

# Influence of pH on Coordination Reactions of Humic Acid with Metal Ions

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## Abstract

The coordination reactions of Humic acid with metal ions were studied. Using the ion exchange equilibrium method, we can find the stability constants of complexes ( $\log K$ ) and the coordination number ( $x$ ) of these reactions. The results showed that in the reactions of HA-Fe<sup>3+</sup>, HA-Zn<sup>2+</sup>, and HA-Cd<sup>2+</sup>, the stability constants of complexes and coordination numbers increased as the pH increased and when ionic strength and temperature conditions were kept the same. For the reaction of HA-Mn<sup>2+</sup>, the stability constants of complexes increased as the pH increased, and the coordination number increased as the pH increased during the range of 3.0 to 5.0; however, it decreased when the pH was increased from 5.0 to 7.0.

*Keywords: pH, Coordination Reaction, Humic acid, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>*

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## 1. Introduction

### 1.1 Humic Acid

Humic acid is a principal component of Humic substances, which are the major organic constituents of soil (humus), peat, coal, many upland streams, dystrophic lakes, and ocean water (Stevenson, 1994). Humic consists of 40-60% carbon, 30-50% oxygen, 1-3% nitrogen, and 0.1-2% sulfur combined in aliphatic and aromatic ring structures associated with carbonyls, alcoholic and phenolic hydroxyl, carboxylates, amines, amides, and other functional groups (Baker, et al., 2007).

Humic acid is the most widely encountered natural complexing ligand, which tends to chelate various metal ions present in the environment. In Humic acid-Metal complexes, Humic acid can change the properties of metal ions. For instance, metal solubility can be increased when metals are complexed with free Humic acid, or decreased when

metals are scavenged by Humic films on mineral surfaces (Zhou, et al., 2015)

The presence of carboxylate and phenolate groups gives the Humic acids the ability to form complexes with ions. Many Humic acids have two or more of these groups arranged so as to enable the formation of chelate complexes (Tipping, 1994). The formation of (chelate) complexes is an important aspect of the biological role of Humic acids in regulating bioavailability of metal ions (Ghabbour, et al., 2001).

### 1.2 Measurement principle of stability constants of complexes ( $\log K$ ) and the coordination number ( $x$ )

A known weight of a well-defined ion exchange resin is added to a solution containing a mixture of a Humic acid and a metal. The resin and Humic acid will compete for the metal and a certain proportion will bind to each (Baker, et al., 2007). By learning Schubert's method, we can find stability constants of complexes and coordination number through

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mathematical methods. This ion exchange equilibrium method can almost be used to all the coordination reactions of Humic acid with any metal ions (Baker, et al., 2007; Qiang, et al., 2006).

Cation exchange equilibrium method is mainly based on the metal ion quantity ( $M_R$ ), which adsorbed by a certain amount of cationic resin (R), is proportional to the metal ions in solution concentration (M) in a fairly large range of concentrations, when the reaction has reached equilibrium. In the systems, with or without a complexing agent, the metal ions distribution coefficient is  $\lambda_0, \lambda$  respectively.

The distribution ratio,  $\lambda$ , of the metal ions between the cation exchange resin and the solution in the presence of a ligand is as follows:

$$\lambda = \frac{[M_R]}{[M]+[MA_x]} \quad \text{eq. (1)}$$

Where  $[M_R]$  is the mole number of metal bound to per g of the resin (mol/g),  $[M]$  is the concentration of free metal ion in the solution (mol/L) and  $[MA_x]$  is the concentration of complexed metal (mol/L).  $[M+M_x]$  is the total molar concentration of metal ions in the equilibrium solution (mol/L) (Baker, et al., 2007).

