COMPLEXATIONS IN ILLITE–FULVIC ACID– Cu^{2+} SYSTEMS

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Abstract—As part of an extended project to illustrate how heavy metals are complexed by natural aquatic particles, we conducted various experiments to study the adsorption of fulvic acid (FA) at aqueous illite surfaces and the complexation of heavy metal copper(II) in illite–FA bi-complexant systems. By analyzing batch adsorption and potentiometric titration data, we found that (i) the adsorption of FA by illite decreases with increases in pH values and its pH adsorption edge resembles those of SiO_2 –FA and montmorillonite–FA systems described by other researchers, (ii) it is possible to effectively simulate the complexation of Cu^{2+} ions in illite–FA bi-complexant systems by taking it to be an additive complexation of two mono-complexant systems (FA– Cu^{2+} and illite– Cu^{2+}) and (iii) FA can inhibit the retention of heavy metals at solid surfaces by forming soluble complexes with metal ions. The above results and conclusions are supported by FT-IR analysis of various illite–FA– Cu^{2+} systems. © 1998 Elsevier Science Ltd. All rights reserved

Key words—illite, fulvic acid, heavy metal, complexation

INTRODUCTION

Reactions at the solid/water interface play an important role in controlling the transportation, speciation and ecotoxicity of heavy metal pollutants in natural aquatic environments. Over the past few years, we have been working to develop a comprehensive model to help explain these reaction mechanisms. Since the composition of natural particles is complex, we believed it necessary in developing our model to consider in detail reaction properties and cross-interactions of each of their main components. In particular, we decided to examine four general reactions: (i) how heavy metals are adsorbed at inorganic solid surfaces, (ii) how metal ions are complexed by natural organic materials (mainly humic substances), (iii) how mineral surfaces interact with organic matter, and (iv) how metal complexation by organics affects the uptake of metal ions by mineral surfaces.

As to the one of these reactions, we reported in earlier papers on our findings related to adsorption properties of illite surfaces (Du *et al.*, 1997a,b). In this paper we deal with the latter three reactions; specifically, we investigate the acid–base properties of fulvic acid, the interaction between illite and fulvic acid (FA) and copper complexation in illite–FA bi-complexant systems.

MATERIALS AND METHODS

Materials

Our sample of illite was obtained from Hebei Province, China and our fulvic acid sample was extracted from the Le An River sediments in southeast China. Detailed information about the preparation of illite samples and about its main element compositions are given in a previous paper (Du *et al.*, 1997a).

Our humic samples, one fulvic acid (FA) and one humic acid (HA), were extracted from the Le An River sediments in southeast China following the procedures outlined in the flow chart in Fig. 1. Their major element compositions on a dry, ash-free basis and their ash contents are given in Table 1. The element analyses were carried out by the Chemistry Institute of Academia Sinica. Ash content was determined by heating the samples at 600°C for 4 hours. For later titration experiments, a 2.5 g/L (ash free content) FA stock solution was made by dissolving the dried FA sample in distilled water. The stock solution was stored in a refrigerator.

Reagents

HNO_3 , NaOH, $\text{Cu}(\text{NO}_3)_2$, NaNO_3 and NaHCO_3 solutions were used as our primary reagents. The diluted HNO_3 was standardized against tris(hydroxymethyl)aminomethane (THAM). The NaOH solution was prepared from BDH concentrated solutions and then standardized using an acid of known concentration. $\text{Cu}(\text{NO}_3)_2$ (Orion Cat. No. 942906) at a concentration of 0.1000 M was used as the standard copper stock solution, and concentrated NaNO_3 was used to maintain various ionic strengths. Concentrated NaHCO_3 buffer solution was used to adjust the pH value of the experimental system to approximately 8.7 before the UV measurement of the FA concentration.

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Fig. 1. Extraction procedure of fulvic and humic acids.

Apparatus

A Beckman DU-650 spectrophotometer was used to quantify the FA concentration in solution. Preliminary experiments showed that the UV absorption of FA was influenced by the pH value and the ionic strength of the sample. Therefore, prior to each measurement, the sample was adjusted to a 0.05 M NaHCO₃ buffer condition (pH ~ 8.7); then the FA concentration was measured at 275 nm with a 0.01 M NaNO₃ and 0.05 M NaHCO₃ mixture solution as a blank.

An automatic system for precise emf titrations, designed by Ginstrup (1973), was used to perform potentiometric titrations. The cell arrangement, similar to that described by Forsling *et al.* (1952), was immersed in an oil thermostat

at 25.0 ± 0.5°C. A glass electrode (Ingold type 201-NS) and an Orion cupric electrode (9429SC) were used for the H⁺ and Cu²⁺ measurements, respectively, with a double junction Ag/AgCl electrode (Orion 90-02) as a reference.

A single beam PE2000 FT-IR spectrometer was used to record the infrared spectra. The DRIFT spectra were taken at a resolution of 4 cm⁻¹ by co-adding up to 200 scans in the range 4000–400 cm⁻¹ using a diffuse reflectance method. For each measurement, the sample was prepared by mixing 1 mg sample with 100 mg finely ground KBr; pure KBr powder was used as a reference.

