Effect of Ionic Strength on Complexing Equilibrium Between Copper (II) and Humic Acid

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EFFECT OF IONIC STRENGTH ON COMPLEXING EQUILIBRIUM BETWEEN COPPER (II) AND HUMIC ACID

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The effect of ionic strength on copper(II) complexing ability of humic acid (HA) was investigated. The conditional stability constants and the copper(II) complexing capacities were evaluated at the ionic strength of 0.005 – 0.1. The copper(II) complexing capacities of HA increased with ionic strength. By extrapolating the conditional stability constants to ionic strength 0, the thermodynamic stability constant was evaluated. The free ligand concentration in the solution containing copper(II) and humic acid was calculated by using the thermodynamic stability constant obtained. The free ligand concentration also increased with ionic strength. The increase of copper(II) complexing ability of HA with ionic strength was discussed from the viewpoints of the dissociation of the acidic functional groups in HA and the conformational change of HA.

KEY WORDS: Humic Acid, copper(II) complexing ability, thermodynamic stability constant.

INTRODUCTION

Humic acids (HAs) are weak-acid polyelectrolytes ubiquitously distributed in natural waters and soils. It is well known that HAs have the complexing ability for heavy metal ions[1]. The speciation of heavy metal ions concerns with the toxicity for plankton in natural waters and the transportation and accumulation of toxic heavy metal ions into the soil environment[2]. Therefore, the knowledge about the complexation between heavy metal ions and HAs is important for environmental chemistry, biology and geochemistry.

The complexing ability of HAs has been quantitatively evaluated by various methods. For example, the conditional stability constants and complexing capacities were calculated by the interpretation mode of Scatchard et al.[3] and Van den Berg et al.[4]. When the complexing abilities of HAs are evaluated by these interpretation modes, the free metal ions and the complex species must be individually determined. Some analytical methods to measure the free and complex species separately such as ion selective electrode[5], voltammetry[6], ion-exchange method[7,8] have been reported. Especially, a macroreticular dextran gel, weak-base anion-exchanger, diethylaminoethyl Sephadex A-25 (A-25) has been found useful for the speciation analysis of trace heavy metal ions in natural waters[9-11]. In these methods, anionic

species such as heavy metal-HA complex and iron(III)-HA colloid are retained on A-25, and then the other species such as cationic or non-ionic species are not retained. Therefore, metal-HA complex species can be separated and determined by the A-25 method[12]. The copper(II) complexing abilities (conditional stability constants and complexing capacities) were also evaluated by a Scatchard plot using the data obtained by the A-25 method[13]. However, only the conditional stability constants but not the thermodynamic stability constant were evaluated in these investigations.

In the present paper, the thermodynamic stability constant of copper(II)-HA complex was evaluated by the A-25 ion-exchanger method. The conditional stability constants and copper(II) complexing capacities at ionic strength, 0.005, 0.030, 0.055 and 0.105 were determined by using the Scatchard plot adopting a two-site model. The thermodynamic stability constant could be evaluated by extrapolating these conditional stability constants to ionic strength zero. The effects of ionic strength on copper(II) complexing abilities were discussed from the viewpoints of the dissociation of acidic functional groups in HA and the conformational change of HA.

EXPERIMENTAL

Reagents and materials

The HA was purchased from Wako Pure Chemicals (Japan), and then extracted and purified as described previously[13]. The elemental analysis was as follows: C, 52%; H; 4.9%; N, 1.2%; ash content, 3.4%. The sodium salts of perchlorate, sulfate, nitrate and chloride were used to adjust ionic strength. The 5×10^{-3} M of sodium acetate/acetic acid buffer was used to adjust pH of the test solution (pH 6).

Measurements

The A-25 ion-exchange resin (Pharmacia LKB Biochemistry, Sweden) was ultrasonically washed in 1M hydrochloric acid solution, decanted from distilled water for several times, and finally stocked in distilled water. A 1.6 ml volume of A-25 was packed into a polypropylene column (40×8 mm i.d., Bio-Rad Labs., U.S.A.), and then washed with water. Subsequently, 10 ml of the buffer solution which has the same matrix as the sample solution was passed through the A-25 column. The preparation of the test solution was as follows: 5 ml of 2.5×10^{-2} M of sodium acetate/acetic acid buffer solution was taken into a 25 ml measuring flask, subsequently an appropriate volume of $NaClO_4$, Cu^{2+} and HA solutions were taken into this, and finally distilled water was added up to the marked line. 8 ml of the test solution containing copper(II) and HA were passed through the column at the flow rate of 10 ml min^{-1}. After desorbing the copper(II)-HA complex retained on A-25 by 0.7 M nitric acid, the copper(II) in the solution was measured by atomic absorption spectrometry (170–50 type, Hitachi LTD Co., Hitachi; Japan). The concentration of copper(II)-HA complex ([CuL]) could be obtained from the amount of copper(II) retained as the complex

on the A-25, and the free copper(II) concentration ($[Cu^{2+}]$) could be calculated by subtracting [CuL] from the total copper(II) concentration ($[Cu^{2+}]_t$). The temperature of the sample solution was 22 ±1.0 °C.

