Copper(II) and Cadmium(II) Sorption onto Ferrihydrite in the Presence of Phthalic Acid: Some Properties of the Ternary Complex

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Copper, cadmium, and phthalic acid (H₂Lp) adsorption by ferrihydrite was examined for binary and ternary systems. In binary systems adsorption was well reproduced using the diffuse layer model (DLM), and H₂Lp adsorption was analogous to that of inorganic diprotic acids in terms of the relationship between the adsorption constants and acidity constants. In ternary systems H₂Lp caused both the enhancement (due to ternary complex formation) and inhibition (due to solution complex formation) of Cu²⁺ and Cd²⁺ sorption depending on the conditions. The DLM could only describe the effect of H₂Lp on metal ion sorption by including ternary complexes of the form \( \text{FeOHML}^- \), where \( \text{FeOH} \) is a surface site and \( M \) is Cu or Cd. The relationship between binary metal adsorption constants and the ternary complex adsorption constants from this and previous studies suggest several properties of ternary complexes. First, ternary complex structures on both ferrihydrite and goethite are either the same or similar. Second, ternary complexes were chelating (with both carboxylate groups coordinated to the surface) to either one Fe or two Fe ions. In contrast trace metal cation adsorption by iron oxides is considered to occur exclusively by inner-sphere co-ordination (19, 20). Studies of ternary cation-ligand-iron oxide systems have identified several different possible mechanisms of coadsorption. At one extreme there is the purely outer-sphere coadsorbed species as proposed for the Cd²⁺-citrate-goethite system based on ATR-FTIR and the constant capacitance model (21). On the other hand, ternary complexes with inner-sphere Cd²⁺ coordinated to either an inner-sphere or outer-sphere Lp⁻ (depending on the conditions) were proposed for the Cd²⁺-Lp⁻-goethite system (11). A similar combination of coadsorbed species was proposed for the Pb²⁺-SO₄²⁻-goethite ternary system (17).

Surface complexation modeling has been widely and successfully used to describe sorption by iron oxides for increasingly complex systems. There is, however, only limited modeling data available for ternary systems with metal ions, ligands, and an iron oxide (5, 11, 21–23). The diffuse layer model (DLM) was chosen for this work because of the availability of a large database of self-consistent adsorption constants for many species (24) and also because of the ability of the DLM to predict adsorption without the need for parameters such as capacitances or charge distribution. In addition, the use of the DLM allows for comparison with adsorption constants for ternary complex formation with several previous studies. The aim of this work is to report the effect of H₂Lp on Cu²⁺ and Cd²⁺ adsorption by ferrihydrite and gain insight into the structure and significance of ternary complexes on ferrihydrite (about which little is known) compared to goethite by comparing the values from this study to other previously reported ternary systems. Some deficiencies of the DLM are also considered in this work.

Methodology
Materials. All reagents used were analytical grade. Ferrihydrite (two-line) was synthesized based on the method described in Schwertman and Cornell (25). Ferrihydrite structure was confirmed by X-ray diffraction of the freeze-dried sample. The specific surface area was determined to be 206 m² g⁻¹ using the N₂ BET method. All solutions were made from 18 MΩ water that had been degassed by lowering the pH to 4 and bubbling with N₂. Solutions were either capped or kept under N₂ and the NaOH used was prepared by diluting a 50:50 (w/w) NaOH: H₂O solution.
Sorption Experiments. Ferrihydrite suspensions were aged overnight, the ionic strength was adjusted, and samples were distributed into a number of 50 mL PP centrifuge tubes. The adsorbate was added (as stock solutions of NO₃⁻ or Na⁺ salts) to each tube followed by HNO₃ or NaOH to yield a pH range. In ternary experiments, metal ion (M²⁺) was always added immediately after the addition of H₂L₀. The tubes were capped and equilibrated for 24~36 h on an end-over-end mixer. The pH was then remeasured, and samples were filtered through a 0.2 µm cellulose acetate membrane filter.

Analytical Methods. The pH was measured using a WTW electrode Sen Tix 20 with an inoLab 740 meter. Dissolved metal concentrations were determined by atomic absorption spectrophotometry (AAS). Ferrihydrite concentration was determined by AAS after acidification of unfiltered suspension. Dissolved H₂L₀ concentration was analyzed by high-performance liquid chromatography.