Adsorption of FA in illite/water suspensions

We carried out our FA adsorption experiment in batch systems using a group of 100 mL plastic bottles. Each

Table 1. Element composition of the fulvic acid and the humic acid (weight%)

	C	H	N	S	O	ash
FA	41.59	6.24	11.62 ^a	<0.45	40.1	32.96 ^b
HA	52.03	5.65	5.96	1.46	34.9	4.64

^aBecause diluted HNO₃ was used to neutralize the extracted FA in the extraction procedure before the concentrated solution was dried (see Fig. 1), the high N content in the FA sample was partly caused by the presence of NO₃.

^bThe ash in the FA sample was in white powder form. The high ash content might have been caused by the large amount of hydroxide and acid used during the extraction procedure. An ICP analysis of the ash showed that its major cation was Na⁺, which indicate that the white powder ash was primarily sodium salt (NaCl or/and NaNO₃). Since a 0.1 M NaNO₃ background electrolyte concentration was used in our experiments, we believe that the sodium salt in the ash do not have much influence on our results.

sample contained 5 mL of 10 g/L illite, 2 mL of 2.5 g/L FA and 1 mL of 1 M NaNO₃. Increments of 0.1 M HNO₃ or 0.1 M NaOH were used to keep the sample pH between 2 and 10. Distilled water was added to bring the total volume of each sample to 100 mL with an illite concentration of 0.5 g/L, an FA concentration of 50 ppm and an ionic strength of 0.01 M NaNO₃. The samples were shaken for 3 hours and left overnight at 25 ± 0.5°C. Afterwards, part of each sample was filtered through a 0.45 µm Millipore membrane and the filtrate was adjusted to a 0.05 M NaHCO₃ buffer condition (pH ~ 8.7); the remainder was used for pH measurement. The FA concentration in the filtrate was determined by UV analysis. The amount of FA adsorbed by illite was then calculated from the difference between the total concentration of FA added and the FA concentration in the filtrate after adsorption.

Complexation of copper in illite-FA bi-complexant systems

The complexation behaviors of copper in systems with 5 g/L illite, 0.2 mM Cu²⁺ but various FA concentrations were investigated by conducting potentiometric titrations. For each titration, a 50 mL suspension containing 5 g/L illite in 0.1 M NaNO₃ was first prepared. N₂ was bubbled successively through 10% NaOH, 10% H₂SO₄, distilled water, 0.1 M NaNO₃, and finally into the suspension to exclude CO₂ until the electrode potential was stable. Afterwards, diluted HNO₃ solution in increments of 0.1 mL was added gradually to eliminate the carbonate impurities in the illite sample. When the system pH dropped below 2.5, 0.1 mL of 0.1000 M Cu(NO₃)₂ and a certain amount of 2.5 g/L FA solution were added. Then, 0.02001 M NaOH solution in 0.1 mL increments was used to titrate the suspension up to a pH of approximately 10. During the titration period, N₂ was bubbled to exclude CO₂ and the solution was stirred magnetically. The equilibrium criterion for each addition of the titrant was that the drift in the measured glass electrode potential was lower than 1 mV/hr. The equilibrium concentrations of H⁺ and Cu²⁺ were respectively calculated from the outputs of the glass and cupric electrodes as

$$E_H = E_H^0 + 59.157 \log[H^+] + E_j \quad (1)$$

and

$$E_{Cu} = E_{Cu}^0 + 29.58 \log[Cu^{2+}] + E_j \quad (2)$$

where E_H^0 is a constant which was determined in each titration using an *in-situ* Gran plot method and then used to calculate the pH value in terms of H⁺ concentration from the output of the glass electrode emf (Du *et al.*, 1997a). E_{Cu}^0 is a constant which was determined prior to the hydroxide titration from the output of the copper electrode after a known amount of standard Cu²⁺ solution was added. E_j is the liquid junction potential, calculated as

$$E_j \text{ (mV)} = -511.5[H^+] + 238.7K_w[H^+]^{-1}, \quad (3)$$

where $\log K_w = -13.8$ is the ionic product of water in 0.1 M medium (Sjöberg *et al.*, 1983). In the measured pH range (3–10) of our experiments, the contribution of E_j is very small and was therefore neglected.

For each titration system we set the equivalence point (V_{eb1}) obtained from the Gran plot of the hydroxide titration as the zero titration point (Du *et al.*, 1997a). This value was chosen because it is the point at which pure acid-base neutralization reactions end and the proton consumption related to complexation reactions begins. For each OH⁻ titration point, the concentration of the total protons added to the system was then calculated as

$$\text{TOT}H = -(V_b - V_{eb1}) \times C_b / (V_0 + V_{at} + V_{Cu} + V_{FA} + V_b), \text{ (mol/L)} \quad (4)$$

and the number of protons reacted (H_R) was determined by

$$H_R = [\text{TOT}H - 10^{-\text{pH}} + 10^{-(\text{p}K_w - \text{pH})}] \times (V_0 + V_{at} + V_{Cu} + V_{FA} + V_b), \text{ (mol)} \quad (5)$$

where C_b is the concentration of NaOH, V_0 the initial volume of the system studied and V_b the volume of NaOH titrated. V_{at} , V_{Cu} and V_{FA} are, respectively, the total volumes of HNO₃, Cu²⁺ and FA added.

