Solid lines represent model predictions based on single-sorbate data fits (log *K* values listed in Table 2). Dashed lines represent simulated chelidamic acid sorption with the adjusted log *K* values listed in Table 4. (a) TOTCheli = 0.04 mM, $TOTSO_4$ = 0.25 mM; (b) TOTCheli = 0.04 mM, $TOTSO_4$ = 1.0 mM.

along with the limited available data on mineral–humate–sulfate interactions, suggest that sulfate can play a major role in the partitioning of humic substances. Since humic substances are known to influence the sorption of trace metal ions, it appears that sulfate can influence metal ion sorption indirectly by modifying the sorption of humic substances.

Prediction of Binary-Sorbate Sorption. Model predictions of competitive sorption based on single-sorbate data fits were in good agreement with data (Figures 6 and 7) for binary systems with both sorbates at intermediate s/s ratios. For the phthalic acid–sulfate system, there was however some overprediction of sulfate sorption (Figure 6a) and a corresponding underprediction of phthalic acid sorption (Figure 6b) at low pH values; there was also some underprediction of chelidamic acid sorption in the presence of sulfate (Figure 7b). Figure 12a shows calculated distributions of sulfate surface species for the sulfate–phthalic acid binary system. Distributions of sorbate surface species in these binary systems were similar to those obtained for the corresponding sorbates in single-sorbate systems at intermediate s/s ratio (e.g., compare Figure 12a with Figure 4a), except that concentrations of the surface species were suppressed in the binary systems.

The sorption of a minor component in the presence of a major component was significantly underpredicted by the model (Figures 8–11). Mesuere and Fish (*18*) observed a similar underprediction of minor-component sorption onto goethite for oxalate–chromate binary systems. Predictions of sulfate (minor component) sorption in the presence of either phthalic acid (Figure 8a) or chelidamic acid (Figure 8b) present at intermediate s/s ratios were in reasonable agreement with data. However, at high s/s ratios

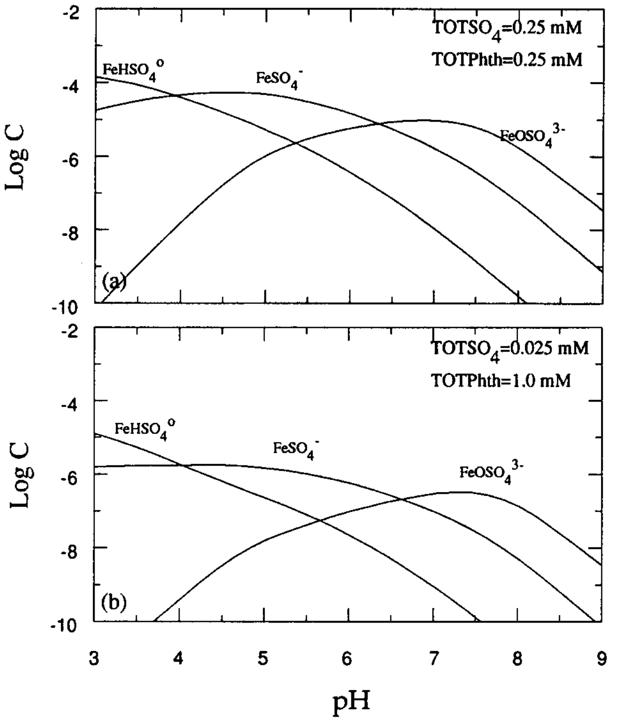

FIGURE 12. Calculated distributions of sulfate surface species on goethite (1.6 g/L) at $I = 0.01$ M and two system conditions: (a) TOTSO$_4$ = 0.025 mM; (b) TOTSO$_4$ = 0.025 mM, TOTPhth = 1.0 mM.

of phthalic acid (Figure 9a) and chelidamic acid (Figure 9b), the model underpredicted sulfate (minor component) sorption by more than a factor of 2, particularly at low pH values. Similar underpredictions were observed for phthalic acid (Figure 10) and chelidamic acid (Figure 11) when present as minor components in the presence of sulfate.

Modeling studies revealed that predictions of minor-component sorption in the presence of a major component were very sensitive to changes in surface complexation log *K* values. A sensitivity analysis was performed to determine the amount of adjustment needed in the log *K* values in order to obtain a better description of minor-component sorption. Table 4 lists the overall and the adjusted log *K* values for the surface species of the minor component; Figures 9–11 show the corresponding model simulations (in dashed lines). Except for one case, all adjustments were within the 99% confidence interval determined for the log *K* values. Log *K* values for the surface species of the major component were kept unchanged. Simulations of minor-component sorption using the adjusted log *K* values indicate that minor changes (increases) in the log *K* values of the surface species could provide a reasonably good description of minor-component sorption.