Modeling of Sorption Data. Equilibrium constants for all aqueous reactions were taken from the Visual Minteq, version 2.51, database (26). Solution complexes for Cu²⁺ and Cd²⁺ include MHL₀⁺, M(L₀)p²⁻, and ML₀, which is the dominant solution complex under all conditions studied. The ferrihydrite surface area (600 m² g⁻¹), site densities, and surface acidity constants of Dzombak and Morel (24) were used in this work. Modeling metal ion sorption requires two different types of sites; a small number of high-affinity sites (termed type 1 sites and denoted =Fe³OH) with a site density of 0.005 mol mol Fe⁻¹ and a larger number of low-affinity sites (termed type 2 sites and denoted =Fe²OH) with a site density of 0.2 mol mol Fe⁻¹. Surface complexation reactions to describe H₂L₀ adsorption were based on those used by Dzombak and Morel (24) for ligand adsorption. The equilibrium constants were optimized with FITSEQ4.0 (27) using the components H⁺, M⁺, L₀⁺, Na⁺, =Fe²OH, and =Fe³OH and the surface potential. The WSOS/DF (the weighted sum of squares of residues divided by the degrees of freedom) was an indicator of the goodness of fit. Values between 0.1 and 20 are generally accepted as reasonably good fits. Data with greater than 90% adsorption can have a disproportionate weighting in FITSEQ4.0 and were not included in the parameter optimization (5). All modeling was performed at a fixed ionic strength, and all equilibrium constants are reported at an ionic strength of zero. The input errors and the weighted average values and uncertainty at the 95% confidence level were determined according to the method of Dzombak and Morel (24).

Results and Discussion

Modeling Sorption in Binary Systems. Phthalic acid sorption by ferrihydrite was determined for a total phthalic acid to ferrihydrite ratio (H₂L₀/Fe) ranging from 0.064 to 30.2 mol mol⁻¹. The results are shown in Figure 1 and are typical of anion sorption. Site heterogeneity is not evident in phthalic acid adsorption, and one site type, the type 2 sites, is sufficient to describe anion sorption onto ferrihydrite using surface species with varying degrees of protonation (24). A diprotic weak acid, there are three surface species to be considered to describe H₂L₀ sorption by ferrihydrite (24). Sorption constants log K₁INT, log K₂INT, and log K₃INT for the formation of the species =Fe³HL₀, =Fe²L₀, and =Fe²OH₂L₀, respectively, were optimized from the experimental data (Table 1). The value of log K₁INT was not constrained by the experimental data in this work, and all the data could be modeled with only =Fe³HL₀ and =Fe²L₀. As is generally found, the more negative surface species are more important at lower anion/ferrihydrite ratios. Parameters could not be optimized from the data sets where the maximum percent adsorption was <10% because of the high inherent uncertainties in calculating the small amount of adsorbed H₂L₀ from the difference between the H₂L₀(signal) and the large amount remaining in solution. Modeled adsorption using the weighted average values is shown in Figure 1 and can reasonably predict the experimental data for the range of conditions measured.

The value for log K₁INT of 15.85 from this work is in close agreement with Ali and Dzombak (14) who reported a value for an analogous reaction of H₂L₀ sorption on goethite to be 15.74. Ali and Dzombak (14) did not optimize a value for log K₂INT but rather modeled all their data for H₂L₀ adsorption by goethite using the two species =Fe³HL₀ and =Fe²OH₂L₀. This was in contrast to sulfate and chelidamic acid adsorption by goethite in the same paper where the species =Fe³H₂O was included in the model though no chemical reason was given for the difference. Both the log K₁INT values optimized in the current paper for H₂L₀ adsorption by ferrihydrite are consistent with the values for inorganic anion adsorption by ferrihydrite. For example the values of log K₁INT determined for a range of inorganic anions form a linear relationship when plotted as a function of the second pKₐ for the anions’ conjugate acids (24, 28). The log K₁INT value for H₂L₀ adsorption on ferrihydrite fits this relationship as is shown in Figure 1.