FT-IR measurements

FT-IR analysis was used to get direct information about FA adsorption in illite suspensions with or without Cu²⁺ ions. For systems without copper, each sample was composed of 30 mg dry illite, 0.3 mL of 1 M NaCl and a certain amount of 2.5 g/L FA solution. Increments of 0.1 M HCl or 0.1 M NaOH were used to bring the system pH to a desired value, and distilled water was added to bring the total volume to 30 mL. After the samples were shaken at room temperature for 4 hours, pH values were measured and the suspensions were centrifuged at 20,000 rpm for 10 minutes at 15°C. The solid part of each sample was dried at 60°C and was then used for DRIFT measurements.

For each sample containing Cu²⁺ ions, a suspension with 30 mg dry illite, 0.3 mL of 1 M NaCl and 0.06 mL of 0.1000 M Cu(NO₃)₂ was first prepared and adjusted to a certain pH value. After the suspension was shaken for 2 hours, an FA solution with a desired concentration and pH was added, the total volume of the system being brought to 30 mL. After the sample was shaken at room temperature for another 2 hours, the final pH value was measured and the suspension was centrifuged at 20,000 rpm for 10 minutes at 15°C. The solid part of the sample was dried at 60°C and was then used for FT-IR analysis.

RESULTS AND DISCUSSION

Acid-base properties in mono-complexant systems

The copper complexation properties of illite were closely studied in our previous work (Du *et al.*, 1997a,b). We found that the surface properties of illite are similar to those of amorphous SiO₂ whose acid-base behavior can be well represented by deprotonation reactions of surface functional groups, and that the complexation properties of fulvic acid can be modelled as those of a mixture of three monoprotic acids (R₁H, R₂H and R₃H). The established copper complexation models for the two mono-complexant systems are summarized in Tables 2 and 3.

We titrated three FA systems (100, 250 and 500 ppm) and then input the obtained TOTH-pH data sets into FITEQL to analyze the acid-base properties of the FA. For determining the dissociation constants of the fulvic acid, the experimental data from different FA concentration systems were combined into one FITEQL file. Assumptions used in analyzing our data were based on the non-electrostatic, discrete site distribution model. Since there is presently no method for experimentally determining the concentration of every kind of acidic site in humic substances, we set both the acidic site concentration (T_n) and the proton

Table 2. Surface characteristic parameters and complexation properties of illite/water suspensions (particle size < 63 μ , 25°C, illite = 5 g/L, I = 0.1 M NaNO₃, Cu²⁺ = 0.1–0.2 mM)

Properties of the supernatant blank of the illite/water suspensions					
Total concentration of $\text{Al}(\text{H}_2\text{O})_6^{3+}$	0.0246				
Proton reactions of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ^a					
$\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{OH}^- = \text{Al}(\text{H}_2\text{O})_6\text{OH}^{2+}$, $\log K = 8.48$					
$\text{Al}(\text{H}_2\text{O})_6^{3+} + 2\text{OH}^- = \text{Al}(\text{H}_2\text{O})_6(\text{OH})_2^+$, $\log K = 17.6$					
Total concentration of $\text{Si}(\text{OH})_4$ (mmol/L)	0.523				
Proton reactions of $\text{Si}(\text{OH})_4$ ^a					
$\text{Si}(\text{OH})_4 = \text{SiO}(\text{OH})_3^- + \text{H}^+$, $\log K = -9.46$					
$\text{SiO}(\text{OH})_3^- = \text{SiO}_2(\text{OH})_2^{2-} + \text{H}^+$, $\log K = -12.56$					
Surface characteristic parameters of illite					
N_2/BET surface area S (m^2/g)	22.3	Specific constant capacitance C (F/m^2)	1.7		
Total proton surface sites H_S (mmol/L)	0.642	Surface site density (sites/ nm^2)	3.5		
Complexation properties of aqueous illite surfaces					
Surface proton reaction	$\equiv\text{SOH} = \equiv\text{SO}^- + \text{H}^+$ $pK_a^{\text{int}} = 4.23$				
Adsorption of Cu^{2+}	$\equiv\text{SOH} + \text{Cu}^{2+} = \equiv\text{SOCu}^+ + \text{H}^+$	$\log K_{\equiv\text{SOCu}^+} = -3.16$			
	$\equiv\text{SOH} + \text{Cu}^{2+} + \text{H}_2\text{O} = \equiv\text{SOCuOH} + 2\text{H}^+$	$\log K_{\equiv\text{SOCuOH}} = -8.51$			

^aThe acidic constants of Al((H₂O)₆)³⁺ and Si(OH)₄ in water solutions are taken from Smith and Martell (1976).

dissociation constant (*K_n*) as adjustable parameters in our calculations. The optimized results were found to be independent of the starting values of *T_n* and *K_n*.

Our modelling procedure was to start with the simplest situation, in which only one fulvic acidic site with a concentration of *T* and a dissociation constant of *K* was considered, and then add acidic sites until we got the best fit of our experimental data using a minimum number of parameters. Doing this, we found that the acid–base properties of the FA could be best represented by those of a mixture of three monoprotic acids (6 parameters, 3 *K* values and 3 *T* values):

Table 3 shows the optimized results and error analyses and Fig. 2 the model calculated titration curves and the experimental data. From Fig. 2, it can be seen that the acid–base properties of various FA systems can be well described using only one set of parameters, which indicates that the dissociation of fulvic acid can be appropriately modelled using the proton reactions of several simple monoprotic acids. It also suggests that the relatively high ash content in the FA sample had little influence on the complexation properties of the FA.