The measurement of acidic functional groups in HA was performed by acid-base titration. A pH meter (M-13 type, Horiba LTD, Tokyo; Japan) and a glass electrode (6366 type, Horiba LTD) were used. The measurements were performed under nitrogen atmosphere at 25±0.5 °C. The acidic functional groups in HA were evaluated according to Cabaniss's report[14]. A ring method was used for the measurement of surface tension[15]. The measurements were done at 20 ± 0.5 °C.

RESULTS

Effect of the ionic strength on adsorption of anionic copper(II) complex on A-25

It has been shown that the anionic copper(II) complexes in solution can be retained on A-25 ion-exchanger[9–13]. In the previous works, it was confirmed that the complexing equilibria between ligands such as glutamic acid or HAs and copper(II) ions would not change during anion-exchange using the A-25[16]. Therefore, the concentration of copper(II) complex obtained from the A-25 method would reflect the complexing equilibria in the solution.

The relation between the ionic strength (I) and the concentrations of the copper(II) complexes retained on the A-25 ([CuL]) are shown in Figure 1. In the case of a complex
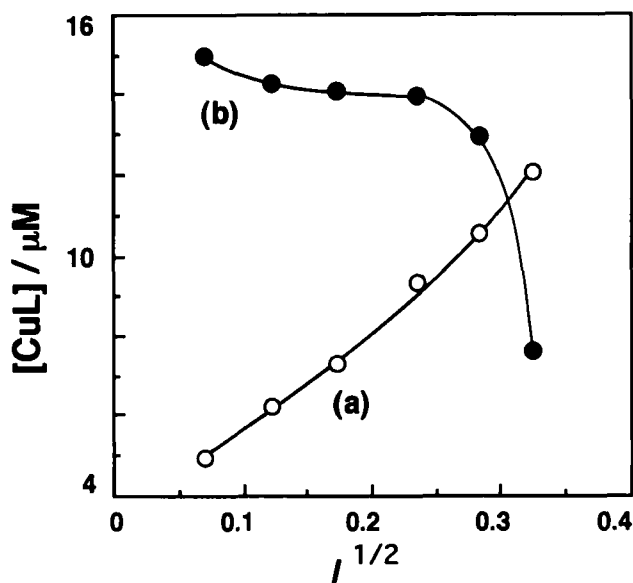

Figure 1 Effect of ionic strength on [CuL].
(a) HA; $[Cu^{2+}]_t$: 30μM, (b) EDTA; $[Cu^{2+}]_t$: 15μM, pH: 6, HA: 20 mg l^{-1}, EDTA: 15μM.

with HA, the [CuL] increased with ionic strength as shown in Figure 1 (a). On the other hand, in the case of an anionic complex with a low-molecular weight ligand such as EDTA, the concentration of copper(II)-EDTA complex was constant up to the ionic strength of 0.080 as shown in Figure 1 (b). The increase of the concentration of copper(II)-HA complex with an increase in ionic strength seems to be due to the increase of copper(II) complexing ability of HA itself through some conformational change of HA.

The concentration of copper(II)-EDTA complex rapidly decreased above the ionic strength 0.080 as shown in Figure 1 (b). This decrease would be due to the reduction of the ion-exchange capacity of A-25 for anionic complex species because of the competition between anionic co-ions and complexes[17].

Effect of the ionic strength on copper(II) complexing ability of HA

In order to quantitatively evaluate the effect of the ionic strength on the copper(II) complex-ing ability of HAs, the conditional stability constants (K_i) and the concentration of binding site (c_{Li}) were calculated by the Scatchard approach[3]. From the mass balance for free copper(II) ions ([Cu^{2+}]) and copper(II)-HA complex ([CuL]), the following equation was derived[13,18],

$$\frac{[CuL]}{[Cu^{2+}]} = - K_i [CuL] + K_i c_{Li} \tag{1}$$

where i means the kind of the binding sites.