Spectroscopic studies on the structure of surface complexes for H₂L₀ and other ligands on iron oxides have observed both inner-sphere and outer-sphere complexes, with higher pH and lower ionic strength favoring the outer-sphere complex (15–17). The DLM does not include outer-sphere complexes; however, anion adsorption can be described by the addition of adsorbed species with varying degrees of protonation (24). The DLM speciation of H₂L₀ adsorbed on
ferricydrite shows that high pH and low ionic strength increase the significance of the \( tF \) species, as is observed spectroscopically for outer-sphere complexes of adsorbed anions. Furthermore, using these species the DLM can predict the main features of anion adsorption including the effects of ionic strength, pH, and adsorption density with a simple and consistent set of reactions (24). A full consideration of the reasons for this, given the discrepancy with the spectroscopic data, is beyond the scope of this work.

For \( \text{Cu}^{2+} \) sorption by ferricydrite (in the absence of \( \text{H}_2\text{L}_p \)), values for \( \log K_{1\text{INT}} \) of 2.91 and \( \log K_{2\text{INT}} \) of 0.58 were determined for the formation of the species \( \text{Fe}^{\text{III}}\text{OCu}^+ \) and \( \text{Fe}^{\text{III}}\text{OCu}^- \), respectively. These are consistent with the cited values of 2.89 and 0.60 (24), and these cited values were used in all modeled \( \text{Cu}^{2+} \) sorption. Therefore the adsorption constants for ternary complex formation are consistent with this database. The experimental and modeled data for \( \text{Cu}^{2+} \) sorption as a function of pH are shown (with the data for \( \text{Cu}^{2+} \) adsorption in the presence of \( \text{H}_2\text{L}_p \)) in Figure 2.

For \( \text{Cd}^{2+} \) sorption by ferricydrite (in the absence of \( \text{H}_2\text{L}_p \)), the optimized value for \( \log K_{2\text{INT}} \) for the formation of the species \( \text{Fe}^{\text{III}}\text{OCD}^+ \) was -2.94, which is in agreement with the reported values of -2.90 (24) and -2.69 (23). The \( \log K_{1\text{INT}} \) value for the formation of the species \( \text{Fe}^{\text{III}}\text{OCD}^- \) was 0.22 (standard deviation 0.03), which is in the reported range of 0.09 \( \sim \) 1.03 (24). The weighted average \( \log K_{1\text{INT}} \) value of Dzombak and Morel (24) was 0.47 (\( \pm 0.03 \) at the 95% confidence interval); however, there is a general trend whereby the optimized \( \log K_{1\text{INT}} \) values for a given data set decreased as the \( \text{Cd}(T)/\text{Fe} \) increased, which could be an indication of more complex site heterogeneity for \( \text{Cd}^{2+} \) (23).

Therefore, modeling \( \text{Cd}^{2+} \) sorption by ferricydrite in the presence of \( \text{H}_2\text{L}_p \) was done both with the \( \log K_{1\text{INT}} \) value of 0.22 from this work and also with the cited value of 0.47 for

### TABLE 1. Optimization of \( \log K_{1\text{INT}} \) and \( \log K_{2\text{INT}} \) for \( \text{H}_2\text{L}_p \) Sorption on Ferricydrite

<table>
<thead>
<tr>
<th>( \text{H}_2\text{L}_p/\text{Fe} ) (mol/mol)</th>
<th>( \text{H}_2\text{L}_p ) (mmol kg(^{-1}))</th>
<th>( \text{ferricydrite} ) (mmol kg(^{-1}))</th>
<th>( I ) (mmol kg(^{-1}))</th>
<th>( \log K_{1\text{INT}} ) ( (=\text{Fe}^{\text{III}}\text{HL}_p) )</th>
<th>( \log K_{2\text{INT}} ) ( (=\text{Fe}^{\text{III}}\text{L}_p^-) )</th>
<th>WSOS/DF</th>
</tr>
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<tr>
<td>0.064</td>
<td>0.6</td>
<td>9.4</td>
<td>0.01</td>
<td>15.85( ^c )</td>
<td>10.23 (0.043)</td>
<td>1.82</td>
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<tr>
<td>0.64</td>
<td>6.0</td>
<td>9.4</td>
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</tr>
<tr>
<td>0.64</td>
<td>0.6</td>
<td>0.94</td>
<td>0.01</td>
<td>15.80 (0.13)</td>
<td>10.23( ^c )</td>
<td>0.93</td>
</tr>
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**weighted average**