The proton dissociation constants of different humic substances have been determined by other researchers using different modelling methods (see Table 4). The models used in most studies incorporated dissociation constants in different pH regions to describe the acid–base chemistry of humic substances, although some models only had constants

in the acidic pH region, which can probably be explained by the fact that the analyzed data did not cover a broader pH range. Our modelling results also show that the deprotonation of humic substances includes proton dissociation reactions in both acidic and alkaline pH regions (Table 3). Compared with the dissociation constants of simple organic acids, the constants in the acidic pH region (*pK*₁ and *pK*₂ of our samples) correspond roughly to those of carboxylic acids and the constants in the alkaline pH region (*pK*₃ of our samples) to those of phenols. This agrees with the fact that the acid capacity of humic substances is due mainly to the dissociation of their carboxyl and phenolic hydroxyl groups. Nevertheless, we should point out that the three monoprotic acid sites proposed in our model do not necessarily correspond to physically real humic binding sites and cannot be treated as true chemical species. The chemistry and structure of humic substances are far too complex for us to be able to determine this.

Copper complexation properties

We studied the pH-dependent Cu²⁺–FA complexation properties by titrating with hydroxide FA systems containing various amounts of Cu²⁺ ions. As can be seen in Figs 2 and 3, for any given pH and humic concentration level, more protons were released in the Cu–FA system (Fig. 3) than in the pure FA system (Fig. 2). After incorporating some assumptions about proton-involving reactions between Cu²⁺ and the three acidic sites of the FA into our complexation model, we analyzed the TOTH-pH titration data sets using FITEQL and calculated the formation constants of the assumed copper–humic species. We then used these constants to predict the copper binding by the FA and compared the model predictions with our experimental data. In calculating the formation constants, we did

Table 3. Acid-base and copper complexation properties of a fulvic acid extracted from river sediments (25°C, I = 0.1 M NaNO₃, FA = 100–500 ppm, Cu²⁺ = 0.1–0.2 mM)

Acid-base properties					
Proton reaction	dissociation constant $pK_a\pm3\sigma$	proton site concentration (mmol/g FA) $T \pm 3\sigma$			
R ₁ H = R ₁ [−] + H ⁺	4.05 ± 0.014	1.11 ± 0.008			
R ₂ H = R ₂ [−] + H ⁺	5.79 ± 0.046	0.62 ± 0.008			
R ₃ H = R ₃ [−] + H ⁺	8.43 ± 0.034	1.15 ± 0.011			
Copper complexation properties					
system	V_Y	log $K_{R_1Cu^+}\pm3\sigma$	log $K_{R_1CuOH}\pm3\sigma$	log $K_{R_3CuOH}\pm3\sigma$	log $K_{(R_1)_2Cu}\pm3\sigma$
250 ppm FA, 0.2 mM Cu ²⁺	6.19	−1.21 ± 0.13	−5.83 ± 0.025	−10.23 ± 0.086	
250 ppm FA, 0.5 mM Cu ²⁺	13.50	−1.12 ± 0.064	−5.81 ± 0.017	−9.96 ± 0.024	
500 ppm FA, 0.2 mM Cu ²⁺	3.48	−0.62 ± 0.053	−5.08 ± 0.023	−8.74 ± 0.065	
500 ppm FA, 0.5 mM Cu ²⁺	11.15	−1.52 ± 0.085	−5.56 ± 0.011	−9.64 ± 0.039	
mean value		−1.12	−5.57	−9.64	
500 ppm FA, 0.2 mM Cu ²⁺	10.75	−1.12	−5.57	−9.64	−1.36 ± 0.053 ^a

^aThis constant was optimized after fixing the formation constants of species R₁Cu⁺, R₁CuOH and R₃CuOH at their corresponding mean values.

not include the Cu²⁺ concentration measured by the cupric electrode into the input data file because (i) we found during the experiments that the cupric electrode was a little less sensitive in the systems with humic substances and (ii) the calculations were less complicated when only the total protons added (TOT) and the corresponding system pH were considered. As to the assumption about copper-humic species, either monodentate or chelate complexes are likely formed in complexation reactions; there are spectroscopic analyses that gave evidence for each possibility (Boyd *et al.*, 1981, 1983). Since the three monoprotic acid sites in our humic complexation model do not necessarily correspond to real binding sites, to simplify model assumptions and calculations, we started by choosing simple, monodentate copper-humic species in modelling the complexation of copper by our samples. We then added more complicated ones only when necessary. The goal was to fit all the experimental data using a minimum number of parameters.

Copper complexation of the extracted fulvic acid. Five Cu²⁺-FA systems with three different FA concentrations (100, 250 and 500 ppm) and two different Cu²⁺ concentrations (0.2 and 0.5 mM) were investigated. We analyzed the TOT-pH data sets of each system and found that they can be well explained if we introduce the following monodentate Cu²⁺-FA reaction assumptions, which consider only the strongest and the weakest acidic sites (R₁H and R₃H), into our model:

The FITEQL-estimated constants for the above

reactions in each analyzed system are given in Table 3. The mean values of the constants for the corresponding reactions were used to simulate the pH-dependent reacted-protons and to predict the pH-dependent copper complexation behaviors in various systems. A good fit exists between the model-calculated H_R -plots and the experimental data up to a pH of about 8.5 (Fig. 3). The reasonable model predictions for copper binding in Fig. 4 support our assumptions about the Cu²⁺-FA interactions.

