Complexation of Cadmium(II) with Soil Fulvic Acid

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Received February 9, 1993

Cadmium(II) complexation by a well characterized soil fulvic acid (FA) from the Okchun Metamorphic Belt were studied at pH of 6.0 in 0.1 M $NaClO_4$ using the ultrafiltration technique. The conditional stability constants thus obtained were log $K=3.90\pm 0.15$ and 3.99 ± 0.12 $L\cdot mol^{-1}$ at fulvic acid concentrations of 101 and 226 $mg\cdot L^{-1}$ respectively. When free cadmium ion concentration was measured directly using an ion selective electrode, log K of 4.12 ± 0.03 $L\cdot mol^{-1}$ was obtained. These results show that fulvic acid forms predominately 1 : 1 complex with Cd^{2+} ions. The maximum binding ability of this polyelectrolyte material was 0.886 mmol Cd/g FA. The average gram formula weight of fulvic acid was estimated to be 1130 daltons.

Introduction

Cadmium is well known for its high toxicity and bioavailability. Its toxicity is due to a strong affinity of Cd^{2+} ion for more polarizable sulfhydryl groups. Since cadmium is chemically quite similar to the biologically important trace element zinc, it can replace zinc bound to enzymes causing these enzymes to become inactive[1]. The environmental concern for cadmium stems from the spread of cadmium in terrestrial and aquatic environments, from increased industrial usage and mining activities. The well documented cases of itai-itai desease in the neighbouring Japan are caused by cadmium poisoning from eating cadmium enriched rice[2].

In natural aquifer systems the salinity, water hardness, and pH are known to affect the cadmium speciation. The comprehensive reviews also state that the total concentration of cadmium is controlled mainly by adsorption on suspended clay materials[3-5] in aquifer systems. However, the naturally occurring humic colloids, known to have high affinity for metal cations ($Z\geq 2+$), can affect the cadmium speciation in aquifer systems[6,7]. Shepard *et al.* reported that some 53% of the total cadmium content is bound to dissolved organic matters in one sample of polluted water[8].

A main component of the dissolved organic carbons (DOC), found in natural aquifer systems, are humic (HA) and fulvic (FA) acids. By forming complexes with metal cations, HA and FA can affect the transportation and availability of trace metals in natural aquifer systems. For the quantification of these processes, the knowledge about two important parameters are required. They are (1) a basic understanding on the nature of humic substances and (2) the measurement of conditional stability constants. Several reviews on these topics are reported in the literature[9-11], where great attentions are paid to potential methods.

In this work, the measurement of the conditional stability constants of Cd^{2+} with soil fulvic acid using ultrafiltration technique is described. Of potential experimental methods, the ultrafiltration technique was chosen for the following reasons: (1) It is applicable to a large number of elements (*e.g.* divalent Cu, Ni, Pb) of environmental concern, provided membranes are carefully washed to avoid contamination; (2) speciation studies can be carried out at low concentration which is limited by the nature of the detector used for the analyses of the filtrate.

Buffle and his coworkers have used ultrafiltration technique in the measurement of complexation properties of metal ions in natural conditions[12,13]. They have also addressed the problems associated with the use of this technique. One problem is the loss of labile metal ions due to adsorption on membranes. A study showed that the loss of metal ions due to adsorption may be very small[14]. Another problem is that the complexation equilibria may shift during the separation stage. It is reported that this effect can be minimized by filtering only 10% of the total solution for analyses[12]. Some of the sample solutions were also analyzed using ion-selective electrode (ISE). Due to relatively high detection limits of ion-selective electrode, however, only those samples with concentrations of free metal ions greater than those of the natural aquifer systems could be measured. The complexation equilibria shift are less problematic when nonseparation techniques are used[11] and humic substances are not known to adsorb on the membranes of ion-selective electrodes[15]. Due to the surface activity of fulvic acid, voltametric techniques could not be applied for such purposes[16]. The low-molecular-weight fulvic acid used in this investigation are extracted from soil samples obtained from the Okchun Metamorphic Belt region of Kuye San according to the method recommended in the literature[17].