The Scatchard plots of HA for various ionic strengths are shown in Figure 2. The relationship between [CuL]/[Cu^{2+}] and [CuL] could be divided in two linear sections. Therefore, a discrete two-site model could be assumed and the conditional stability constants and the copper(II) complexing capacities were evaluated for the two discrete binding sites of copper(II).

Copper(II) complexing capacity (N_i) means the number of moles of copper(II) bound to 1g of HA (mol Cu^{2+} per g of HA), and then can be written as follows:

$$N_i = \frac{[c_{Li} \, (mol \, l^{-1})]}{[HA \, (g \, l^{-1})]} \tag{2}$$

The values of conditional stability constants and copper(II) complexing capacities calculated at various ionic strength are summarized in Table 1. The K_0 in Table 1 means the average stability constant of copper(II) binding sites in the HA and this can be defined as follows[19]:

$$K_0 = \sqrt{K_1 K_2} \tag{3}$$

As shown in Table 1, the average stability constants (K_O) and the total copper(II) complexing capacities ($N_t = N_1 + N_2$) increase with the ionic strength. The increase of copper(II) complexing ability with an increase in ionic strength seems to be because the dissociation
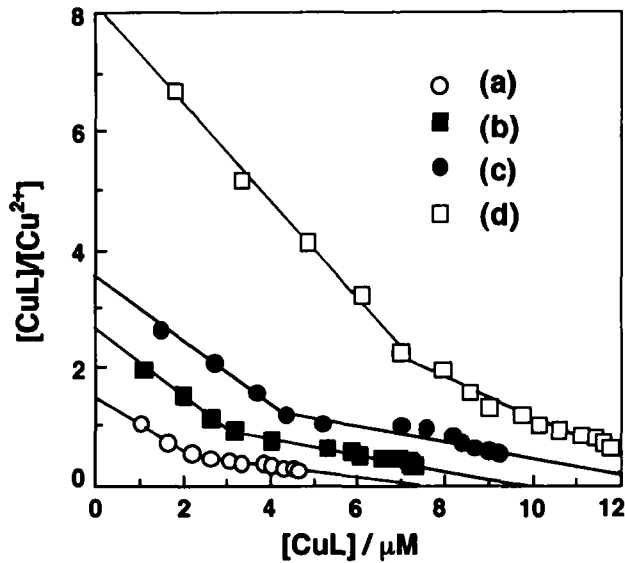
Figure 2 Scatchard plot of HA for various ionic strengths.
$I = 0.005$ (a), 0.030 (b), 0.055 (c), 0.105 (d), pH 6.0, HA 20 mg l^{-1}.

of acidic functional groups is promoted by the electrostatic effect[14] and then the coordination of copper(II) to HA becomes easy. The interpretation was supported by the fact that the amounts of acidic functional groups (C_A), which is measured by acid-base titration, also increase with the ionic strength.

From the relation between ionic strength (I) and logarithm of conditional stability constants (log$K$) (Figure 3), the thermodynamic stability constant ($K°$) could be evaluated by extrapolating $I^{1/2}=0$. The results were as follows: log$K_0°$; 5.30, log$K_1°$; 5.62, log$K_2°$; 4.99.

On the other hand, the concentration of the free ligand can be calculated by Eqn. (4),

Table 1 Copper(II) complexing abilities of humic acid for various ionic strength at pH 6, HA: 20 mg l^{-1}.

	Ionic strength			
	0.005	*0.030*	*0.055*	*0.105*
logK_1	5.64	5.68	5.71	5.92
logK_2	5.00	5.05	5.19	5.55
logK_0	5.32	5.34	5.45	5.74
N_1[a]	172	234	332	491
N_2	198	260	312	249
N_t	370	494	644	740
C_A[b]	13.1	16.7	19.1	26.0

a) copper(II) complexing capacity; μmol per g of HA.
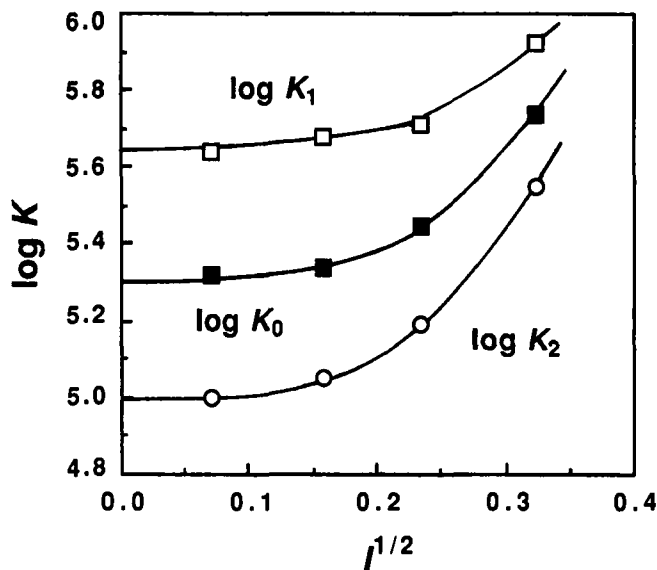b) amount of acidic functional groups in humic acid; determined by potentiometry; meq per g of humic acid.

