

Analysis of Copper Binding in the Ternary System Cu^{2+} /Humic Acid/Goethite at Neutral to Acidic pH

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Binding of heavy metal and actinide ions to natural colloids, such as humic substances (HSs) and metal (hydr)-oxides, plays an important role in the ecotoxicological behavior of these ions. Several thermodynamic models have been constructed to predict the speciation of these ions in metal/HS or metal/oxide binary systems. However, in natural environments the adsorption of HSs on oxides can influence the binding of target metals, leading to deviation from the additivity of calibrated binary models. In this study binding of copper (Cu^{2+}) to the purified Aldrich humic acid (PAHA)/goethite complex in the neutral to acidic pH region was investigated by measuring Cu^{2+} binding isotherms. The measured isotherms were compared with the results obtained for the binary systems under similar conditions. The comparison revealed that Cu^{2+} binding in the ternary system is enhanced with respect to the sum of Cu^{2+} binding in the corresponding binary systems. From the analysis of the charging behavior of the adsorbed PAHA as well as the smeared-out potential profile near the PAHA/goethite interface, the increase of Cu^{2+} binding to the complex was mainly attributed to the decrease of proton competition to the functional groups of the adsorbed PAHA and the change of the electrostatic potential in the vicinity of the goethite surface.

Introduction

Natural colloids, such as natural organic materials (NOMs) and metal (hydr)oxides, are ubiquitous in soil and aquatic systems (1). Natural colloids are recognized to play an important role in the ecotoxicological behavior of heavy metal and actinide ions, because the migration and toxicity of these ions are directly related to their speciation, which can be significantly altered by the binding to natural colloids (2, 3). In the past couple of decades many experimental studies have been carried out to investigate the binding of metal ions to either NOMs or oxides (4–10), and thermodynamic models have been constructed to describe this binding (6,

8, 11–14). The NICA (nonideal competitive adsorption)–Donnan model (12, 13) and WHAM–model VI (11) are examples for metal binding to humic substances (HSs), a representative group of NOMs. For metal ion binding to oxides the CD–MUSIC (charge distribution–multisite ion complexation) model (8, 14) is the most sophisticated approach, but also the 2pK TLM (triple-layer model) (6, 9) is used regularly.

In natural environments different colloids coexist and interact with each other. An important example of this interaction is that oxide surfaces are frequently covered by adsorbed NOMs (15). The adsorption of NOMs on oxide surfaces can alter both the surface properties of the oxides and the degree of protonation of the NOMs (16, 17). As a result, the bound amount of a given metal in a given ternary system (Me/NOM/oxide, where Me represents the metal ion) may deviate from the sum of the bound amounts in the binary systems (Me/NOM and Me/oxide), depending on the system conditions (18–23). The effects of the NOM–oxide interaction on metal binding in a given ternary system can be evaluated either by comparing the metal binding in the corresponding binary systems assuming no interaction between NOM and oxide with that in the ternary system (21–23) or by direct modeling of the ternary system (16, 23, 24). The modeling of ternary systems is not a simple task, especially when one wants to describe the system over a broad range of conditions with a single set of parameters. Some first attempts to do this were made by Vermeer et al. (16), but these calculations aimed at a better understanding rather than at a precise description of experimental data, and only proton (H^+) binding was studied. In an attempt to describe experimental data Filius et al. (24) developed the LCD (ligand and charge distribution) model for Me/fulvic acid (FA)/oxide systems. FA is a low molar mass NOM that is assumed to adsorb on the oxide surface with a part of its functional groups, which do not directly bind to the surface, in the Stern layer. Under this assumption it is possible to describe the binding of both FA and small ions to oxide surfaces by combining the CD–MUSIC and NICA–Donnan models. The LCD model could successfully describe H^+ and calcium (Ca^{2+}) binding to the FA/goethite ($\alpha\text{-FeOOH}$) complex (23, 24). However, the basic LCD model cannot be applied to the ternary systems containing NOM with a high molar mass, such as humic acid (HA). The size of HA molecules may exceed the thickness of the Stern layer over which the charges of adsorbed molecules are distributed in the basic LCD model, and consequently, the model would oversimplify the electrostatic potential profile near the surface. Therefore, for the moment we have to rely on the comparison of experimental or calculated results of binary systems containing HA with experimental results of equivalent ternary systems to unravel the effect of the HA–oxide interaction on metal binding.

Although the change of the binding behaviors of metals by NOM–oxide interaction has been recognized, the underlying mechanisms are still unclear. This may be related to the fact that most studies employed adsorption edge measurements, that is, measuring the fraction of metal bound as a function of pH at constant metal concentrations (19–21, 23). With this expression the effect of dissolved NOM in the bulk solution as a competitor for the metal is not separated from the binding to the NOM/oxide complex. This problem will be avoided if one plots the bound amount of a target metal to NOM/oxide complex as a function of its free concentration at different pH values (i.e., isotherm measurement). The objective of the present research is to shed light on the effect of the mutual interaction between HA and oxide

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on metal binding in the neutral to acidic pH region. To achieve this, binding isotherms of copper (Cu^{2+}) to the purified Aldrich HA (PAHA)/goethite complex were investigated as a function of PAHA loading, Cu^{2+} concentration, pH, and salt concentration. The acid to neutral pH region was chosen because in the alkaline pH region the adsorption of NOM is small (17) and most likely the major effect of NOM is the reduction of metal activities by forming stable complexes between dissolved NOM and metal ions (18–21). Tipping et al. (18) also investigated the Cu^{2+} /HA/goethite system and reported the effects of HA adsorption on Cu^{2+} binding. However, the experimental conditions employed by them are too limited to extract the underlying mechanisms. The present study will give a further explanation to the findings of Tipping et al. by investigating the change of Cu^{2+} binding upon the adsorption of PAHA with the help of the results of the potentiometric titrations of the PAHA/goethite complex (17).