Experimental

Materials and Reagents. The humic and fulvic acids were extracted by base digestion of air dried soils. Briefly, 1.5 kg of the air dried soil in 15 L of 1 M HCl was shaken for 16 h at room temperature. The supernatant was discarded and the residue was neutralized to pH 7 using 1 M NaOH. Subsequently, 15 L of 0.1 M NaOH was added to the residue and the resulting suspension was stirred under N_2 atmosphere for 24 h. The solid suspension was removed by centrifugation, leaving the dark coloured supernatant containing dissolved humic substances. The humic acid fraction was removed by acid precipitation (pH 1) with 6 M HCl. The fulvic acid fraction remaining in the supernatant was isolated by sorbing it on a column of XAD-8 resins. FA was eluted from the column by 0.1 M NaOH, and NaF was added and left overnight to remove trace of silicate impurities. FA was resorbed on XAD-8 resins, washed with a small volume of 0.1 M HCl, and was eluted by 0.1 M NaOH. The FA solution was passed through a cation exchange column of Dowex 50×8 (H^+) to remove Na. The protonated final product was freezed dried and was kept in a vacuum desicator over P_2O_5 in darkness.

FA stock solution (1510 mg·L^{-1}) was prepared by dissolving the accurately weight solid material in 6.0 m*l* of NaOH (carbonate free, Baker Co.). After 2 h of continuous shaking, the solution was diluted to 1.0 L with 0.1 M $NaClO_4$ containing 10^{-3} M of MES (2-morpholineethane sulfonic acid) buffer and pH adjusted to 6.0 using minimum quantity of 0.1 M $HClO_4$. The Cd(II) stock solution was prepared by dissolving CdO (Aldrich Co.) in 1.0 M $HClO_4$. When all the oxide is dissolved, the solution was diluted using 0.1 M $NaClO_4$ (10^{-3} M MES) and pH adjusted to 6.0 using 0.1 M NaOH (carbonate free). The concentration of the Cd(II) stock solution was 2.0×10^{-2} M, as was analyzed by atomic absorption spectrophotometer (AAS, Instrumental Laboratory Video 12). All reagents were analytical grade and double deionized water was used to prepare solutions. All glasswares was soaked in acid bath and washed repeatedly with double deionized water prior to use. The pH was measured using glass electrode (Metrohm Co.) coupled to a digital pH meter (Metrohm type 632).

Ultrafiltration Procedure. A series of the smaple solution (20 m*l*) were prepared using the FA and Cd(II) stock solutions. In all sample solutions the concentration of FA was maintained constantly (101 mg·L^{-1} or 226 mg·L^{-1}) and Cd^{2+} concentration was varied from 1.0×10^{-5} M to 6.0×10^{-3} M. An identical series of the reference solution (20 m*l*) were also prepared in the same manner using the $NaClO_4$ solution (pH 6.0) in place of the FA stock solution. The sample and reference solutions were allowed to stand for three days to equilibriate with occasional shaking.

The sample solutions were filtered using a ultrafiltration cell (Amicon Co. 8010) and YM 2 membrane filter (molecular weight cut-off 1000 daltons, Amicon Co.), under 40 Psi N_2 pressure. Membrane filters were first soaked in double deionized water for several hours and repeatly washed with water to remove all trace of coating materials. The sample solution was continuously stirred during the filtration to prevent clogging on the membrane surface. The proper functioning of the membrane was assured when the flow rate was maintained constantly at 0.1 m*l*/min. First 0.5 m*l* was discarded (dead space of the cell), and subsequent 2.0 m*l* of the filtrate was collected and its Cd concentration was measured using AAS. Those sample solutions containing a large excess of Cd^{2+} ions formed precipitates. These samples were centrifuged for 30 min at 4000 rpm in centrifuge tubes using a benchtop centrifuge. After carefully discarding most of the supernatant solution, the samples were further centrifuged for 30 min. The tube was tilted at an angle for 1 h to separate and discard remaining supernatant solution. Small volumes of deionized water (2.0 m*l*) were introduced to wash the inner walls of the tube without disturbing the precipitate surface. The FA precipitate was digested by the standard nitric acid attack and Cd content was analyzed by AAS.