(95% confidence interval)

<table>
<thead>
<tr>
<th>( H_2L_p(T)/Fe ) (mol/mol)</th>
<th>( H_2L_p(T) ) (mmol kg(^{-1}))</th>
<th>( \text{Fe} ) (mmol kg(^{-1}))</th>
<th>( \text{I} ) (mmol kg(^{-1}))</th>
<th>( \log K_{1\text{INT}} ) ( (=\text{Fe}^{\text{III}}\text{HL}_p) )</th>
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<td>0.93</td>
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\( ^a \) Data sets are given in Figure 1. The \( \log K_{1\text{INT}} \) values are given for \( I = 0 \) (with standard deviations in parentheses). \( ^b \) Values could not be determined from data sets with higher \( \text{H}_2\text{L}_p(T) \) as described in the text. \( ^c \) No convergence of this value so the value was fixed at the weighted average for consistency. \( ^d \) For \( \log K_{2\text{INT}} \) only one value could be determined so no average or confidence interval can be given.

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**FIGURE 2.** Experimental (symbols) and modeled (lines) results for \( \text{Cu}^{2+} \) (a and b) or \( \text{Cd}^{2+} \) (c and d) sorption by ferricydrite in the presence of \( \text{H}_2\text{L}_p \). Model results use the weighted average adsorption constants from Tables 1 and 2. Actual values of \( I, \text{[Fe]}, \) and \( \text{M}(T) \) are given in Table 2. \( \text{H}_2\text{L}_p(T) \) concentrations in mmol kg\(^{-1}\) are 0 ( ), 0.6 ( ), 6.0 ( ), and either 28 or 30 (for \( \text{Cu}^{2+} \) or \( \text{Cd}^{2+} \), respectively, )
consistency with the database of Dzombak and Morel (24). The experimental and modeled data (using the log $K_{INT}$ value of 0.22) for Cd$^{2+}$ sorption as a function of pH are shown (with the data for Cd$^{2+}$ adsorption in the presence of H$_2$Lp) in Figure 2.

**Modeling of Cu$^{2+}$ and Cd$^{2+}$ Sorption by Ferrihydrite in the Presence of H$_2$Lp.** The experimental results for Cu$^{2+}$ and Cd$^{2+}$ sorption by ferrihydrite in the presence of H$_2$Lp are shown in Figure 2. The upper two graphs (Figure 2a,c) have a low M$_2$/Fe ($<0.005$) ratio while the lower two graphs (Figure 2b,d) have a high M$_2$/Fe ($>0.005$) ratio. The adsorption of H$_2$Lp was not noticeably affected by the presence of metal ions (data not shown) because the H$_2$Lp concentration was so much greater than that of Cu$^{2+}$ or Cd$^{2+}$. Phthalic acid either enhanced or decreased Cu$^{2+}$ and Cd$^{2+}$ adsorption depending on the H$_2$Lp concentration, pH, and M$_2$/Fe ratio. The presence of 0.6 mmol kg$^{-1}$ H$_2$Lp enhanced M$^{2+}$ sorption in all cases. For H$_2$Lp concentrations of 6 mmol kg$^{-1}$, the sorption of Cu$^{2+}$ was enhanced for pH $< 5$ but was inhibited at higher pH values, while Cd$^{2+}$ adsorption was only enhanced. For 28 mmol kg$^{-1}$ H$_2$Lp, the adsorption of Cu$^{2+}$ was significantly inhibited, particularly at the higher pH values and for the data with Cu$_{III}$/Fe $\approx 0.025$ mol mol$^{-1}$. But for 30 mmol kg$^{-1}$ H$_2$Lp, the adsorption of Cd$^{2+}$ was enhanced in most conditions but inhibited at higher pH. All and Dzombak (3) observed H$_2$Lp only enhancing Cu$^{2+}$ sorption by goethite for data with Cu$^{2+}$/surface site ratios (0.08 and 0.33 mmol mol$^{-1}$) that were comparable to the data in Figure 2b (0.13 mmol mol$^{-1}$). However, the highest concentration of H$_2$Lp in their study was 1 mM compared to 28 mmol kg$^{-1}$ in the current study. All data with 6 mmol kg$^{-1}$ H$_2$Lp in the current study showed enhanced Cu$^{2+}$ sorption to ferrihydrite, with inhibition only evident at higher H$_2$Lp.