Before Cu^{2+} binding to the PAHA/goethite complex is studied, the binary systems (i.e., H^+ and Cu^{2+} binding to PAHA and their adsorption on goethite) and H^+ binding to the PAHA/goethite complex without Cu^{2+} must be understood. Except Cu^{2+} adsorption on goethite, these measurements have been done before (17, 25), and the obtained results were described with the NICA–Donnan model in the case of H^+ and Cu^{2+} binding to PAHA (25) and with the CD–MUSIC model in the case of H^+ adsorption on goethite (17). Results of Cu^{2+} adsorption on goethite will be discussed in the first part of this paper, and the remaining part will be devoted to the Cu^{2+} /PAHA/goethite system.

Experimental Section

Chemicals and Materials. Throughout the experiments, analytical or higher grade chemicals of Wako Pure Chemical Industries, Ltd. were used, and the water was purified with a “Milli-Q” unit (Millipore Co.).

HA was purchased from Aldrich–Chime in sodium form. The purification of this HA was described elsewhere (17). The final product was freeze-dried and is denoted as PAHA. Before use, PAHA was dissolved overnight in KOH solution with pH 10 to a concentration of 2 g/L. The high pH prevents the effects of incomplete dissolution of PAHA in subsequent experiments (26).

The goethite sample was synthesized according to Hiemstra et al. (27). The BET (N_2) specific surface area of the freeze-dried goethite was 82 m^2/g . According to Venema et al. (8) goethite made by this recipe contains particles that are crystalline (approximately 90% of the 110 face and 10% of the 021 face) with a needlelike shape with an average length of 150 nm and width of 15 nm. By potentiometric titrations at different salt concentrations the point of zero charge (pzc) of this goethite was determined to be 9.24 (17).

Cu^{2+} /Goethite. The measurements of Cu^{2+} adsorption isotherms on goethite were performed at pH 4 and 6 and salt concentrations of 0.1 and 0.01 M KNO_3 . Two replicate batches were prepared at each condition. At pH 6 the samples were prepared under a continuous flow of moisturized argon. The goethite stock suspension (10.3 wt %) was weighed in 50 mL polypropylene centrifuge tubes: 2.5 g at pH 4 and 0.1 g at pH 6. To make the salt concentration of the batches 0.1 or 0.01 M KNO_3 , small amounts of 1 or 0.1 M KNO_3 solutions were added, and total volumes of 20 mL were reached by additions of preboiled pure water. The total Cu^{2+} concentrations were varied from 2.26×10^{-5} to 1.13×10^{-3} M at pH 4 and from 2.28×10^{-4} to 1.69×10^{-3} M at pH 6 by adding 1.15×10^{-3} or 1.15×10^{-2} M $\text{Cu}(\text{NO}_3)_2$ solutions. After the pHs of the batches were adjusted by adding small amounts of 0.1 or 0.01 M HNO_3 and/or KOH solutions, they were equilibrated for 24 h at 298 K. Several hours before completion of the equilibration the pHs of the batches were readjusted if necessary. After the final pH values of the samples were

logged, they were centrifuged at 22100g (Sakuma Ltd., M201-IVD), followed by filtration with 0.025 μm mixed cellulose ester membrane filters (Millipore Co.). The concentrations of the dissolved Cu^{2+} in the filtrates were measured with an ICP-AES instrument (Shimadzu Co., ICP51000-IV). The adsorbed amounts of Cu^{2+} were calculated by subtracting the dissolved Cu^{2+} concentrations from the initial Cu concentrations. The equilibrium Cu^{2+} concentrations were calculated from the dissolved ones using the ECOSAT program (28) by correcting the hydrolysis of Cu^{2+} .

Cu^{2+} /PAHA/Goethite. Copper binding isotherms to the PAHA/goethite complex were obtained as the averages of three replicates at each condition. The goethite stock suspension (2.28 g/L) was prepared in a polycarbonate bottle and stirred at pH 4 overnight under an argon atmosphere. After 5 mL of the stock suspension and appropriate amounts of the PAHA stock solution were pipetted to achieve ratios of 0.022, 0.088, and 0.176 g of PAHA/g of goethite into 50 mL polypropylene centrifuge tubes, small amounts of 0.1 or 0.01 M HNO_3 , 3 mL of 1 or 0.1 M KNO_3 , and pre-boiled pure water were added to make the pH of the samples 4 or 6, the salt concentration 0.1 or 0.01 M KNO_3 , and the final volume 30 mL. The samples were shaken for 72 h at 298 K. Subsequently, additions of 1.25×10^{-2} or 1.25×10^{-3} M $\text{Cu}(\text{NO}_3)_2$ solutions were made to attain the appropriate ranges of the total Cu^{2+} concentrations: typically 4.18×10^{-5} to 2.51×10^{-3} M at pH 4 and 1.18×10^{-4} to 1.70×10^{-3} M at pH 6. After the pHs of the samples were adjusted they were further equilibrated for 72 h. The equilibration time was determined on the basis of the time dependence of Cu^{2+} binding at 0.088 g of PAHA (total)/g of goethite (Figure S1 in the Supporting Information). During the equilibration the pH was occasionally monitored and readjusted if necessary. The samples were centrifuged at 43600g for 30 min (Kubota Co., 7930). Blank samples without goethite at the highest PAHA loading were also centrifuged to check whether PAHA (or its weak aggregates) sediment during centrifugation, and there was no noticeable change in PAHA concentration. In the aqueous phase there are two different types of Cu^{2+} , free Cu^{2+} including its hydrolysis products ($[\text{Cu}^{2+}]_{\text{free}}$) and Cu^{2+} bound to PAHA ($[\text{Cu}^{2+}]_{\text{PAHA}}$). The sums of these species, i.e., $[\text{Cu}^{2+}]_{\text{aq}} = [\text{Cu}^{2+}]_{\text{free}} + [\text{Cu}^{2+}]_{\text{PAHA}}$, were measured with the ICP-AES instrument after aliquots of the supernatants were acidified to pH 1. The other aliquots of the supernatants were diluted with HNO_3 to approximately pH 4, and the total organic carbon concentrations were measured with a TOC analyzer (Shimadzu Co., TOC-Vc) to provide the dissolved PAHA concentrations. The TOC analyzer was calibrated with PAHA solutions of known concentrations before each measurement. The activities of Cu^{2+} in the remaining supernatants were measured with a copper-selective electrode (CuISE, Metrohm, Ltd.) combined with a Ag/AgCl reference electrode (Metrohm, Ltd.) with 1 M KNO_3 as an inner solution, giving $[\text{Cu}^{2+}]_{\text{free}}$ after correction of the activity coefficients and the contribution of the hydrolysis products. From these measurements the bound amounts of Cu^{2+} to the PAHA/goethite complex in molarity ($[\text{Cu}^{2+}]_{\text{comp}}$) were obtained by $[\text{Cu}^{2+}]_{\text{comp}} = [\text{Cu}^{2+}]_{\text{total}} - [\text{Cu}^{2+}]_{\text{aq}}$ and the amounts bound to the dissolved PAHA by $[\text{Cu}^{2+}]_{\text{PAHA}} = [\text{Cu}^{2+}]_{\text{aq}} - [\text{Cu}^{2+}]_{\text{free}}$, where $[\text{Cu}^{2+}]_{\text{total}}$ is the total concentration of Cu^{2+} . The adsorbed amounts of PAHA were obtained by subtracting the dissolved PAHA amounts from its total amounts. In the experiments at pH 6 all pH and CuISE measurements were conducted under a continuous flow of moisturized argon.