Ion-Selective Electrode Method. The stock FA solution (1204 mg·L^{-1}, pH 6.0) and $CdCl_2$ stock solution (6.5×10^{-2} M, pH 6.0) in 0.1 M KNO_3 (10^{-3} M MES) were prepared in similar manners. A series of sample and references solutions were made, in which the FA concentration was kept constant (100 mg·L^{-1}) and Cd^{2+} concentrations were varied from 2.5×10^{-5} M to M to 1.2×10^{-3} M. The analyses were carried out using Cd(II) ISE (Model No. 94-48, Orion Co.) and a double junction reference electrode (Model No. 90-02) coupled to an EA-920 expandable ion analyzer from the Orion Co. The Cd(II) ISE was gently polished with a polishing strip prior to use. The Cd(II) ISE was calibrated using a series of Cd standrad solutions prior to each analysis. The electrode response was observed to be linear in the experimental range pM 2.1 to 4.7, with Nernstian slope of −28.2 mV.

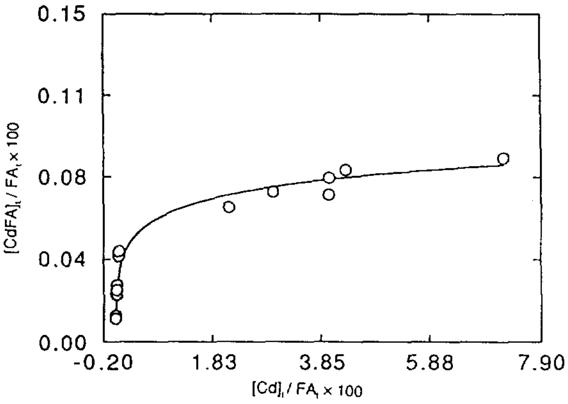

Figure 1. The illustration of binding of Cd^{2+} on fulvic acid.

Results and Discussion

Humic substances (HUS) are polyelectrolytes having a number of chelating sites. The incremental stability constant K_i at the i-th site can be written as

$$K_i=[\text{Cd-HUS}_i]/[\text{HUS}_i][Cd^{2+}] \qquad (1)$$

where [Cd-HUS$_i$] is the concentration of cadmium complexed with the i-th chelating site, [HUS$_i$] is the concentration of the i-th chelating site of HUS, and [Cd^{2+}] is the concentration of the free Cd^{2+} ion[18]. The overall stability constant is then

$$K=\sum_{i=1}^{n}[\text{HUS}_i]K_i/\sum_{i=1}^{n}[\text{HUS}_i] \qquad (2)$$

As neither the concentration of a single type of chelating site nor the incremental stability constant can be measured, the expression shown in Eq. (1) can be simplified if it is assumed that Cd^{2+} bind at identical and independent sites, resulting in

$$K=[\text{Cd-FA}]/[\text{FA}]_f[Cd^{2+}]_f \qquad (3)$$

where K now represents the conditional stability constant, [Cd-FA] is the concentration of the bound cadmium, $[\text{FA}]_f$ is the concentration of the free and ionized FA binding sites, and $[Cd^{2+}]_f$ is the free ion concentration. This simplification is valid at low metal-to-humus ratios if 1 : 1 complexes (one cadmium binding site per FA) predominate. Although other models are also used in determining the conditional stability constants of metal complexes with humic substances in the

Table 1. Complexation Data of Cd^{2+} with Soil Fulvic Acid in 0.1 M $NaClO_4$ at pH=6.0.

