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EQUILIBRIUM STUDIES OF THE INTERACTIONS OF Zn(II) AND Cu(II) IONS WITH HUMIC ACID BY POTENTIOMETRIC TITRATION, IR AND FLUORESCENCE SPECTROSCOPY

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ABSTRACT:

The interactions of Zn(II) and Cu(II) with humic acids (HA) were characterized by potentiometric titration, IR and fluorescence spectroscopy. The equilibrium constants determined were: Log([Zn(Cat)]/[Zn^{2+}][Cat]) = 15.25, Log([$Zn(Cat)_2$]/[ZnCat][Cat]) = 9.80, Log([Zn(Cat)(Sal)]/[Zn(Cat)][Sal]) = 8.59, Log([Zn(Cat)(Pht)]/[Zn(Cat)][Pht]) = 3.71, Log([$Zn(OH)(Cat)_2$][H^+]/[$Zn(Cat)_2$]) = -8.91, for the Zn(II) system, and Log([Cu(Cat)]/[Cu][Cat]) = 18.45, Log([$Cu(Cat)_2$]/[CuCat][Cat]) = 14.18, and Log([Cu(Cat)(Sal)]/[Cu(Cat)][Sal]) = 8.44 for the Cu(II) system. The amounts of each group detected by potentiometric titration were: phenol = 0.666, carboxylic = 1.042, catechol = 0.540, phtalic = 1.163, and Salicylic = 0.810 mmoles per gram of HA, and the speciation curves were calculated.

KEYWORDS: Humic Acid, Zn(II), Cu(II), Speciation, Potentiometric Titration.

RESUMO:

As interações dos ions Zn(II) e Cu(II) com Ácidos Húmicos (HA) são caracterizadas por titulação potenciométrica, IV e Espectroscopia de Fluorescência. As constantes de equilíbrio determinadas são: Log([Zn(Cat)]/[Zn^{2+}][Cat]) = 15,25, Log([$Zn(Cat)_2$]/[ZnCat][Cat]) = 9,80, Log([Zn(Cat)(Sal)]/[Zn(Cat)][Sal]) = 8,59, Log([Zn(Cat)(Pht)]/[Zn(Cat)][Pht]) = 3,71, Log([$Zn(OH)(Cat)_2$][H^+]/[$Zn(Cat)_2$]) = -8,91, para o sistema Zn(II), e Log([Cu(Cat)]/[Cu][Cat]) = 18,45, Log([$Cu(Cat)_2$]/[CuCat][Cat]) = 14,18, e Log([Cu(Cat)(Sal)]/[Cu(Cat)][Sal]) = 8,44 para o sistema Cu(II). A quantidade de cada grupo detectada por titulação potenciométrica é: Fenol = 0,666; Carboxílico = 1,042; Catecol = 0,540; Ftálico = 1.163 e Salicílico = 0,810 mmoles por grama de HÁ, e as curvas de especiação foram calculadas.

PALAVRAS CHAVE: Ácido Húmico, Zn(II), Cu(II), Especiação, Titulação Potenciométrica.

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1. INTRODUCTION

Humic acids (HA) are a complex mixture of compounds, with different sizes, molar masses and several functional groups. The major groups are: carboxyl, phenol, catechol, phthalic and salicylic. Knowledge of the amount of each group present in this mixture is important in order to understand the interaction of humic substances (HS) with metal ions in the environment. The stability of complexes formed between HA and metal ions (HA-M) varies and is dependent on the pH, metal, ionic strength, and concentration of HA.[1,2,3]

A recent definition of the conformational nature of HA states that they should be regarded as supramolecular associations of self-assembling heterogeneous and relatively small molecules derived from the degradation and decomposition of biological material. A major aspect of the humic supramolecular conformation is that it is stabilized predominantly by weak dispersive forces instead of covalent linkages. Hydrophobic (van der Waals, π–π, CH-π) and hydrogen bonds are responsible for the apparent large molecular size of HA, the importance of the former increasing with pH.[2]

Metal complexation is important to understand the transport and availability of metals in soils and natural waters, and in the case of toxic metal contamination humic substances (HS) lower significantly the amount of free metal ion, reducing its toxicity to humans. This subject has gained considerable attention for many years and several methods have been employed to investigate HA-metal ion complexation.[4-18] However, none of these studies gives details regarding HA complexation.