Data Modeling. For the modeling of the Cu^{2+} adsorption on goethite the CD–MUSIC model (8, 14) was applied. This model describes ion adsorption on crystalline metal (hydr)-oxides, and it can be divided into two parts: the charge distribution part (CD) and the surface complexation part (MUSIC). The CD part, which describes the electrostatic

interaction between metal ions and oxide surfaces, assumes three planes at the oxide/water interface: 0-, 1-, and d (or 2)-planes. The 0-plane is the surface of the (hydr)oxide and the d-plane the starting plane of the diffuse layer. The region between the 0- and d-planes is the Stern layer, inside which the 1-plane is placed. The charge of H^+ is placed on the 0-plane, and the charges of the 1:1 electrolyte ions that form ion pairs with surface sites are placed on the d-plane. The charges of adsorbed metal ions are distributed on the 0- and 1-planes. The distribution is determined either by the Pauling bond valence concept with predetermined structures of adsorbed ions (29) or simply by finding a best fit to the model (8). No charge is assumed to be present between the 0- and 1-planes and 1- and d-planes. The capacitance between the 0- and 1-planes is C_1 , and that between the 1- and d-planes C_2 . In the CD model the value of C_2 is assumed to be 5 F/m^2 (8). The value of the Stern layer capacitance, C_{stern} , can be accessed from the results of H^+ adsorption without metal ions, and subsequently, C_1 is calculated using the relationship

$$\frac{1}{C_{\text{stern}}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

Once the values of the capacitances are known the potential differences between the planes can be calculated. Beyond the d-plane the potential profile is given according to the Gouy–Chapman theory.

For the MUSIC part, which describes surface complexation, spectroscopic, crystallographic, and potentiometric information is combined. Crystallographic information indicates that there are three types of oxygen sites present on the goethite surface: singly, doubly, and triply coordinated by the underlying iron ions (i.e., FeO , Fe_2O , and Fe_3O , respectively). According to theoretical considerations and potentiometric results, only the singly and triply coordinated sites participate in protonation and deprotonation of the surface in the normal pH range (8, 29):



The formal charges of the sites in these equations follow from the Pauling bond valence concept (14). The protonation constants in eqs 2 and 3 are very similar and set to equal the pzc of the goethite (8).

Metal complexation with these surface sites can be modeled in a similar way, but the situation is more complicated due to various stoichiometries of metal surface complexation. A metal ion can bind to different surface sites with various binding modes, depending on pH and the metal concentration. XAFS (X-ray absorption fine structure) measurements enable one to directly determine the structures of metal complexes on (hydr)oxide surfaces. However, for Cu^{2+} adsorption on goethite, a couple of discrepant results have been reported, reflecting the different goethite preparations and uncertainties in the XAFS measurements and their interpretation (30–32). In this study the Cu^{2+} surface complexes identified in the literature were imported to the CD–MUSIC model to describe the Cu^{2+} adsorption on goethite. This was done by using the site densities and ion pair formation constants reported by Venema et al. (8), proton affinity constants determined in ref 17, and C_1 calculated by eq 1 with $C_{\text{stern}} = 0.79 \text{ F/m}^2$ (17) and optimizing the metal ion adsorption parameters. The parameter optimization was conducted using the ECOSAT program combined with the FIT program (33).