Method	$[Cd]_t$ (mol/L)	$[Cd]_{1f}$ (mol/L)	$[Cd]_{2f}$ (mol/L)	$[Cd]_{1s}$ (mol/L)	$[Cd]_{2s}$ (mol/L)	$[Cd]_{1f}$ (mol/L)	$[Cd]_{2f}$ (mol/L)	log *K* (L/mol)	log *K* (L/mol)
UF	9.99E-06	5.16E-06	5.50E-06	4.82E-06	4.49E-06	8.47E-05	8.50E-05	4.04	3.98
	2.02E-05	1.10E-05	1.10E-05	9.26E-06	9.24E-06	8.02E-05	8.02E-05	4.02	4.02
	3.98E-05	2.20E-05	2.21E-05	1.78E-05	1.77E-05	7.16E-05	7.18E-05	4.05	4.05
	5.94E-05	4.08E-05	4.43E-05	1.86E-05	1.51E-05	7.09E-05	7.44E-05	3.81	3.66
	7.97E-05	5.61E-05	6.08E-05	2.36E-05	1.89E-05	6.59E-05	7.05E-05	3.80	3.65
	1.02E-04	7.01E-05	7.41E-05	3.17E-05	2.77E-05	5.78E-05	6.18E-05	3.89	3.78
	1.98E-04	1.54E-04	1.59E-04	4.43E-05	3.93E-05	4.52E-05	5.02E-05	3.80	3.69
	$[FA]_t$=0.101 (g/L)×8.86E-04 (mol/g)=8.94E-05 (mol/L) average value=3.90± 0.15								
UF	4.07E-05	1.39E-05	1.68E-05	2.68E-05	2.40E-06	1.73E-04	1.76E-0	4.04	3.91
	8.43E-05	3.62E-05	3.53E-05	4.81E-05	4.90E-05	1.52E-04	1.51E-0	3.94	3.96
	1.03E-04	4.45E-05	4.55E-05	5.82E-05	5.72E-05	1.42E-04	1.43E-0	3.96	3.94
	1.99E-04	1.11E-04	1.06E-04	8.81E-05	9.31E-05	1.12E-04	1.07E-0	3.85	3.91
	4.03E-04	2.48E-04	2.42E-04	1.55E-04	1.61E-04	4.48E-05	3.89E-0	4.15	4.23
	$[FA]_t$=0.226 (g/L)×8.86E-04 (mol/g)=2.00E-04 (mol/L) average value=3.99± 0.12								
ISE	3.21E-05		1.63E-05		1.58E-05		7.27E-05		4.12
	3.72E-05		1.94E-05		1.78E-05		7.07E-05		4.11
	6.03E-05		3.24E-05		2.79E-05		6.06E-05		4.15
	6.70E-05		3.85E-05		2.85E-05		6.00E-05		4.09
	$[FA]_t$=0.100 (g/L)÷1130 (g/mol)=8.85E-05 (mol/L) average value=4.12± 0.03								

(UF: Ultrafiltration; ISE: Ion selective electrode). (suffix t: total; f: free; s: soluble; 1 and 2 correspond to replicate experiment).

literature[19], Eq. (3) was used in the determination of the conditional stability constants in this study.

The results of the Cd fulvate complexation study using the ultrafiltration is shown in Figure 1. Filtration through UM 05 (molecular weight cut-off 500 daltons) is known to be influenced by sorption. Thus the concentration of cadmium in filtrate from filtrations through YM 2 membrane (molecular weight cut-off 1000 daltons) was assumed to represent the concentration of free cadmium ions as in other studies[12,18]. The experiment was conducted at the natural pH range (pH=6.0) where hydrolysis products are not known to occur. The concentration of the bound cadmium, [Cd-FA], was taken as the difference between total cadmium concentration, $[Cd]_t$, and concentration of cadmium in filtrate, $[Cd^{2+}]_f$. The Figure 1 shows the experimental relationship of Eq. (3). At low concentration ratios of Cd to fulvic acid, [Cd-FA] increases linearly with increasing $[Cd]_t$. The experimental points start to deviate from the slope at higher concentration ratios, finally reaching the condition where the concentration of the bound cadmium does not change with further increase of $[Cd]_t$. This saturation value is the maximum binding ability (MBA) of the fulvic acid for cadmium ion[20]. In the absence of a known molecular weight, which is often the case for humic and fulvic acids, the formation function can be expressed in terms of binding site concentration, $[FA]_t$, which is the product of the fulvic acid concentration (0.101 or 0.226 $g \cdot L^{-1}$) and MBA (0.886 mmol Cd/g FA)[19].

Experimental data for the Cd fulvate complexation study are summarized in Table 1. The given concentrations of Cd and fulvic acid are indicated as $[Cd]_t$ and $[FA]_t$ respectively. The concentrations $[Cd^{2+}]_f$ and [Cd-FA] are obtained from the ultrafiltration data, where

$$[Cd]_t = [Cd^{2+}]_f + [Cd\text{-}FA] \tag{4}$$

Since the total binding site concentration is the sum of free and Cd bound sites,