There are two things that need more explanation. First, although the proposed Cu²⁺-FA complexation model gave results that match the experimental data very well up to a pH of about 8.5, at pH > 8.5, the model underestimated the protons-released, especially for the systems with higher copper concentrations (0.5 mM) (Fig. 3). This discrepancy might be attributable to the formation of copper hydroxide precipitates at higher pH values. Due to design limitations in FITEQL, we could not include any precipitation reactions in our model calculations. Given the many uncertainties of the characteristics of humic substances and the many possibilities of Cu²⁺-humic interactions, we decided not to try other methods to fit the experimental data too precisely. Second, the model, which considers the formation of R₁Cu⁺, R₁CuOH and R₃CuOH complexes, explains the copper-binding data fairly well for all systems, except for the one with 500 ppm FA and 0.2 mM Cu²⁺ (Fig. 4). For this system, the model predicts a lower copper complexation level than was actually measured. This suggests that the reactions represented by equations 9–11 do not cover all significant Cu²⁺-FA reactions. Since this system had a combination of relatively higher FA but lower Cu²⁺ concentrations, in which the concentration of the strongest FA acidic site (R₁H) (1.11 mmol/g × 0.5 g/L = 0.555 mM) was much higher than that of

Fig. 2. Experimental data and model descriptions of the potentiometric titrations of different FA and HA systems.

Cu^{2+} ions (0.2 mM), we assumed that there is an additional Cu^{2+} –FA reaction,

which forms a bidentate species. After fixing the constants for the reactions in equations 9–11 at their corresponding mean values and adding equation 12 to our model, we re-analyzed the TOTH-pH data sets of the system with 500 ppm FA and 0.2 mM Cu^{2+} . The obtained constant is given in Table 3. The model including the formation of $(\text{R}_1)_2\text{Cu}$, together with the other three species, R_1Cu^+ , R_1CuOH and R_3CuOH , greatly improved the fit of the data (dashed line in Fig. 4). These results suggest that our Cu(II)–FA complexa-

tion model can give a good fit of the copper-binding data under our experimental conditions, but that it may not be reliable in predicting results accurately in systems with different conditions.

Adsorption of fulvic acid at aqueous illite surfaces

In our batch adsorption experiment, we found that the FA adsorption at the aqueous illite surfaces decreased with increases in pH values, the major adsorption occurring at $\text{pH} < 4$ (Fig. 5). The reason for this becomes clear when the charge properties of our illite and the fulvic acid samples are considered. Zeta potential measurements of the illite suspensions showed that the illite had a weak negative charge even at a pH as low as 2 (Du *et al.*,

Fig. 3. pH-dependent protons-reacted (H_R) in systems of FA and Cu^{2+} ions. Points: experimental data. Solid lines: model simulation in which the formation of species R_1Cu^+ , R_1CuOH and R_3CuOH was considered. Dashed line: model simulation in which the formation of species R_1Cu^+ , R_1CuOH , R_3CuOH and $(\text{R}_1)_2\text{Cu}$ was considered.

Table 4. Proton dissociation constants (pK_a) of humic substances

Discrete site distribution model					
Modelling using a group of monoprotic acids (R _n H)				ELEC ^a	Reference
R ₁ H → R ₁ + H	R ₂ H → R ₂ + H	R ₃ H → R ₃ + H	R ₄ H → R ₄ + H		
4.05–4.71	5.79–6.73	8.43–9.01		No	this paper
4.21	6.95			Yes	Bolton <i>et al.</i> , 1996
4	6	8	10	No	Westall <i>et al.</i> , 1995
					Tipping and Hurley, 1992
3.3–3.3/2	3.3–3.3/6	3.3 + 3.3/6	3.3 + 3.3/2	Yes	
9.6–5.5/2	9.6–5.5/6	9.6 + 5.5/6	9.6 + 5.5/2		
~2.5	~4.5			Yes	Tipping <i>et al.</i> , 1988
					Backes and Tipping, 1987
3.155				Yes	
1.8	3.4	4.2	5.7	Yes	Ephraim <i>et al.</i> , 1986
Modelling using a group of diprotic acids (H ₂ X)					
H ₂ A → HA + H	HA → A + H	H ₂ B → HB + H	HB → B + H		
4.0	5.32	7.43	9.23	No	Bolton <i>et al.</i> , 1996
3.7	4.3				Lövgren <i>et al.</i> , 1987
Continuous site distribution model					
μ _I	σ _I	μ _{II}	σ _{II}		
3.62	2.31	12.3	1.68	No	Perdue and Lytle, 1983
3 ~ 4		8 ~ 9		Yes	de Wit <i>et al.</i> , 1993

^aIn the ELEC column, "Yes" indicates that electrostatic effect was considered in the model, "No" indicates that it was not.
 μ : mean pK_a value; σ : standard deviation for the distribution of pK_i about μ .

1997a). The dissociation constant (pK) for the strongest acidic site of our FA sample (R_1H) was about 4 (Table 3). This suggests that at $pH < 4$, the FA behaved essentially like an uncharged molecule and that less charge-induced repulsion therefore existed between the illite and the protonated FA. At higher $pH (> 4)$, more and more FA functional groups were ionized. The increased negative charge caused a strong electrical repulsion between the FA molecules and the illite surfaces, which can

explain the decreasing FA adsorption as the pH became greater than 4.