The inhibited M$^{2+}$ sorption generally observed at higher pH could be due to either H$_2$Lp and M$^{2+}$ competing for surface sites or competition between M$^{2+}$ adsorption and the formation of M-Lp complexes in solution. Modeling the data using the binary adsorption constants for a variety of scenarios clearly shows that one of these two forms of competition is the formation of solution M-Lp complexes that causes the observed inhibition of M$^{2+}$ adsorption. For example, if the solution complexes are omitted from the model, M$^{2+}$ adsorption is predicted to increase in all cases due to adsorption of H$_2$Lp. The observed effect of H$_2$Lp inhibiting Cu$^{2+}$ and Cd$^{2+}$ adsorption contrasts to the effect of SO$_4^{2-}$ on the ferrihydrite adsorption of Cu$^{2+}$ and Cd$^{2+}$ which only increased as the SO$_4^{2-}$ concentration increased up to 20 mmol kg$^{-1}$ (22, 23). The difference between the sulfate and phthalate ligands is the relative strength of the interaction with M$^{2+}$ in solution. In general, the anion of a weaker acid, which has a higher affinity for a proton, will have a higher affinity for other cations. This was also demonstrated in Figure 1 where anion affinity for protons and for the Fe$^{3+}$ cation on the ferrihydrite surface is compared. It is for this reason that inhibition of Cu$^{2+}$ and Cd$^{2+}$ adsorption is observed at higher H$_2$Lp$^{2-}$ concentrations but not for sulfate.

With only the binary sorption constants the model predicts inhibition of M$^{2+}$ adsorption with increasing H$_2$Lp$^{2-}$ concentration (details not shown). However, in general, the modeled inhibition is greater than the observed inhibition and no significant enhancement of M$^{2+}$ adsorption is predicted. This suggests that there is some interaction between the M$^{2+}$ and H$_2$Lp on the ferrihydrite surface (which would not be evident in the binary experiments), and this interaction is enhancing M$^{2+}$ adsorption. In previous work the enhanced Cu$^{2+}$ sorption by goethite in the presence of H$_2$Lp was successfully modeled by including a ternary surface complex with stoichiometry $\text{FeOHCuL}_p$ (5); however, all their data had a sufficiently high Cu$_{III}$/Fe-FeOOH ratio that only one goethite site type was needed to describe cation adsorption. In this work the effect of H$_2$Lp on M$^{2+}$ adsorption was studied at two M$_2$/Fe ratios; the low Cu$_{III}$/Fe ratio of 0.0017–0.0020 or Cd$_{III}$/Fe ratio of 0.0082–0.0094, which is significantly above the type 1 site density so that the type 2 sites will be most important, and the high Cu$_{III}$/Fe and Cd$_{III}$/Fe ratio of 0.025–0.030 and 0.0082–0.0094, respectively, which is sufficiently above the type 1 site density so that the type 2 sites will be significant. In this way the role of ternary complexes on both high- and low-affinity sites could be assessed.

The initial approach to modeling in this work was to add one ternary complex ($\text{FeOHOML}_p$) on the type 2 sites, with an equilibrium equation for surface complex formation of $\text{[FeOHOML}_p$] = $\text{[FeOH]}$[$\text{M}^{2+}$]$_{\text{II}}$[$\gamma_c$]$_{\text{K}_{TC}^{\text{TC}}}$ (1) = molar concentration; $\gamma_c$ = aqueous phase activity coefficient for species with charge $\chi$. However, while each data set could be fitted by including this species, the optimized values of log $K_{TC}^{\text{TC}}$ ranged from 9.3 to 9.7 for the data sets with Cu$_{III}$/Fe $\approx 0.025$ but ranged from 10.6 to 10.9 for the data sets with Cu$_{III}$/Fe $\approx 0.002$. An acceptable model needs to be able to describe all the experimental data in a consistent way, and
the above results indicated that another surface complex might be involved on the high-affinity sites. For this reason, an additional ternary complex, \( =\text{FeOHCuL}^0 \), was added to the model. Values for \( \log K_{\text{TC}}^{\text{FeOHCuL}} \) and \( \log K_{\text{TC}}^{\text{FeOHCuL}} \) were optimized from the experimental data, and the results are shown in Table 2.