$$[FA]_t = [FA]_f + [Cd\text{-}FA] \tag{5}$$

the concentration of the free and available binding site, $[FA]_t$, was calculated using Eq. (5). The conditional stability constants are calculated at each experimental points in the linear range using Eq. (3), and they are shown in Table 1. The calculated values of log *K* obtained from the two replicate sets of experimental data are found to fall within the experimental range. Therefore, the average values were taken as the overall conditional stability constant of the Cd fulvate complex. The average log *K* values at fulvic acid concentrations of 101 $mg \cdot L^{-1}$ and 226 $mg \cdot L^{-1}$ were 3.90± 0.15 and 3.99± 0.12 $L \cdot mol^{-1}$ respectively, showing that the complexations of Cd^{2+} by fulvic acid is nearly independent of fulvic acid concentration under these experimental conditions.

When applying Eq. (3) in the calculation of the conditional stability constants, it was assumed that 1 : 1 complex predominate. For verification, Eq. (3) was rewritten in the following manner

$$\log[Cd\text{-}FA]/[Cd^{2+}]_f = \log[FA]_f + \log K \tag{6}$$

Eq. (6) is nearly identical to the Hill plot[19], a plot of $\log[\upsilon/(1-\upsilon)]$ verse log *M*, where υ is defined as

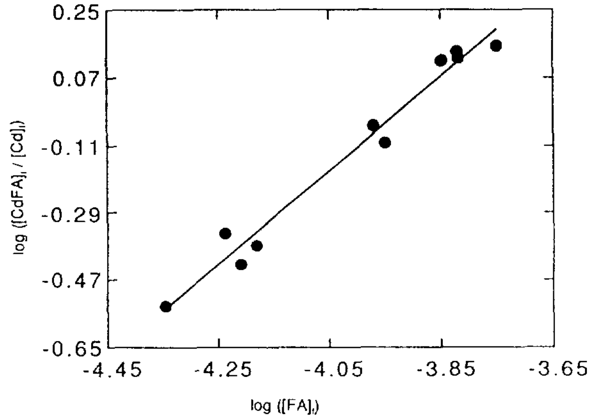

Figure 2. The linear correlation of Eq. (6), which verifies that 1 : 1 complexes predominate.

$$\upsilon = \text{Site bound/Total number of binding sites}$$

and M is the metal ion conentration, and with the equation of the Zunino and Martin shown below[20]

$$\log[M_b/(\mathrm{MBA}-M_b)]=\log K+n\log M \tag{7}$$

where M_b and M are the bound and free metal concentrations, and MBA is the maximum binding ability. If the assumption that only 1 : 1 complex predominate is valid, then a plot of $\log[\text{Cd-FA}]/[\text{Cd}^{2+}]_f$ verses $\log[\text{FA}]_f$ should yield a straight line with a slope of 1. The plot using the data in Table 1 is shown in Figure 2. It shows a straight line fit of the data with a slope of 1.2± 0.1, suggesting that the assumption is appropriate under these Cd to fulvic acid concentration ratios and experimental conditions.

The method of speciation analysis can have profound effect on the results, because each method measures different aspects of the system. In order to verify the results obtained from the ultrafiltration study, the experiment was repeated under similar experimental conditions using the nonseparation method. The experimental data for the Cd^{2+} fulvate complexation study using Cd(II) ISE is also summarized in Table 1. The average value of $\log K$ thus obtained was 4.12± 0.03 $\text{L}\cdot\text{mol}^{-1}$, which is only slightly larger than that obtained earlier using the ultrafiltration technique.

There are many factors which can alter the results of speciation studies involving metal ions and fulvic acid. The method utilized in the speciation analysis can influence the results. The characteristics of fulvic acids are known to vary significantly from one another depending on their origin (*e.g.* source materials, aging, botanical and climatic conditions of the region), and fulvic acids having different characteristics are used by other laboratories. Investigations are often conducted under different experimental condition (*e.g.* FA concentration, pH and ionic strength). Furthermore, conditional stability constants, reported in the literature, are calculated based on different models. A summary of some recent studies on the Cd^{2+} fuvlic acid complexation studies are shown in Table 2.