The consistent underpredictions of minor-component sorption, observed here and in Mesuere and Fish (*18*), indicate that a small amount of sorbate is bound more strongly at the goethite surface. Discrepancies between data and model predictions may thus be attributed, at least in part, to the heterogeneity of surface sites. A small fraction of surface sites may be available for the sorption of certain kinds of sorbates and, therefore, may not experience direct competition from a second sorbate of a different kind. For example, on the basis of CIR-FTIR (cylindrical internal reflection–Fourier transform infrared) spectroscopic studies, Yost et al. (*59*) proposed that a salicylate ion forms two bonds involving one carboxyl and one phenolic oxygen, with each Fe atom of goethite resulting in a chelate structure. Only those iron atoms coordinated to two OH ligands would be able to form such a complex. This particular type of Fe atom, however, is found in relatively few places on goethite such as along the edges and surface defects (*59*). Tejedor–Tejedor et al. (*41*) concluded that, unlike salicylate, sorbates such as phthalate and *p*-hydroxybenzoate do not form bidentate chelate structures on the goethite surface. Thus, such compounds may not compete directly with salicylate for a small fraction of goethite surface sites capable of forming chelate structures.

Effects of such heterogeneity may not be apparent in single-sorbate systems but become evident in sorption from binary systems, especially when one sorbate is present as a minor component. However, when both sorbates are present at intermediate or high s/s ratios, most sorption would occur on a common group of sites, and the effect of a small heterogeneity in surface sites would be minimal. This is consistent with reasonable predictions of sorption when both sorbates were present at intermediate s/s ratios (Figures 6 and 7).

Predictions of minor-component sorption behavior are also influenced by the model used to calculate the Coulombic term in the generalized two-layer model. As shown in Figure 4b,d, the negatively charged surface species are predicted to be dominant at low s/s ratio. Calculated concentrations of these surface species are sensitive to changes in the calculated Coulombic contribution to

TABLE 4

Adjusted Log K^{int} Values for Surface Species of Minor Component Used To Describe Sorption of a Minor Component in the Presence of a Major Component

major component	concn, mM	minor component	concn, mM	surface species of minor component	overall log K^{int} value	adjusted log K^{int} value
phthalic acid	1.0	sulfate	0.025	$\equiv FeHSO_4^0$	13.83 ± 0.14	13.96
				$\equiv FeSO_4^-$	8.41 ± 1.23	9.19
				$\equiv FeOSO_4^{3-}$	−6.04 ± 0.40	*b*
chelidamic acid	0.8	sulfate	0.025	$\equiv FeHSO_4^0$	13.83 ± 0.14	14.93[a]
				$\equiv FeSO_4^-$	8.41 ± 1.23	*b*
				$\equiv FeOSO_4^{3-}$	−6.04 ± 0.40	*b*
sulfate	1.0, 0.25	phthalic acid	0.05	$\equiv FeHL_p^0$	15.74 ± 0.33	16.07
				$\equiv FeOHL_p^{2-}$	2.17 ± 0.18	2.35
sulfate	1.0, 0.25	chelidamic acid	0.04	$\equiv FeH_2L_c^0$	14.05 ± 0.36	14.21
				$\equiv FeHL_c^-$	7.92 ± 0.63	8.43
				$\equiv FeOHL_c^{3-}$	−6.24 ± 0.41	-6.06

[a] Exceeds the 99% confidence interval determined for this constant. [b] Same as overall log K^{int} value.

sorption and decrease with decreasing charge at the surface (see mass law equations in Table 2). In a binary system with a major−minor combination of sorbates, the surface charge decreases significantly compared to a system with only the minor component due to sorption of the major component (*36*). Therefore, even a small overprediction of Coulombic effect in such binary systems would contribute to an underprediction of sorption of a minor component. This phenomenon is evident from the significant differences between the calculated distributions of the minor component surface species in the presence of a major component (shown in Figure 12b for a sulfate−phthalic acid system) and those in a single-sorbate system (shown for sulfate in Figure 4b).

While the underprediction of minor-component sorption clearly has some relation to the highly negatively charged surface species and the Coulombic description used in the generalized two-layer model, surface site heterogeneity is likely to have more bearing on the underprediction. Mesuere and Fish (*18*) obtained similar underpredictions of minor-component sorption with the triple-layer model and less negatively charged surface species. Consideration of sorbate-specific site heterogeneity may improve the prediction of minor-component sorption, but the additional parameters introduced would be difficult or impossible to measure.

Thus, the generalized two-layer model, with the assumption of homogeneous surface sites and with a simple description of the oxide−water interface, could predict sorption on goethite in binary systems over a range of conditions. Although there were some underpredictions of minor-component sorption, for the most part predictions based on equilibrium constants extracted from single-sorbate data were accurate for the multicomponent systems. These results provide a validation of the extrapolation of single-sorbate data to multi-sorbate systems through surface complexation modeling. With multiple sorbates, however, ternary surface complex formation sometimes must be considered, and the formation of these species cannot be determined from single-sorbate data alone *(60)*.

Acknowledgments

This work was supported by the United States Department of Agriculture (USDA Grant 92-34214-7321), by the Donors of The Petroleum Research Fund administered by the American Chemical Society, and by the National Science Foundation (NSF Grant BCS-9157086). The authors thank Dennis Prieve and Annette Jacobson for their helpful suggestions during the course of this work.

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Received for review November 28, 1994. Revised manuscript received October 26, 1995. Accepted December 1, 1995.[⊗]

ES940723G

[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1996.