Only a value for \( \log K_{\text{TC}} \) could be optimized from the data with a Cu/Fe of \( \sim 0.0017 \), as would be expected because the type 2 sites are not significant until the type 1 sites are appreciably occupied. The values ranged from 12.29 to 12.48, and all the WSOS/DF were between 1.6 and 5.5. A value for \( \log K_{\text{TC}} \) could be optimized from the data with Cu/Fe of \( \sim 0.025 \), and these values ranged from 9.02 to 9.52. Values for \( \log K_{\text{TC}} \) could be optimized from two data sets with a Cu/Fe of 0.025. Although the standard deviations for \( \log K_{\text{TC}} \) were comparatively large reflecting the minor role the type 1 sites play under these conditions. The values for \( \log K_{\text{TC}} \) with Cu/Fe of \( \sim 0.025 \) were reasonably consistent with those from Cu/Fe of \( \sim 0.0017 \) given the high standard deviation. Furthermore, the modeling of the data with Cu/Fe of \( \sim 0.0017 \) was not significantly affected by fixing the value of \( \log K_{\text{TC}} \) to the weighted average value that was determined from the data with Cu/Fe of \( \sim 0.025 \). This demonstrates that the model is consistent across all the conditions studied.

Similarly, using the same model framework and a \( \log K_{\text{INT}} \) for Cd of 0.22 (optimized from this study), the \( \log K_{\text{TC}}^{\text{FeOHCDL}} \) and \( \log K_{\text{TC}}^{\text{FeOHCDL}} \) optimized from the Cd data were 9.86 and 7.56, respectively (Table 2). If the \( \log K_{\text{INT}} \) for Cd is taken as 0.47 (24), then the values of \( \log K_{\text{TC}} \) and \( \log K_{\text{TC}} \) change only slightly to 9.81 and 7.46, respectively.

Numerous other ternary complex stoichiometries were tested in the modeling of the data. These included varying states of protonation, and ternary complexes involving one or two types of sites. No other ternary stoichiometries provided a consistent set of model parameters to describe all the data. Another variable is including or excluding H2Lp adsorption on the type 1 site. Anion adsorption can be modeled with only the type 2 sites. It is possible that H2Lp also absorbs on type 1 sites (with the same log \( K_{\text{INT}} \)), but this would only be evident from the effect of site competition on cation adsorption. The ternary complex model discussed above includes H2Lp adsorption on both site types, as excluding H2Lp adsorption on the type 1 sites meant that a consistent model framework was not possible, in particular for the data with Cu/Fe of \( \sim 0.0017 \) and 28 mmol kg\(^{-1}\) H2Lp.

Figure 2 shows the sorption of Cu2\(^+\) and Cd2\(^+\) by ferrihydrite in the presence of H2Lp with the modeling results that include ternary complex formation (using the weighted average values from Table 2) with the associated binary adsorption constants. By including the ternary complexes, the model can predict the effect of H2Lp on M2\(^+\) sorption, and the discrepancies between the experimental and the predicted values of M2\(^+\) adsorption in the presence of H2Lp are of comparable magnitude to those in the absence of H2Lp. Ali and Dzombak (5) only observed H2Lp enhancing Cu2\(^+\) adsorption for experiments with up to 1 mM H2Lp. However, using the parameters from Ali and Dzombak (5) to model the effect of higher concentrations of H2Lp on Cu2\(^+\) sorption by goethite (details not shown) shows a very similar behavior to the effect seen on ferrihydrite.