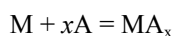
In the absence of ligand in solution, the distribution ratio,  $\lambda_0$ , is given by:

$$\lambda = \frac{[M_R]}{[M]} \quad \text{eq. (2)}$$

The following equation can be derived:

$$\lambda = \frac{[M_R]}{\left[\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)\right]} \quad \text{eq. (3)}$$

Assume the equation of coordination reaction of Humic acid with metal ion is



M is the metal ion; A is the complexing agent; x is Coordination number. Stability constants of complexes  $K_f$  is:

$$K_f = \frac{[MA_x]}{[M][A]^x} \quad \text{eq. (4)}$$

Eq. (1) (2) (3) are reduced to:

$$K_f = \frac{[M_R] \left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)}{\frac{[M_R][A]^x}{\lambda_0}} = \frac{\left(\frac{\lambda_0}{\lambda-1}\right)}{[A]^x} \quad \text{eq. (5)}$$

Logarithm on both sides, we have:

$$\log\left(\frac{\lambda_0}{\lambda-1}\right) = \log K_f + x \log[A] \quad \text{eq. (6)}$$

The pH, ionic strength, temperature, and cation exchange resin are under the condition of constant quality; changing the concentration of Humic acid ( $A_1, A_2, A_3, A_4$ ), can be obtained with more corresponding values ( $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ ). If the concentration of the complexing agent is much greater than the concentration of metal ion concentration, the initial concentration can be considered equal to the equilibrium concentration of free complexing agents. Thus, by using  $\log(\lambda_0 / (\lambda - 1))$  as the vertical axis; using  $\log[A]$  as the abscissa map, stability constants of complexes ( $\log K_f$ ) can be obtained from the intercept, and coordination number (x) calculated from the slope.

## 2. Reviews

### 2.1 The coordination reaction of Humic acid with $Fe^{3+}$ ion

By doing experiments about effects of acidity on stability constants of complexes and the coordination number on coordination reaction of Humic acid with  $Fe^{3+}$  ion, the following linear relation was been obtained from Fig.1 and Fig.2 (Qiang, et al., 2006).

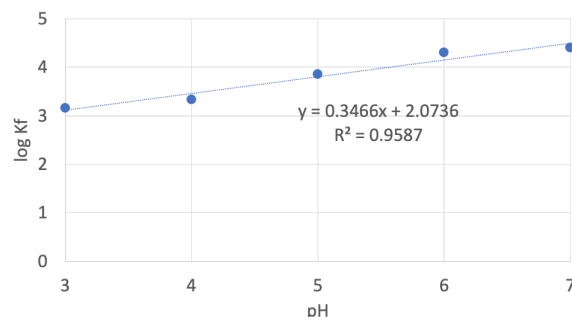


Fig.1 Effect of acidity on stability constants of complexes of HA -  $Fe^{3+}$

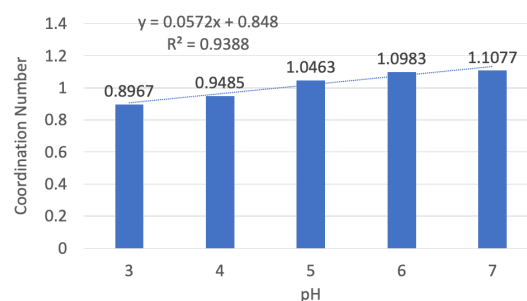


Fig.2 Effect of acidity on coordination number of HA-  $Fe^{3+}$

The results show that the stability constants of complexes and coordination number are increasing as the pH is increased when ionic strength and temperature conditions are kept the same. The results suggest that a higher pH can increase the coordination reaction to the right.

Equations (7) and (8) are used to describe the effect of acidity on stability constants of complexes and coordination number of HA - Fe<sup>3+</sup>.

$$\log K_f = 0.3466 * \text{pH} + 2.0736 \quad \text{eq. (7)}$$

$$x = 0.0572 * \text{pH} + 0.848 \quad \text{eq. (8)}$$

The variation result from both acid effect of Humic acid and hydrolysis effect of Fe<sup>3+</sup> ions. When the pH is low, the acid effect of Humic acid is very serious. It reduces the ability of the Humic acid ligand, resulting in a lesser extent of complex reactions to right, and resulting in small stability constants of complexes ( $\log K_f$ ). With the gradual increase in pH, acid effect of Humic acid decreases; coordination ability gradually increases (Qiang, et al., 2006); the degree of coordination reactions to the right increases, so the stability constants of complexes ( $\log K_f$ ) increase.

At the same time, with the hydrolysis effect of Fe<sup>3+</sup> increasing, competitive conduct of OH<sup>-</sup> will make the right degree of coordination reaction decreases, and thus the relative complexing ability of Humic acid declines, which leads to coordination number increases.