Schulthess and Huang (1991) have comprehensively studied the humic and fulvic acid adsorption by Al and Si oxides and by clay minerals kaolinite (1:1 type) and montmorillonite (2:1 type). By comparing the behaviors of the clay minerals with those of their component oxides, namely amorphous Al and Si oxides, they found a strong adsorption of humic substances at the Al sites on the Al oxide

Fig. 4. Copper complexation by the fulvic acid sample, plotted as free Cu^{2+} ions as a function of pH . Points: experimental data. Solid lines: model predictions in which the formation of species R_1Cu^+ , R_1CuOH and R_3CuOH was considered. Dashed line: model prediction in which the formation of species R_1Cu^+ , R_1CuOH , R_3CuOH and $(R_1)_2Cu$ was considered.

Fig. 5. Adsorption of the fulvic acid at the aqueous illite surfaces.

and kaolinite and a weak adsorption at the Si sites on the Si oxide and montmorillonite. They attributed the different adsorption properties of the two clay minerals to the differences between their chemical structures, which determine the different site proportions (Si site: Al site) at the two clay surfaces. The pH adsorption edge of FA at illite surfaces in our study (Fig. 5) resembles those of FA at SiO₂ and montmorillonite surfaces described in their studies. This is not surprising since illite is similar to montmorillonite in that it is also a 2:1 type clay mineral in which the exposed surface is dominated by Si sites. This conclusion is also in agreement with our previous research result that the surface behavior of illite resembles that of amorphous SiO₂ (Du *et al.*, 1997a).

According to Schulthess and Huang (1991), the adsorption of humic substances (RH) by clay minerals might be explained as the result of H-bond formation, as represented by the following equation:

Under this assumption, the mechanism of FA adsorption by illite can be accounted for by assuming that the functional groups of FA (RH) form H-bonds at the illite surfaces.

Copper complexation in bi-complexant systems

Experimental results. We studied the copper complexation behaviors in three bi-complexant systems containing 0.2 mM Cu²⁺, 5 g/L illite and various FA concentrations (100, 250 and 500 ppm). The pH-dependent copper complexations in the three systems, together with those in the illite-Cu²⁺ (c.f. Du *et al.*, 1997b) and FA-Cu²⁺ mono-complexant systems, are depicted in Fig. 6. Experimental data representing the variation of reacted protons as a

function of pH in the three bi-complexant systems are shown in Fig. 7. The information in Fig. 6 can be summarized as follows:

(i) In the bi-complexant system with the lowest FA concentration (100 ppm), the decrease of free Cu²⁺ with the increase of pH closely matched that in the system without FA, which indicates that the copper complexation was primarily due to copper adsorption by the illite surfaces.

(ii) In the bi-complexant system with the highest FA concentration (500 ppm), the behavior of the pH-dependent copper complexation was similar to that in the system with only 500 ppm FA as complexant. This implies that the complexation of copper by fulvic acid controls copper distribution.

(iii) In the bi-complexant system with 250 ppm FA, at lower pH values (pH < 5), the copper complexation closely matched that in the corresponding FA-Cu²⁺ mono-complexant system. When the pH was greater than 5, fewer free Cu²⁺ ions remained in the bi-complexant system than in each of the two separate mono-complexant systems (FA-Cu²⁺ and illite-Cu²⁺). It is probable that copper was additively bound to the illite and the FA; this suggests that the illite surfaces and the FA functional groups might compete with each other in determining copper speciation.

Model simulations. We developed a surface complexation model successfully explain the copper complexation behaviors in illite-Cu²⁺ (Table 2) and FA-Cu²⁺ (Table 3) mono-complexant systems, respectively. Since there is little interaction between FA and illite surfaces (Fig. 5) in the main copper-binding pH range (pH 4–6, Fig. 6), and since a weak adsorption of FA by Si sites (the dominant surface site of illite) has been demonstrated (Schulthess and Huang, 1991), we decided to combine the two mono-complexant system models to explain our experimental data and to describe cop-

Fig. 6. Copper complexation in the illite- Cu^{2+} , FA- Cu^{2+} mono-complexant systems and in the illite-FA- Cu^{2+} bi-complexant systems, plotted as free Cu^{2+} ions as a function of pH.

per speciation in the bi-complexant systems. In the model calculations, the reactions between the FA and illite were ignored. Model simulations were performed by using the parameters and constants given in Tables 2 and 3 with the help of the SOLGAS-WATER computer program (Eriksson, 1979).

Copper Speciation

The model-calculated copper speciation in the bi-complexant systems and the related experimental data are presented in Fig. 8(a)–(c). The reasonably good fit between the model simulations and the data indicates that the complexation of Cu^{2+} in the bi-complexant systems can be taken to be a combination of individual bindings by the illite surfaces and the fulvic acid. In other words, it implies that there is a weak interaction between illite and FA,

or at least that the interaction has little influence on their individual binding properties.

A further analysis of the copper species related to the illite surfaces and the fulvic functional groups helps explain the experimental results shown in Fig. 6. From the information given in Tables 2 and 3, we calculated the total illite and FA site concentrations in the bi-complexant system with 100 ppm FA, the former (0.642 mM) being much higher than the latter (0.288 mM). This suggests that the illite surfaces were the major binding sites in this system. It is apparent that the copper species at the illite surfaces, $\equiv\text{SOCu}^+$, was the main copper complex (Fig. 8(a)). In the bi-complexant system with 250 ppm FA, the total illite and FA site concentrations were 0.642 and 0.721 mM, respectively. The closer values imply that the illite surfaces and the

Fig. 7. pH-dependent protons-reacted (H_R) in bi-complexant systems. Points: experimental data. Lines: model simulations using the parameters and constants in Tables 2 and 3.