Figure 3 Estimation of thermodynamic constants.

$$[L^-] = \frac{[CuL]}{K_0([Cu^{2+}]_t - [CuL])} \tag{4}$$

where [CuL] and K_0 values could be obtained experimentally.

The plots of [CuL] or [L$^-$] obtained by the calculation are shown as the function of total copper(II) concentration ([Cu^{2+}]$_t$) in Figure 4. These results show that both the [L$^-$] and [CuL] increase with the ionic strength. This tendency is in good agreement with that in the amount of acidic functional groups and the copper(II) complexing capacities. The dissociation of functional groups in HA seems to be promoted with increasing ionic strength. Moreover, the total copper(II) complexing capacity (N_t), which is calculated from Eqn. (2), also increases with ionic strength. These results are in good agreement with the experimental values at I=0.005, 0.030, 0.055 and 0.105 in Table 1.

DISCUSSION

As the ionic strength is higher, the complexing ability of a low molecular weight organic ligand generally becomes lower because of the competition between co-ions and the metal ion. However, the copper(II) complexing ability of HA increased with ionic strength. It is thought that the conformational change of HA caused by the presence of ionic species would affect the copper(II) complexing ability. HA is a random-copolymeric structure with the anionic polyvalent charge, and then the conformation of HA could be variable with the condition of solution (e.g. pH, ionic strength, temperature, polarity of solvent and so on).
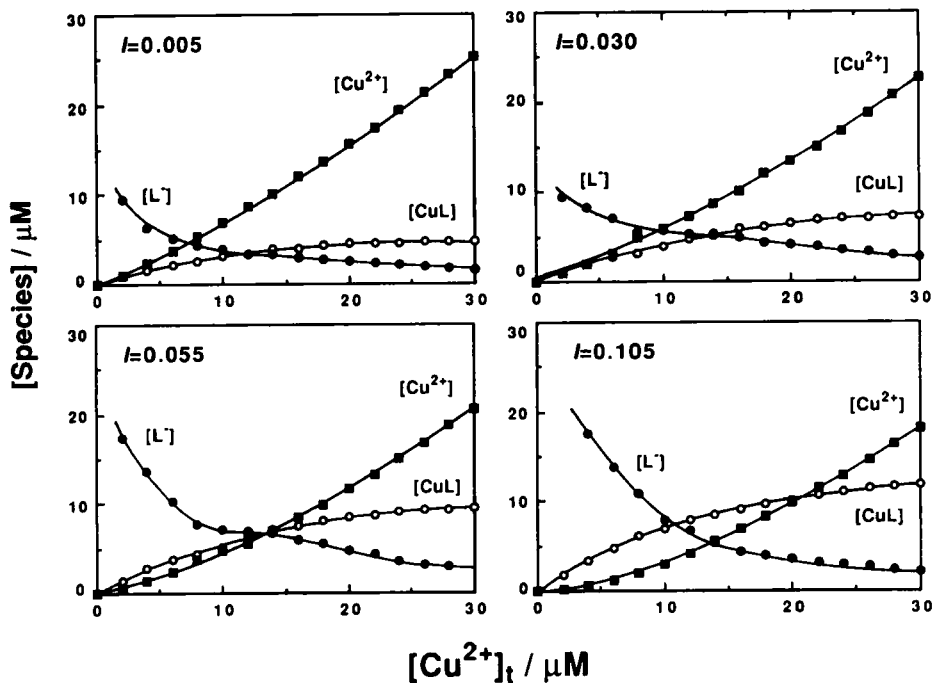
Figure 4 Effect of ionic strength on [L⁻].
Experimental values of $\log K_0$ and [CuL] were used to evaluate [L⁻].

The high ionic strength weakens the repulsion between anionic charges in HA molecule and makes it more spherical in polyelectrolyte[20]. In the spherical structure of HA, the acidic functional groups, which are hydrophilic groups, seem to have a tendency to orient themselves to the solvent (water). Therefore, the surface negative charges may be larger, and then the heavy metal ions will be accumulated around the HA spherical molecules.