Results

Cu^{2+} /Goethite. The adsorption isotherms of Cu^{2+} on goethite measured as a function of the equilibrium concentration of

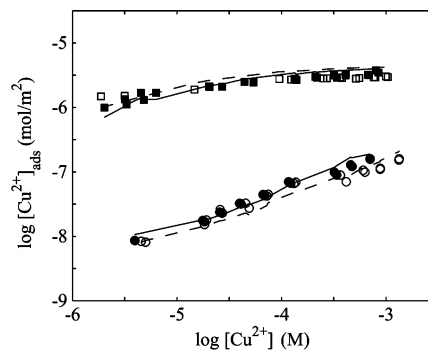
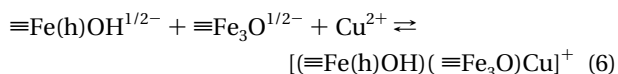
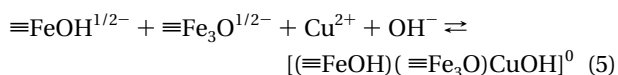
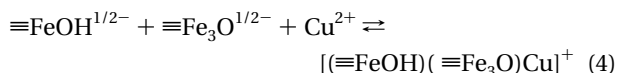


FIGURE 1. Adsorption isotherms of Cu^{2+} on goethite and the results of the CD–MUSIC fitting: pH 4 (●, ○) and 6 (■, □); 0.1 M (●, ■, solid curves) and 0.01 M (○, □, dashed curves) KNO_3 .

Cu^{2+} at pH 4 and 6 and the salt concentrations 0.1 and 0.01 M KNO_3 are depicted in Figure 1. The adsorption of Cu^{2+} on goethite strongly depends on pH: the adsorbed amount increases by about 2 orders of magnitude when pH increases by 2 units. On the contrary, the dependence of Cu^{2+} adsorption on the salt concentration is small, and only at pH 4 and at relatively high $[\text{Cu}^{2+}]$ the adsorbed amount slightly increases with an increase of the salt concentration. These trends agree with the results obtained by Robertson and Leckie (9). The dependency of Cu^{2+} adsorption on pH and the lack of dependence on salt concentration indicate the formation of inner-sphere surface complexes between Cu^{2+} and the surface sites of goethite.

The Cu^{2+} adsorption isotherms were fitted with the CD–MUSIC model, using the surface complexes reported in refs 30–32. Combinations of monodentate and bidentate complexes and/or the inclusion of the hydrolysis of these species were tested in preliminary calculations to make the model more flexible. However, all trials failed. Finally, it turned out that in addition to the bidentate surface complexes of Cu^{2+} and its hydrolysis product with the singly and triply coordinated sites (eqs 4 and 5, respectively) (31) some high-affinity sites (eq 6)



were necessary to describe the obtained Cu^{2+} adsorption accurately. $\equiv\text{Fe(h)OH}^{1/2-}$ represents the singly coordinated sites that have a high affinity for Cu^{2+} . This approach is similar to that of Robertson and Leckie (9). These authors have reported that in the application of the 2pK TLM to Cu^{2+} adsorption on goethite adding a few high-affinity sites improved the model fits substantially. The high-affinity sites may be located at edges or correspond to defects on the crystal faces. The work of Spadini et al. (34) indirectly supports this. These authors reported that cadmium (Cd^{2+}) ions preferentially adsorbed on crystal growth points of goethite and that the higher affinity of Cd^{2+} for hydrous ferric oxide than goethite could be attributed to the higher fraction of crystal edges on the former. In this study the site density of the $\equiv\text{Fe(h)OH}^{1/2-}$ sites was optimized to be 0.02% of that of the singly coordinated sites.

The result of the CD–MUSIC fitting is presented in Figure 1, and the optimized metal complexation constants and the

TABLE 1. CD—MUSIC Parameters for the Cu²⁺ Adsorption on Goethite^a

Surface Properties and Protonation					
log K _{1,3} ^b , log K _{3,1}					9.24
N _s ^c (number of sites/nm ²), FeOH + Fe(h)OH					3.45
N _s (number of sites/nm ²), Fe(h)OH					6.90 × 10 ⁻⁴
N _s ^c (number of sites/nm ²), Fe ₃ O					2.70
log K _{K+} = log K _{NO₃} ^c					-1
C ₁ ^d (F/m ²)					0.94
C ₂ ^d (F/m ²)					5
Cu ²⁺ Surface Complexation					
surface species	log K	Z ₀ ^e	Z ₁ ^e	R ² ^f	RMSE ^g
(=FeOH)(=Fe ₃ O)Cu ⁺	9.50	0.9	1.1	0.9873	0.10523
(=FeOH)(=Fe ₃ O)CuOH ⁰	16.8	0.9	0.1		
(=Fe(h)OH)(=Fe ₃ O)Cu ⁺	11.2	0.9	1.1		

^a The parameter values in italics were fixed throughout the optimization. ^b The same protonation constant was assumed for Fe(h)OH. ^c Site densities of the singly and triply coordinated surface sites and ion pair formation constants from ref 8. ^d The value of C₁ was calculated using eq 1 with C_{stern} = 0.79 F/m² from ref 17 and C₂ = 5 F/m² from ref 8. ^e The optimized charge of Cu²⁺ placed on the 0-plane (Z₀) and 1-plane (Z₁) was assumed to be the same for the three complexes. ^f Correlation coefficient between the measured adsorbed amounts and the fitted ones. ^g Root-mean-square of errors between the measured adsorbed amounts and the fitted ones in unit of log(mol/m²).

charge distributions are summarized in Table 1 together with the other parameters. The charge distributions of the adsorbed Cu²⁺ in the three surface complexes were assumed to be identical with the OH group placed on the 1-plane and optimized by trial and error. This version of the model can describe the pH and salt concentration dependency of the Cu²⁺ adsorption well.