The calculated speciation for the ternary system with Cu/Fe \( \approx 0.025 \) is shown in Figure 3 to illustrate the significance of ternary complexes. Species are arranged in three groups: first, solution Cu2\(^+\)-Lp complexes; second, sorbed ternary complexes \( =\text{FeOHCuL}^0 \) and \( =\text{FeOHCuL}^0 \); and third, sorbed Cu2\(^+\) binary complexes \( =\text{FeOCu}^+ \) and \( =\text{FeOOCu}^+ \). For all H2Lp concentrations, ternary complexes account for up to approximately 35% of the Cu, peaking from pH 5.5 to 6. At lower pH, metal solution complexes dominate, while at higher pH, adsorbed binary M2\(^+\) dominates the speciation. We observed a similar species distribution in the Cd2\(^+\)-Lp-ferrihydrite ternary system. The extent of ternary complex formation is similar to that calculated and calibrated with spectroscopic data for Cd2\(^+\) sorption by goethite in the presence of H2Lp by Boily et al. (11) where a maximum of about 40% Cd2\(^+\) as ternary complexes occurred in the pH region just below that where binary adsorption complexes become dominant. The ternary complexes identified by Boily et al. (11) involved an inner-sphere Cd2\(^+\) and either an inner- or outer-sphere H2Lp compared to the DLM where there are no outer-sphere species.

**Ternary Complex Structure.** The ternary complex structures for the Cd2\(^+\)-Lp-goethite and Pb2\(^+\)-SO42\(^-\)-goethite systems were discussed above. Although there has been no spectroscopic investigation of the cation-Lp-SO42\(^-\)-ferrihydrite system, it has been postulated that the mechanism for the SO42\(^-\)-induced enhancement of metal sorption on ferrihydrite and goethite might be the same or similar (23). This was based on an investigation of the effect of SO42\(^-\) on Cu2\(^+\), Cd2\(^+\), Pb2\(^+\), Zn2\(^+\), and Co2\(^+\) sorption by ferrihydrite. A linear relationship was found between sorption constants for ternary complex formation (log \( K_{\text{INT}} \)) and metal sorption (log \( K_{\text{INT}} \)) in binary systems, and the data for the Cu2\(^+\)-SO42\(^-\)-goethite system (6) also fitted the same relationship. It is possible to compare the sorption constants for ternary complex formation in the Cu2\(^+\)-Lp-ferrihydrite system with previously reported values for Cu2\(^+\)-Lp-goethite (6). Ali and Dzombak (6) used the species \( =\text{FeOHL}^2 \) as opposed to \( =\text{FeL}^2 \) used in this work. However, in the region of the Cu adsorption edge, the neutral phthalate surface species \( =\text{FeHL}^0 \) that was used in both studies with similar formation constants accounts for >97% of the binary adsorbed phthalate. These data are shown in Figure 4 along with data for cations adsorbing in the presence of SO42\(^-\) (6, 22, 23). For both ligands Figure 4 shows that ternary complex stability increases with the increase in the stability of the adsorbed cation. This is consistent with the spectroscopically determined ternary complex structures for these ligands with Cd2\(^+\)
or Pb\(^{2+}\) on goethite (11, 17, 18) which showed the cation binding on the surface. No spectroscopic studies have been done on the structure of the ternary surface complexes on ferrihydrite, but the fact that both data points for goethite closely fit the relationships for ferrihydrite in Figure 4 suggests that the ternary complex structures on ferrihydrite could be expected to be the same or at least similar to those formed on goethite.

In addition, the fact that the log \(K^{TC}\) values for ternary complexes with Lp\(^{2-}\) are higher than the corresponding values for SO\(_4^{2-}\) would suggest that the stability of the ternary complex also depends on the strength of the ligand–metal interaction, as would be intuitive. The log \(K\) values for forming the solution complex CuA\(^9\), where A is either Lp\(^{2-}\) or SO\(_4^{2-}\), are 4.02 and 2.36, respectively. The difference between these two values is similar to the difference between log \(K^{TC}\) for Cu-Lp and Cu-SO\(_4\) ternary complexes on both ferrihydrite (9.43 and 7.83, respectively) and on goethite (10.91 and 9.68, respectively) (5) and, more generally, to the difference between the intercepts of the two lines in Figure 4. It should be noted that having a ligand with a higher value of log \(K^{TC}\) does not necessarily mean that the ligand will increase cation adsorption more significantly. Because the corresponding solution complexes are also formed more strongly the converse can be true, depending on the ligand concentration. For example, sulfate enhanced Cu\(^{2+}\) adsorption up to 20 mmol kg\(^{-1}\) sulfate (22) whereas H\(_2\)Lp inhibited Cu\(^{2+}\) adsorption at concentrations greater than about 6 mmol kg\(^{-1}\) in the current work.

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**Literature Cited**


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