Fig. 8. Distribution of copper species in bi-complexant systems with 0.2 mM Cu^{2+} , 5 g/L illite and various FA concentrations. Points: experimental data. Lines: model calculations. (a) FA = 100 ppm; (b) FA = 250 ppm; and (c) FA = 500 ppm.

FA functional groups can compete in binding Cu^{2+} ions. It can be seen from Fig. 8(b) that both the copper-illite surface complex, =SOCu^+ , and the copper-fulvic complex, R_1CuOH , were the domi-

nant copper species. When the FA was at 500 ppm, its total site concentration was 1.439 mM, much larger than that of the illite (0.642 mM). In this case, the FA functional groups were the main copper

complexants. Figure 8(c) shows that the copper species related to the FA, (R₁)₂Cu and R₁CuOH, predominated in the entire pH range of copper complexation (pH 3–6).

The influence of FA or water soluble organics on the uptake of Cu²⁺ ions by clay minerals kaolinite and montmorillonite has been studied by other researchers (Inskeep and Baham, 1983; Dalang *et al.*, 1984). They found that for systems with the same total metal concentration, less copper was adsorbed at solid surfaces in the bi-complexant systems than in those without organics, which is in accord with our results.

We can conclude from the above that in natural water systems fulvic acid, the lower molecular weight and water-soluble fraction of humic substances, can compete with solid surfaces to bind heavy metal ions by forming soluble complexes. This process inhibits the retention of heavy metals by sediments but favors their transportation in aquatic environments. The distribution of metal ions between surface and soluble complexes is dependent on the relative concentrations of the solid and soluble complexants.

Variation of Reacted-protons as a Function of pH

Figure 7 shows our experimental data and model estimates of reacted-protons in the three bi-complexant systems. As can be seen, the model fairly well described the proton changes in the bi-complexant systems with relatively lower FA concentrations (100 and 250 ppm), but overestimated the protons-released in the system with the higher FA concentration (500 ppm). Since at higher FA concentrations, it is likely that more FA functional groups bind with illite surfaces, thereby influencing macroscopic reaction results (e.g., the number of protons released), the model overestimation might be due to the fact that we did not consider the FA-illite interaction in our model. This can be further analyzed as follows.

At low pH values, FA was adsorbed at the illite surface (Fig. 5), the likely reaction mechanism being that H-bonds formed between illite and FA (see equation 13). It follows that fewer illite surface hydroxyl groups and fulvic acidic sites were available for binding copper ions, and so the adsorption of FA by illite indirectly influenced the number of protons-reacted in the experimental system, even though no H⁺ or OH⁻ was released in the reaction. Assuming that H-bonds were formed between the strongest acidic sites of our FA sample (R₁H) and the illite surface hydroxyl groups, we added equation 13 to our initial model, which only incorporates the reaction equations in Tables 2 and 3, and then re-calculated the protons released in the 500 ppm FA bi-complexant system. This gave an improved description of the experimental data below pH 4.5 (not shown in Fig. 7).

Since little FA was adsorbed by the illite at pH above 5 (Fig. 5), the model including equation 13 still did not fit the data related to the 500 ppm FA bi-complexant system at higher pH levels. This discrepancy might be attributed to the influence of reactions related to the complexation of copper ions, e.g., the formation of ternary complexes. Dalang *et al.* (1984) discuss the formation of ternary complexes between kaolinite, FA and Cu²⁺ ions, suggesting two alternative reaction mechanisms, either that Cu²⁺ acts as a bridge between FA and solid surfaces or that FA acts as a bridge between Cu²⁺ and solid surfaces. Similar mechanisms might be at work in our illite-FA-Cu²⁺ systems. However, given the complex chemical structure of fulvic acid, its copper-binding functional groups might not react with illite surfaces and it is also possible that its oxygen-containing groups other than those containing OH can react with the solid surfaces. These uncertainties make it difficult to consider the formation of ternary complexes in our model calculations. Experiments which include analyses of both free and total soluble Cu(II) ions in the bi-complexant systems and measurements of the amount of FA adsorbed in copper-containing illite suspensions may be needed to adequately explain the reactions in the illite-FA-Cu²⁺ systems.

A Brief Discussion on Another Chemical Speciation Model, WHAM

WHAM (Windermere humic aqueous model) is a recently developed computer program for calculating equilibrium chemical speciation in surface and ground water systems, sediments and soils (Tipping, 1994). It incorporates an electrostatic, discrete site model to simulate humic complexation reactions. To account for reactions related to clay minerals, cation-exchange reactions are considered; some other reactions, such as the precipitation of aluminum and iron oxides and the adsorption-desorption of fulvic acid, are also handled in the program. Although WHAM covers a broad range of reactions related to different materials common in natural systems, one of its weaknesses, in our opinion, is that the cation-exchange mechanism it uses probably does not adequately represent the complexation mechanism of clay minerals since specific adsorption at surface hydroxyl groups is the predominant reaction when trace elements are bound (Davis and Kent, 1990). This might be one reason why WHAM is suitable especially for problems where the chemical speciation is dominated by organic matter. Our model differs from Tipping's mainly in that we consider the specific adsorption at clay mineral surfaces by incorporating surface complexation principles. Since it reasonably well described copper complexation and speciation in the bi-complexant systems dominated by either illite (Fig. 8(a)) or fulvic acid (Fig. 8(c)), we believe that