The surface tension of HA solution was measured with this perspective. The surface tensions of the solution containing 50 mg l^{-1} HA in various ionic strength are shown in Figure 5. The surface tension decreased with increasing ionic strength. The larger surface charges of HA, the larger amounts of HA adsorb on the surface. Therefore, the surface free

Table 2 Calculation of N_t using K_0 for various I.

I	$-\log\Gamma_0$	$[CuL]/\mu M$	N_t
0.005	0.964	4.98	338
0.015	0.931	6.21	423
0.030	0.871	7.30	495
0.055	0.736	9.34	621
0.080	0.562	10.6	670
0.105	0.373	12.1	719

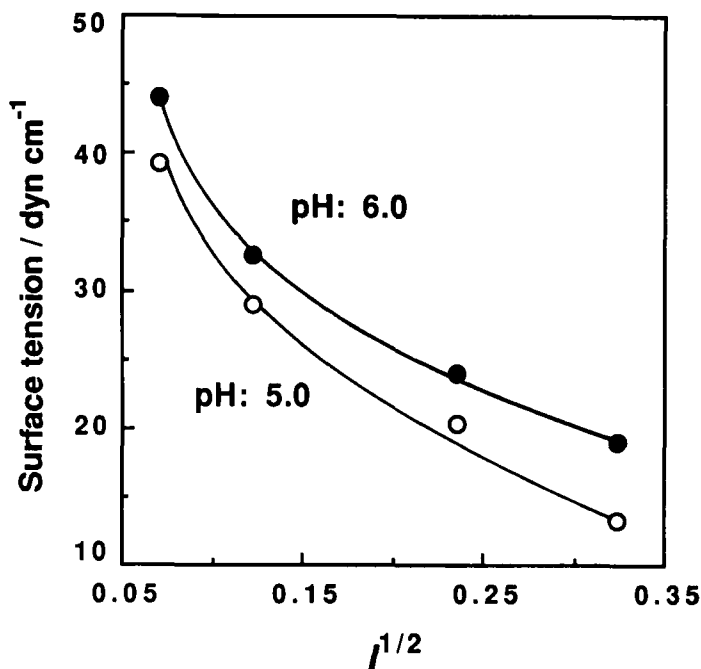$[Cu^{2+}]_t$:30 μM, pH 6, HA: 20 mg l^{-1}.

Figure 5 Effect of ionic strength on surface tension at 50 mg l^{-1} of HA.

energy (that is, surface tension) will decrease. The absolute viscosity of HA was also measured in the solution containing 0.1M NaOH and 0.1M $NaClO_4$. The obtained value of 0.02 is in agreement with the values of the spherical polymers reported by Kumada *et al.* $(0.02 - 0.05)^{21}$. From these results, it is predicted that the HA molecule becomes more spherical with increasing ionic strength.

The conformation of HA in the ionic solution would be largely changed by the kinds of inorganic anions. Therefore, the copper(II) complexing ability of HA will be also affected differentially by the kinds of anions. The copper(II) complexing abilities, in the presence of nitrate, sulfate and chloride, are summarized in Table 3. The orders of the average stability constants (K_0) and the copper(II) complexing capacities (N_t) were $SO_4^{2-} > NO_3^- > Cl^-$. This result was in good agreement with the decreasing effects of inorganic anion on the critical micellar concentration of anionic surfactants such as sodium dodecyl sulfate[22]. This is mainly due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in the presence of the additional electrolyte and consequently the decrease of the electrical repulsion between them in the micelle. The same phenomena must occur in the case of HA. Therefore, the large value of copper(II) complexing ability in the case of SO_4^{2-} can be attributed to the fact that HA molecules prefer a more spherical conformation in the presence of SO_4^{2-}.

In conclusion, it was found that the copper(II) complexing abilities of HA increased with ionic strength. This fact will give important information for the evaluation of the dynamic

Table 3 Copper(II) complexing abilities of humic acid with various anions.

	$SO_4{}^{2-}$	$NO_3{}^-$	Cl^-
$\log K_1$	5.90	5.72	5.62
$\log K_2$	5.43	5.23	5.07
$\log K_0$	5.67	5.48	5.35
N_1	392	342	238
N_2	369	254	181
N_t	761	596	419

pH: 6.0, I: 0.055, HA: 20 mg l^{-1}.

changes of heavy metal ion species in the environment such as in estuaries where the ionic strength changes dramatically. This seems to be because (1) the dissociation of the acidic functional groups in HA is promoted with increasing ionic strength, (2) HA molecules cause the conformational change to become spherical, and the structure facilitates the coordination of copper(II).

Acknowledgement

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