Table 2. Summary of the Conditional Stability Constants of Cd^{2+} Fulvate Complexes

Fulvic acid source	pH	I (M)	Method	$\log K_1$	$\log K_2$	Reference
Sewage sludge	5.0	0.1	PT	3.04	2.27	[22]
Soil	6.0	0.1	ISE	4.12		
	6.0	0.1	UF	3.90		[this work]
	〃	〃	〃	3.99		
Water	5.0	0.1	ISE	3.47		
	6.0	0.1	〃	3.68		[21]
	7.0	0.1	〃	3.90		
Soil	6.0	0.1	UF	3.60		[15]
Soil	5.0	0.1	ISE	3.80		
	6.0	0.1	〃	4.08		[21]
	7.0	0.1	〃	4.32		
Sewage sludge	6.5	0.01	ISE	4.7-5.2	3.8	[23]
	6.5	0.01	DPASV	5.6		

(PT: Potentiometric titration; ISE: Ion selective electrode; DPASV: Differntial pulse anodic stripping voltammetry; UF: Ultrafiltration)

The conditional stability constants obtained using the sewage sludge extracted fulvic acid differ significantly from one labroatory to another and with the method of speciation analysis. This may be due to many water soluble organic impurities (*e.g.* polysaccarides) present in sewage sluge which can influence the results. However, the results of this investigation compare very well with that obtained water-derived fulvic acids by Saar and Weber[21] and based on a similar scientific model, and with the results of Buffle and his coworkers[15]. Therefore, the characteristics of the metal ion binding site of fulvic acid samples may be similar with one another. In this investigation, the conditional stability constants were expressed in terms of binding site concentration. They can also be expressed in FA molecular weight terms, if it is known. Saar and Weber found that there are 1.0± 0.3 Cd^{2+} binding sites per average fulvic acid molecule[21]. Based on this information, the average gram formula weight (AGFW) can be estimated from the MBA data, yielding a value of 1130. This value of the AGFW compares very well with the recently published data on average molecular weight of soil fulvic acids of 1010 by flow field-flow fractionation and 1200 by other methods[24]. When the AGFW value of 1010 is used in the calculation using Eq. (3), the conditional stability constants in Table 2 become slightly changed to 3.97± 0.15 (UF, 101 $\text{mg}\cdot\text{L}^{-1}$), 3.90± 0.12 (UF, 226 $\text{mg}\cdot\text{L}^{-1}$), and 4.06± 0.03 $\text{mg}\cdot\text{L}^{-1}$) respectively.

Conclusion

Fulvic acid is a naturally occurring polyelectrolyte, which has a wide variety of aromatic and aliphatic structures bearing many oxygen-containing functional groups, such as -COOH and -OH. Fulvic acid is a modifer of metal ion chemistry in natural aquifer systems. The conditional stability constants were determined using both the separation and nonseparation methods. Similar results were obtained, which suggest that the versatile ultrafiltration technique can be used in complexation studies of humic substance and many other heavy metal ions of environmental concern (e.g. Ni^{2+}, Cu^{2+}

and Pb^{2+}), provided extra cares are taken to minimize the effects of sorption and chemical equilibrium shift. This work has shown that, although fulvic acid cannot be defined clearly in structural terms, it can be investigated and described in terms of its group properties.

Acknowledgement. This work was supported in part by Korea Advanced Institute of Science and Technology.

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Estimation of Bioconcentration Factors in Fish for Organic Nonelectrolytes Using the Linear Solvation Energy Relationship

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Received February 15, 1993

Bioconcentration factors (BCF) in fish of organic nonelectrolytes are well correlated by a linear solvation energy relationship (LSER) of the form:

$$\log \mathrm{BCF} = -0.95 + 4.74\, V_I/100 - 4.39\,\beta + 0.88\,\alpha$$

where V_I is the intrinsic solute molecular volume and β and α are the solvatochromic parameters that measure hydrogen bond acceptor basicity and donor acidity of the compound. The LSER model can not only correlate the property with an accuracy comparable to molecular connectivity model but also provide a quantitative information on the nature and relative strength of solute-target system interactions affecting the property of interest. Such an information can hardly be obtained from molecular connectivity model.

Introduction

Over the past decades the chemical contamination of our environment has aroused increasing concern. A proper assessment of the risk to men and environment by exposure to these chemicals generally includes attempts to measure or predict the concentration in various environmental compartments in conjunction with toxicological data. However, the concentration data or the toxicological data are often not adequate for realistic assessments, and basic physical