Cu²⁺/PAHA/Goethite: Effects of pH and Salt Concentration. The total Cu²⁺ binding in these systems is the result of copper binding to the PAHA/goethite complex ([Cu²⁺]_{comp}) and that to dissolved PAHA ([Cu²⁺]_{PAHA}). In Figure 2 Cu²⁺ binding to the PAHA/goethite complex is compared with that to the dissolved PAHA at a ratio of 0.088 g of total PAHA/g of goethite in 0.1 M KNO₃. For the same comparisons at other conditions see Figure S2 in the Supporting Information. Figure 2A presents the results at pH 4 and Figure 2B at pH 6. At both pH values the adsorbed amounts of PAHA are around 0.075 g of PAHA/g of goethite (see Figure S3C,D in the Supporting Information). The relatively large errors in the Cu²⁺ concentration resulted from the large uncertainties in the CuISE measurements, especially at low [Cu²⁺] and/or low dissolved PAHA concentration, because at these conditions the supernatants were poorly buffered with respect to Cu²⁺. At low Cu²⁺ concentration (log [Cu²⁺] ≤ -4 at pH 4 and log [Cu²⁺] ≤ -5 at pH 6) the fraction bound to the complex is larger than that bound to the dissolved PAHA. With increasing [Cu²⁺] the trend is reversed, and with increasing pH the fraction of Cu²⁺ bound to the PAHA/goethite complex increases.

In Figure 3 the Cu²⁺ binding isotherms to the PAHA/goethite complex at 0.088 g of PAHA (total)/g of goethite, two pH values (pH 4 and 6), and two salt levels (0.1 and 0.01 M KNO₃) are presented as double logarithmic plots. The isotherms depend on both pH and the salt concentration. With an increase of the pH the Cu²⁺ binding increases strongly, and with an increase of the salt concentration it decreases at relatively low [Cu²⁺], and increases at relatively high [Cu²⁺]. The latter is reflected in the slope of the isotherms, which is steeper at 0.1 M KNO₃ than at 0.01 M KNO₃.

In Figure 4 the four measured Cu²⁺ binding isotherms presented in Figure 3 are compared with calculated binding isotherms. Each point of the calculated Cu²⁺ isotherms (solid curves) is the sum of the bound amount of Cu²⁺ to an

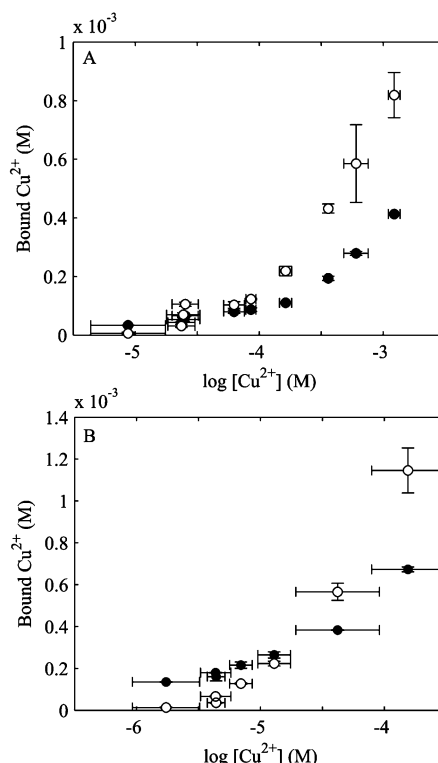


FIGURE 2. Cu²⁺ binding isotherms to the PAHA/goethite complex (●) and the dissolved PAHA (○) at 0.088 g of PAHA (total)/g of goethite and 0.1 M KNO₃: pH 4 (A) and 6 (B).

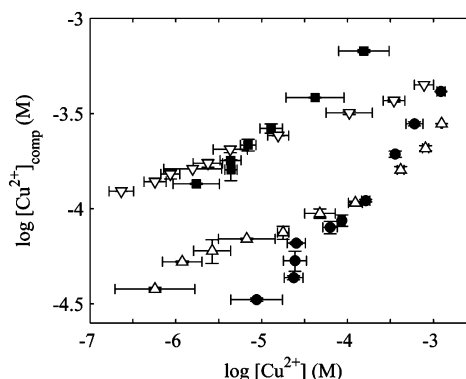


FIGURE 3. Cu²⁺ binding isotherms to the PAHA/goethite complex at 0.088 g of PAHA (total)/g of goethite: pH 4 (●, △) and pH 6 (■, ▽); 0.1 M (●, ■) and 0.01 M (△, ▽) KNO₃.

equivalent amount of adsorbed PAHA (dotted curves) plus that to bare goethite (dashed curves) at the same condition. Therefore, the solid curve represents Cu²⁺ binding in the absence of any interaction between PAHA and goethite. To have the same conditions (amount of adsorbed PAHA, amount of goethite, pCu, pH, salt concentration), the Cu²⁺ isotherms to PAHA or goethite were calculated by the ECOSAT program using the NICA–Donnan and CD–MUSIC models, respectively. The parameters for the NICA–Donnan model are obtained from Table S1 in the Supporting Information and those for the CD–MUSIC model from Table 1. The adsorbed amounts of PAHA on goethite in the presence and absence of Cu²⁺ are presented in Figure S3 in the Supporting Information.

The bound amount of Cu²⁺ to the PAHA/goethite complex is larger than the noninteracting sum at all conditions. At pH 4 and 0.01 M KNO₃ this difference is more than 1 order of magnitude at low log [Cu²⁺]. Increasing the pH from 4 to 6 leads to a decrease of this difference and decreasing the salt