## 2.2 The coordination reaction of Humic acid with Mn<sup>2+</sup> ion

By doing experiments about the effects of acidity on stability constants of complexes and coordination number on coordination reactions of Humic acid with the Mn<sup>2+</sup> ion, from the experiment, Fig.3 and Fig.4 are obtained (Qiang, et al., 2008).

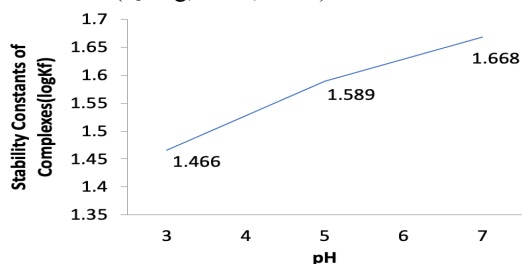


Fig.3 Effect of acidity on stability constants of complexes of HA - Mn<sup>2+</sup>

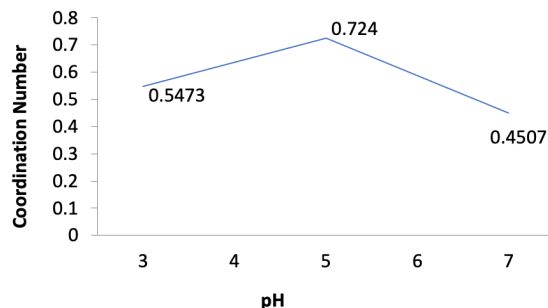


Fig.4 Effect of acidity on coordination number of HA- Mn<sup>2+</sup>

Effects of acidity to the coordination reaction of Humic acid with Mn<sup>2+</sup> ion also can be analyzed by using the ion-exchange equilibrium method. The results show that the stability constants of complexes and coordination number are increasing as the pH is increased, if the ionic strength and temperature are under the condition of constant quality.

We can use equation (9) to describe the effect of acidity on stability constants of complexes ( $\log K_f$ ) of HA - Mn<sup>2+</sup>.

$$\log K_f = 0.0504 * \text{pH} + 1.3225 \quad \text{eq. (9)}$$

Coordination number increased as pH is increased during the range of 3.0 to 5.0, but decreased when pH is increased from 5.0 to 7.0.

The variation result from both acid effect of Humic acid and hydrolysis effect of Mn<sup>2+</sup> ions. When the pH is low, the acid effect of Humic acid is very serious. With the gradual increase in pH, it is the same influence to  $K_f$  just like the reaction of HA-Fe<sup>3+</sup>: acid effect of Humic acid decreases; the degree of complexation reactions to right increases. So the stability constants of complexes ( $\log K_f$ ) increase.

At the same time, the hydrolysis effect of Mn<sup>2+</sup> increases; the competition of OH<sup>-</sup> increase the number of hydroxyl groups around the metal ions, changing the radius of hydration of metal ions, thus changing the coordination number of the coordination reaction (Qiang, et al., 2008).

## 2.3 The coordination reaction of humic acid with Cd<sup>2+</sup> ion and Zn<sup>2+</sup>

By doing experiments about effect of acidity on stability constants of complexes and coordination

number on coordination reaction of Humic acid with  $\text{Cd}^{2+}$  and the Humic acid and  $\text{Zn}^{2+}$  respectively, following Fig.5 and Fig.6 and be drawn (Baofeng, et al., 2005).

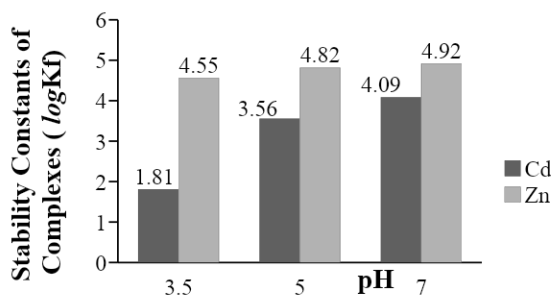


Fig.5 Effect of acidity on stability constants of complexes of  $\text{HA-Cd}^{2+}$  and  $\text{HA-Zn}^{2+}$  respective

Figure 5 shows, when pH increased from 3.5 to 7.0, stability constants of complexes ( $\log K_f$ ) of  $\text{HA-Cd}^{2+}$  increased from 1.81 to 4.09, and stability constants of complexes ( $\log K_f$ ) of  $\text{HA-Zn}^{2+}$  increased from 4.55 to 4.92.