Of the techniques available, potentiometric titration was selected since it allows the calculation of the amount of each functional group and it can also be used to measure the interaction of each group. In this study, the interactions of Cu(II) and Zn(II) were characterized by potentiometric titration, fluorescence and IR spectroscopy. The IR spectra are compared with those in the literature.[19-21]

2. EXPERIMENTAL

The potentiometric titration of HA (from Aldrich) in the absence and presence of copper(II) and zinc(II) was carried out with a Corning 350 pH/ion analyzer fitted with blue-glass and Ag-AgCl reference electrodes. The potentiometric apparatus was calibrated with standard HCl and KOH solutions to read $-\log [H^+]$ directly, and the pKw for water at $\mu = 0.100$ M was 13.78. Samples of 0.100 g of HA were diluted with 40 ml of bidistilled water (in the presence of $KMnO_4$) in a sealed thermostated vessel at 25.0 °C. The experimental solution of HA alone, adjusted to 0.100 M ionic strength with KCl, was titrated with 0.100 M standard CO_2-free KOH until the pH reached approximately 11, and back titrated with 0.100 M HCl. Solutions containing HA plus Cu(II) and HA plus Zn(II) were studied potentiometrically with 0.0350 mmol and 0.0700 mmol of metal ion. The argon was cleaned using two vessels of 0.100 M KOH solution and bubbled at the inlet and outlet of the thermostated cell. Computations of the triplicate experiments were all carried out with the BEST7 program, and the species diagrams were obtained with the aid of the SPECIES program.[22-25]

Infrared spectra of the humic acid fractions were recorded using samples in KBr pellets (1 mg of Aldrich humic acid per 100 mg of KBr) with a Shimadzu Resolution 1.04 FT-IR spectrometer. The KBr (FT-IR grade, Aldrich Co.) was dried by heating and kept under vacuum in desiccators prior to use.

In the fluorescence titration, stock solutions of HA were prepared by dissolving 0.0080 g of HA in 200 mL. Samples of 10 mL of stock solution were used to prepare the experimental solutions. Aliquots of 50 µL of $1.09\text{x}10^{-2}$ mol/L Cu(II) solution were added to the experimental solutions, and an interval of 30 minutes allowed the solutions to reach equilibrium.

The transmittance intensity of the experimental solutions was measured using a SimAminco SPF-500 spectrofluorometer. Emission and excitation slits were sets at a 10 nm band width. The wavelength emission was 510.5 nm and the excitation wavelength was 366 nm. Stern-Volmer graphics were obtained from these data for the HA-Cu(II) system at pH 9.

3. RESULTS AND DISCUSSION

3.1 The coordinating groups of humic acids

The potentiometric curve of HA is shown in Figure 1, together with the curves of the metal systems. In all the curves the buffers are not well defined. It can be seen that the curves of metal systems are below the curve of HA alone, indicating the coordination of the metal ions; copper(II) interacting more strongly than zinc(II). The amount of each group detected in the supramolecular structure of HA, as well as the pKa values, were determined with the help of the BEST7 program when possible, and the results are shown in Table 1.

3.2 Metal systems

The equilibrium constants determined (Table 2) allow the calculation of the distribution of the groups coordinated with the metal ions, showing the preference of each group for the metals. Figure 2 shows the distribution for the HA-Zn(II) system. Above pH 4, the Zn(II) ion coordinates to the catechol group, Zn(Cat), and also the phtalic group, Zn(Cat)(Pht), reaching a maximum at near neutral pH. A second catechol group coordinates to the Zn(II) ion resulting in $Zn(Cat)_2$ and a hydroxo species, $Zn(OH)(Cat)_2$. A mixed group interaction, catechol and salicylic, Zn(Cat)(Sal), also forms at higher pH.