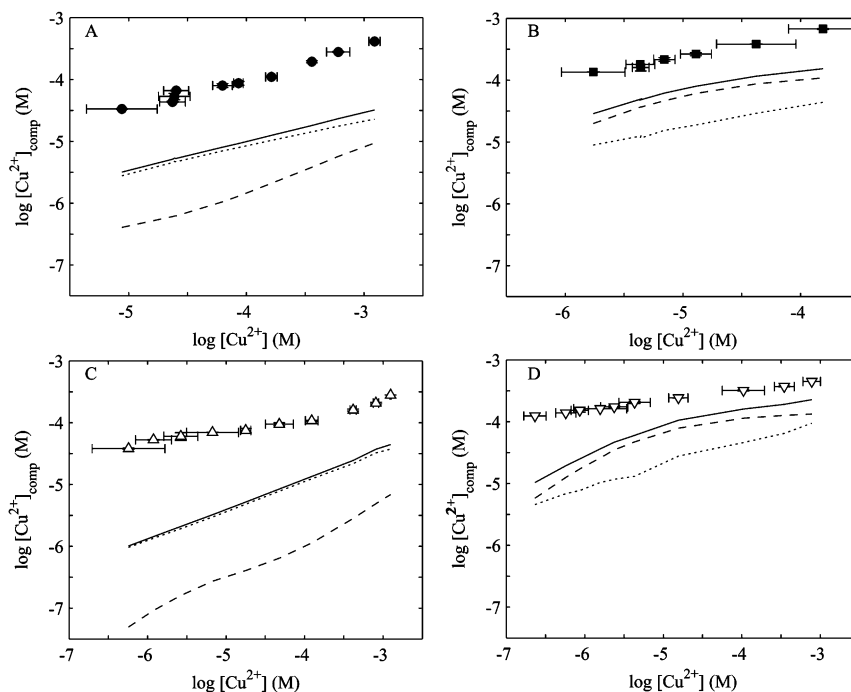


FIGURE 4. Comparison of the measured Cu^{2+} binding isotherms to the PAHA/goethite complex at 0.088 g of PAHA (total)/g of goethite with the calculated isotherms to PAHA (dotted curves, amount equivalent to the adsorbed amount) and bare goethite (dashed curves) and the sums of the PAHA and goethite isotherms (solid curves, noninteracting PAHA and goethite): (a) pH 4, 0.1 M KNO_3 ; (b) pH 6, 0.1 M KNO_3 ; (c) pH 4, 0.01 M KNO_3 ; (d) pH 6, 0.01 M KNO_3 .

concentration from 0.1 to 0.01 M KNO_3 to an increase of this difference at relatively low $\log [\text{Cu}^{2+}]$, but to a decrease at high $\log [\text{Cu}^{2+}]$. Tipping et al. (18) have reported a similar enhancement of Cu^{2+} binding to a HA/goethite complex in the acidic pH region.

Cu^{2+} /PAHA/Goethite: Effects of the PAHA (Total)/Goethite Ratio. The dependence of the Cu^{2+} binding isotherms to the PAHA/goethite complex on the PAHA (total)/goethite ratio measured at 0.1 M KNO_3 are presented in parts A and B of Figure 5 for pH 4 and 6, respectively. Similarly as before the measured isotherms (symbols) are compared with the calculated ones (curves, noninteracting PAHA and goethite). At pH 4 the difference between the measured isotherms and the calculated ones strongly depends on the PAHA/goethite ratio: the lower the ratio, the larger the enhancement of Cu^{2+} binding. At pH 6 the calculated and measured isotherms are relatively close to each other, and the trend with respect to the PAHA/goethite ratio is somewhat obscure.

Discussion

XAFS measurements of Cu^{2+} /HA/goethite complexes at pH 5 and 0.1 M KNO_3 by Alcacio et al. (35) revealed the structures of the ternary complexes among Cu^{2+} /HA/goethite. At relatively low HA adsorption (≤ 0.94 mg of HA/ m^2 of goethite) the obtained Cu K-edge spectra were "goethite-like", and the authors attributed this to the bridging between HA and goethite by Cu^{2+} ions (type A ternary complex (35)). On the other hand, at relatively high HA adsorption (≥ 2.3 mg of HA/ m^2 of goethite) the spectra were "humic-like", which was attributed to the binding of Cu^{2+} to the HA that adsorbed on goethite (type B ternary complex (35)). At 0.176 g of PAHA (total)/g of goethite, where the adsorbed amounts of PAHA are 2.0 mg/ m^2 at pH 4 and 1.1–2.0 mg/ m^2 at pH 6, Cu^{2+} ions most probably bind to the functional groups of the adsorbed PAHA, and at the lower PAHA (total)/goethite ratios some of the Cu^{2+} ions may bridge between PAHA and goethite or directly bind to the goethite surface under the influence of the adsorbed PAHA. Keeping the possible change of dominant

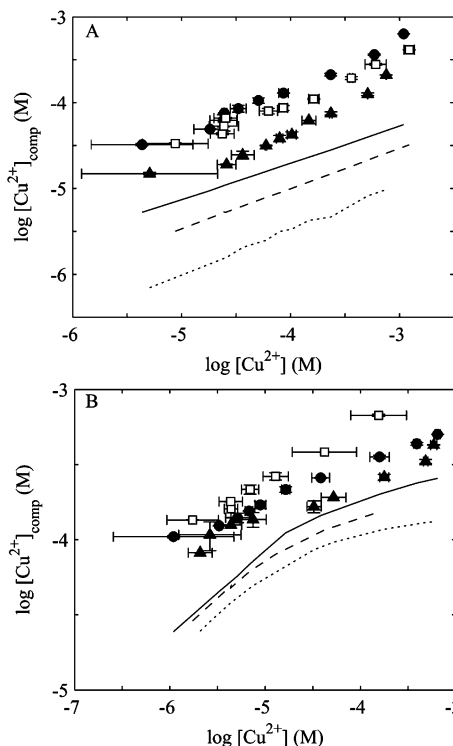


FIGURE 5. Cu^{2+} binding isotherms to the PAHA/goethite complex at 0.1 M KNO_3 , pH 4 (A) and 6 (B), and different PAHA (total)/goethite ratios: $\bullet$, 0.176; $\square$, 0.088; $\blacktriangle$, 0.022 g of PAHA/g of goethite. The curves represent the sums of Cu^{2+} isotherms on PAHA plus that on bare goethite assuming no interaction between PAHA and goethite: solid curves, 0.176; dashed curves, 0.088; dotted curves, 0.022 g PAHA (total)/g goethite.