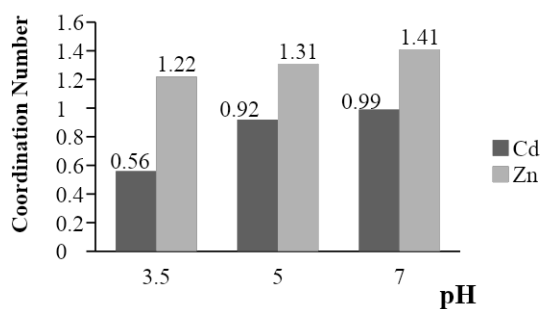


Fig.6 Effect of coordination number of  $\text{HA - Cd}^{2+}$  and  $\text{HA - Zn}^{2+}$  respective

Figure 6 shows, when pH increased from 3.5 to 7.0, coordination number of  $\text{HA - Cd}^{2+}$  increased from 0.56 to 0.99, coordination number of  $\text{HA-Zn}^{2+}$  increased from 1.22 to 1.41. In the two coordination reactions, both stability constants of complexes and the coordination number of  $\text{HA - Cd}^{2+}$ , and  $\text{HA-Zn}^{2+}$  will increase as the pH value is gradually increased.

This is because when the pH value is low, the concentration of  $\text{H}^+$  in a solution is relatively high, certain weak binding sites in Humic acid are saturated, and thus the metal ions and Humic acid binding is inhibited. When pH value is increased, free functional groups, especially weak acidic carboxyl group, increases. The Humic acid molecule surface

electrostatic repulsion increases, therefore Humic acid changes its structure from reunion status to a stretched mesh structure when pH is low (Baofeng, 2005). Therefore metal ions are more accessible to the inner surface in order to combine with internal binding sites to enhance the stability of the reaction.

From Fig. 5 and Fig. 6, it is also concluded that both stability constants of complexes ( $\log K_f$ ) and coordination number of  $\text{HA-Zn}^{2+}$  is greater than the constants of the reaction of  $\text{HA-Cd}^{2+}$  when they are in the same pH conditions. This is because the affinity ability of Humic acid and metal ions are related to the atomic coefficient and ionic radius. The ionic radius of smaller elements have a higher affinity with the HA. Element Zn has a smaller atomic coefficient and ionic radius than element Cd, so  $\text{Zn}^{2+}$  has a higher affinity with the HA than  $\text{Cd}^{2+}$  when they are in the same pH condition. Therefore,  $\log K_{\text{Zn}}$  is larger than  $\log K_{\text{Cd}}$ .

### 3. Conclusions

Acidity affects both the acid effect of Humic acid and the hydrolysis effect of the  $\text{Fe}^{3+}$  ion. It creates opposite reaction directions, but not the same degree of influence. In certain experimental range, with the increase of pH, both stability constants of complexes and coordination number of  $\text{HA- Fe}^{3+}$  increases, which promotes coordination reactions. A higher pH value increases both stability constants of complexes and coordination number.

Acidity affects both the acid effect of Humic acid and the hydrolysis effect of the  $\text{Mn}^{2+}$  ion, just like the reaction of  $\text{HA- Fe}^{3+}$ . Higher pH value is positive to coordination reaction and increases stability constants of complexes. The coordination number increases with pH when it rises from 3.0 to 5.0, but decreases when the pH rises further up from 5.0 to 7.0.

To the reactions of  $\text{HA-Zn}^{2+}$  and  $\text{HA-Cd}^{2+}$ , both the stability constants of complexes and coordination numbers were increased as the pH is increased, when ionic strength and temperature conditions are kept the same. It is also concluded that both stability constants of complexes ( $\log K_f$ ) and the coordination number of  $\text{HA-Zn}^{2+}$  is greater than the constants of the reaction of  $\text{HA-Cd}^{2+}$  when they are in the same pH conditions.

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