Fig. 9. FT-IR spectra for various illite-FA- Cu^{2+} systems at pH about 3. (a) 1 g/L illite, pH 3.13; (b) 1 g/L illite, 200 ppm FA, pH 2.90; (c) 1 g/L illite, 200 ppm FA, 0.2 mM Cu^{2+} pH 3.42; (d) 1 g/L illite, 500 ppm FA, pH 3.14; (e) 1 g/L illite, 500 ppm FA, 0.2 mM Cu^{2+} pH 3.16; and (f) FA dry sample. Note: The peak at 1385 cm^{-1} in the dry FA sample (f) is due to the stretching vibration of impurity NO_3^- , which was used in the extraction of FA from river sediments (For details, refer to our previous work (Du *et al.*, 1997b,a)).

our model is more suitable for systems with chemical speciation determined by both inorganic solid surfaces and organic ligands.

FT-IR analysis

Figures 9 and 10 present the DRIFT spectra of various FA-illite- Cu^{2+} systems at acidic and neutral pH levels. The several notable differences between the spectra of the pure illite (Fig. 9(a) and Fig. 10(a)) and the adsorbed illite (c.f. especially Fig. 9(d), the spectrum of the sample with the most adsorption) samples provide direct evidence for FA adsorption by the illite. First, the hydrogen-bonded OH stretching vibration band (around $3300\text{--}3400\text{ cm}^{-1}$) of the FA adsorbed illite samples was more intense than that of the pure illite samples. This might indicate that the reaction mechanism between FA and illite is hydrogen-bonding. Second, the peak at 1790 cm^{-1} and the doublet peaks at 1681 and 1613 cm^{-1} of the pure illite samples were

replaced respectively by a shoulder peak and a single peak at 1660 cm^{-1} of the adsorbed ones. The peak at 1660 cm^{-1} might have been due to the C=O stretching vibration of the FA sample. Third, there are new absorption bands at 3080 , 2930 and 1530 cm^{-1} in the adsorbed samples. These peaks might be respectively associated with the aromatic and aliphatic C-H stretch bands and the carboxylate anion's asymmetric stretching vibration in the FA sample.

Comparing the above spectral characteristics of the adsorbed samples of various compositions and of those at different pH levels, we find that the adsorption of FA increased with the increase in its concentration (Fig. 9(b) and (d), Fig. 10(b) and (d)). We also find that more FA was adsorbed at lower pH values (Fig. 9(b) and Fig. 10(b), Fig. 9(d) and Fig. 10(d)), which is consistent with the results obtained from the batch adsorption experiments (Fig. 5). Furthermore, no apparent increase of FA

Fig. 10. FT-IR spectra for various illite-FA- Cu^{2+} systems at pH about 6.8. (a) 1 g/L illite, pH 6.80; (b) 1 g/L illite, 200 ppm FA, pH 6.94; (c) 1 g/L illite, 200 ppm FA, 0.2 mM Cu^{2+} pH 6.78; (d) 1 g/L illite, 500 ppm FA, pH 6.68; (e) 1 g/L illite, 500 ppm FA, 0.2 mM Cu^{2+} pH 6.68; and (f) FA dry sample.

adsorption is shown in the spectra of the copper-containing samples (Fig. 9(c), (e), Fig. 10(c) and (e)) than in those of the copper-free ones (Fig. 9(b), (d), Fig. 10(b) and (d)). This agrees with the conclusion based on our analysis of the potentiometric titrations and the model-calculated copper speciation in the bi-complexant systems, i.e., that fulvic acid tends to compete with solid surfaces in binding heavy metal ions by forming soluble complexes in natural water systems.

CONCLUSIONS

To summarize, our investigation into the adsorption of fulvic acid at illite surfaces and the copper complexation behaviors in FA-illite bi-complexant systems has yielded the following results and conclusions:

(1) The acid-base properties of our FA samples could be effectively modelled by considering them to be a mixture of three monoprotic acids (R_1H , R_2H and R_3H);

(2) The copper complexation in the studied FA systems could be explained by assuming that copper bound mainly with the strongest and weakest humic acid sites (R_1H and R_3H) to form monodentate complexes (R_1Cu^+ , R_1CuOH and R_3CuOH), except for one system in which an additional copper-FA reaction was needed to fully characterize the complexation mechanism;

(3) The adsorption of FA by illite decreases with increases in pH values and its pH adsorption edge resembles those of SiO_2 -FA and montmorillonite-FA systems. The adsorption mechanism might be explained by assuming that the functional groups of FA react with the water molecules held by electrostatic forces near the illite surfaces to form H-bonds.

(4) The weak interaction between FA functional groups and illite surfaces has little influence on the copper complexation in FA-illite bi-complexant systems. The uptake of copper can be effectively simulated by taking it to be a combination of indi-

vidual bindings by the illite surfaces and the fulvic acid.

(5) In natural water systems, fulvic acid can compete with solid surfaces to bind heavy metal ions by forming soluble complexes. This process inhibits the retention of heavy metals by sediments but favors their transportation in aquatic environments. The distribution of metal ions between surface and soluble complexes is dependent on the relative concentrations of the solid and soluble complexants.

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