forms of the bound Cu^{2+} as a function of the PAHA loading in mind, the question that remains unsolved is the following: What is the driving force for the enhancement of Cu^{2+} binding reported in the previous sections? The formation of

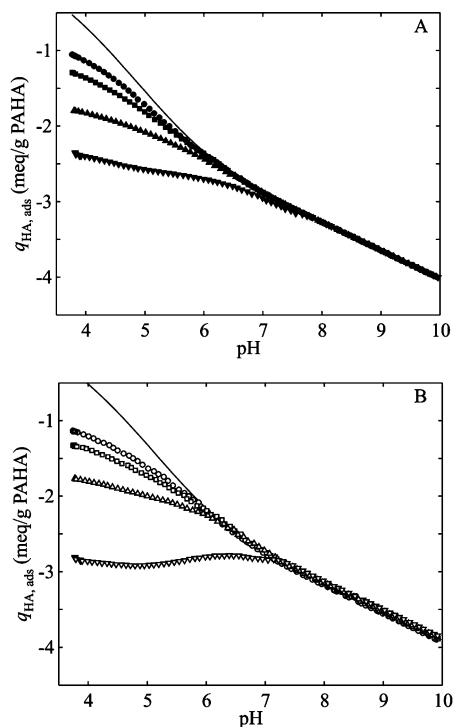


FIGURE 6. Charge of PAHA adsorbed on goethite ($q_{\text{HA,ads}}$) as a function of pH at 0.1 M KNO_3 (A, closed symbols) and 0.01 M KNO_3 (B, open symbols) for different PAHA (total)/goethite ratios: $\bullet$, $\circ$, 0.22; $\blacksquare$, $\square$, 0.13; $\blacktriangle$, $\triangle$, 0.088; $\blacktriangledown$, $\triangledown$, 0.044 g of PAHA/g of goethite. The solid lines represent the charge/pH curves of free PAHA. The results are replotted from ref 17.

the type A ternary complex might be one option. However, even at the highest PAHA/goethite ratio the enhancement still remains. Besides, with this mechanism only it seems to be difficult to explain the dependence of the enhancement on pH and the salt concentration.

From the H^+ binding experiments to the PAHA/goethite complex in the absence of Cu^{2+} , we discovered that upon the adsorption of PAHA H^+ is released from its functional groups at neutral to acidic pH and the electrostatic potential at the PAHA/goethite interface becomes less positive (17). This is because at this pH range the absolute value of the negative charge of PAHA in the bulk solution is small compared with that of the positive charge of goethite, and upon PAHA adsorption, H^+ is desorbed from the PAHA functional groups near the surface due to the strong positive potential of goethite. On the basis of these observations, there can be two mechanisms for the Cu^{2+} binding enhancement: (i) the change of H^+ competition for the functional groups of the adsorbed PAHA; (ii) the change of Cu^{2+} activity at the PAHA/goethite interface. In Figure 6 the charge/pH curves of the PAHA adsorbed on goethite at 0.1 and 0.01 M KNO_3 in the absence of Cu^{2+} as described in ref 17 are replotted. Take the Cu^{2+} binding to the PAHA/goethite complex at 0.088 g of PAHA (total)/g of goethite, pH 4, and 0.1 M KNO_3 as an example. From Figure 6A, in the absence of Cu^{2+} the charge of the adsorbed PAHA ($q_{\text{HA,ads}}$, closed triangles) at this condition corresponds to that of PAHA in the bulk solution (solid line) at around pH 5.5. In the presence of Cu^{2+} the adsorbed amounts of PAHA are slightly smaller than those in the absence of Cu^{2+} (Figure S3C in the Supporting Information), and a more negative charge might be induced on the adsorbed PAHA. Hence, it may be reasonable to assume that the H^+ activity in the vicinity of the functional groups of the adsorbed PAHA at this condition approximately equals that at pH 5.5–6 in the bulk solution. Considering Cu^{2+} binding isotherms to PAHA in the bulk solution, an

increase of pH from 4 to 6 at 0.1 mol/L KNO_3 results in an increase of Cu^{2+} binding by 1 order of magnitude (25). This seems to correspond to the difference between the bound amount of Cu^{2+} to the PAHA/goethite complex and the noninteracting sum at this condition (Figure 4A). In other words, Cu^{2+} binding to the complex is enhanced because H^+ competition for the functional groups of the adsorbed PAHA is diminished upon PAHA adsorption (the type B ternary complex). Meanwhile, according to our calculation of the smeared-out potential profile at the PAHA/goethite interface (17), the electrostatic potential near the goethite surface, where the adsorbed Cu^{2+} ions on goethite are located, becomes less positive compared with that in the absence of PAHA. This change of the potential leads to an increase of the Cu^{2+} activity and, in turn, to an increase of its adsorbed amount on goethite and/or the formation of the type A ternary complex. Tipping et al. (18) attributed the enhancement of Cu^{2+} binding in acidic pH to the additional high-affinity sites created by HA adsorption, which might correspond to these mechanisms.

The possible effect of the heterogeneity of HA on the above interpretation should be mentioned here. HA solution is a mixture of fractions with different molar masses. Because high molar mass fractions preferentially adsorb on an oxide surface, the fractionation takes place upon adsorption (36, 37). This will be a source of artifacts for the evaluation of the metal binding enhancement in a ternary system, because the molar mass distribution of HA in the supernatant solution may differ from that of the original solution. However, it is expected that this effect is not so serious because metal bindings to different size fractions of HA are reported to be similar to each other (38). To further validate the above two mechanisms, similar experiments with polyelectrolytes of well-defined compositions and single sizes as models of HA are demanded.

The above interpretation also explains the dependence of the enhancement of Cu^{2+} binding to the PAHA/goethite complex on pH, salt concentration, and PAHA (total)/goethite ratio. First, with increasing pH, the induced negative charge on the adsorbed PAHA decreases as shown in Figure 6 and the level of H^+ competition to the functional groups of the adsorbed PAHA approaches the bulk level. This leads to a decrease of the enhancement of Cu^{2+} binding to the PAHA/goethite complex, although the potential near the surface becomes further less positive and compensates the above decrease somewhat. Second, the primary effect of changing the salt concentration is the change of the degree of charge screening, which may result in enhancement or diminishment of Cu^{2+} binding to the PAHA/goethite complex. At low $\log [\text{Cu}^{2+}]$ a decrease of the salt concentration can result in an increase of the Cu^{2+} binding enhancement since the degree of H^+ competition is reduced, comparing parts A and B of Figure 6. On the other hand, at high $\log [\text{Cu}^{2+}]$, where the potential in the vicinity of the goethite surface might be more positive because of the accumulation of Cu^{2+} in this region, a decrease of the salt concentration may result in a decrease of the enhancement of Cu^{2+} binding to the complex. Finally, the above two mechanisms can also explain the dependence of the enhancement of Cu^{2+} binding on the PAHA/goethite ratio. With a decrease of this ratio the H^+ competition to the functional groups of the adsorbed PAHA is reduced as shown in Figure 6. Furthermore, the potential in the vicinity of the goethite surface becomes less positive compared with the potential at relatively high PAHA loading, because the adsorbed PAHA takes a more flat configuration at low loading (17). Both mechanisms lead to the enhancement of Cu^{2+} binding to the complex. It should be mentioned that the above discussion contradicts the results of Alcacio et al. (35) to some degree. According to the authors, the type A complex dominates at relatively low PAHA/goethite ratio. On the other

hand, our results suggest that Cu^{2+} binds to the PAHA/goethite complex via the formation of both the type A and B complexes. In our opinion, if there are some functional groups available for Cu^{2+} after the formation of the type A complex, the further binding of Cu^{2+} to these groups is possible, forming the type B complex. This can also be justified because a PAHA molecule is three-dimensionally structured and has more than 100 functional groups per molecule.

It is also of interest to compare the above results with those in other ternary systems: Ca^{2+} binding to the Strichen fulvic acid (SFA)/goethite complex by Weng et al. (23), Cd^{2+} binding to the PAHA/hematite complex by Vermeer et al. (22), and uranyl (UO_2^{2+}) binding to the Suwannee River HA (SRHA)/hematite complex by Lenhart et al. (21). At relatively low pH the bound amounts of Ca^{2+} and Cd^{2+} to the HS/oxide complexes are smaller than the corresponding noninteracting sums, and at relatively high pH the trend reverses. On the other hand, the UO_2^{2+} binding to the SRHA/hematite complex is similar to that of Cu^{2+} to the PAHA/goethite complex in this work. Although direct comparison is difficult because of the different HS loadings and the difference of the HSs and oxides used, the following interpretation might be made. The binding of the metal ions such as Ca^{2+} and Cd^{2+} is sensitive to the change of electrostatic potential near the binding sites because these ions bind relatively weakly to the (surface) functional groups of HSs and oxides and the electrostatic contribution to their binding is generally large. Upon adsorption HS and oxide partially neutralize each other. Hence, at relatively low pH these ions may be released from the functional groups of the adsorbed HS due to the (strong) positive potential of the oxide surface, although the increased adsorption to the oxide surface due to the less positive potential of the surface compared with that of the bare surface compensates this somewhat. This situation is analogous to the H^+ release from the adsorbed HS (22, 23). On the other hand, metal ions such as Cu^{2+} and UO_2^{2+} specifically bind to the (surface) functional groups of HSs and oxides. The bound amounts of these ions to the HS/oxide complexes increase at neutral to acidic pH with respect to the sums of their bound amounts in the equivalent binary systems because H^+ competition at the HS/oxide interface is smaller than in the bulk solution and the potential near the interface becomes less positive due to the adsorption of HS.

The conclusion obtained in this study can be generalized to metals that specifically bind to NOM and oxide and is of great use in relation to the improvement of risk assessments for the contamination by such metals. One such example is the underground disposal of radioactive wastes from nuclear power plants. The results obtained in this study suggest that even at low concentration of NOM, which might be the case in the underground where the radioactive wastes are disposed, the binding of a target contaminant to mineral surfaces covered by the adsorbed NOM can be different from that to the bare surfaces and that the experimental results obtained in the simple binary systems without NOM should be considered with some caution if they were used for the prediction of the binding. It is also noteworthy to mention that in natural environments metals other than target metals, such as calcium, magnesium, aluminum, and iron, are present with relatively high concentrations and possibly have an influence on the binding of the target metals, not only because these metals compete for the same binding sites with the target metals, but also because they change the electrostatic and/or structural properties of NOM, oxide, and their complex. This is of great interest and will be investigated when we move on to the modeling of metal binding in ternary systems.

Supporting Information Available

Relevance of Aldrich HA as a model of HA, the NICA–Donnan parameters used for the calculation of bound amounts of Cu^{2+} to dissolved PAHA (Table S1), the time dependence of the Cu^{2+} binding to the PAHA/goethite complex with 0.088 g of PAHA (total)/g of goethite (Figure S1), the comparison of the Cu^{2+} binding to the complex with that to the dissolved PAHA at other conditions than depicted in Figure 2 (Figure S2), and the adsorbed amounts of PAHA in the absence and presence of Cu^{2+} (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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