The distribution of groups coordinated to Cu(II) is shown in Figure 3. Copper coordinates to the HA above pH 3. Its preference for the catechol group is shown, Cu(Cat), being 100 % coordinated at pH 5.0. Above this pH value a second catechol group coordinates, represented by Cu(Cat)2. A salicylic group also coordinates, and coordination of salicylic and catechol groups to Cu(II) is represented by Cu(Cat)(Sal).

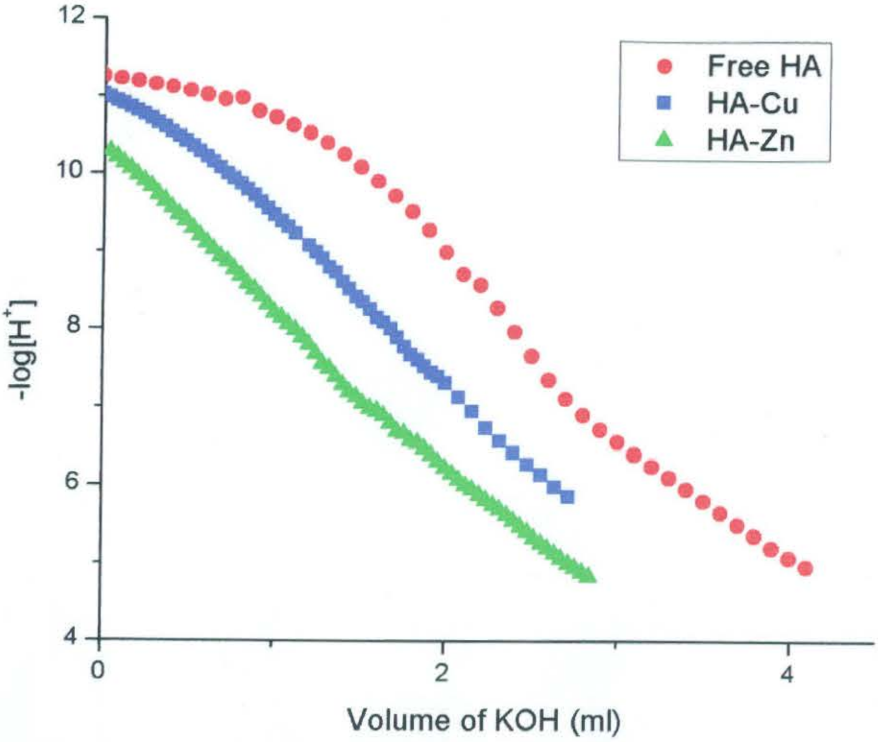

Figure 1 – Potentiometric titration curves of HA, HA in presence of Cu(II) and HA in presence of Zn(II); μ = 0.100 M (KCl), T = 25.0 °C.

Table 1 – Amounts of oxygenated groups detected in HAs obtained from Aldrich, and their pKa values, μ = 0.100 M (KCl), T = 25.0 °C.

Group	mmoles/g of HA*	pKa*
Phenol	0.666 (6)	9.66 (6)
Carboxylic	1.042 (19)	6.35 (2)
Catechol	0.540 (13)	7.97 (22) 13.30
Phtalic	1.163 (30)	2.76 (6) 4.71 (6)
Salicylic	0.810 (4)	3.29 (25) 13.40

*The number in parentheses is the average deviation of the measurement.

Table2: Equilibrium constants for the interactions of HA coordinating groups with Zn(II) and Cu(II) ions, $\mu = 0.100$ M (KCl), T = 25.0 °C.

Quotient	Log Q Zn(II)*	Log Q Cu(II)*
[M(Cat)]/[M][Cat]	15.25 (30)	18.45 (28)
[M(Cat)$_2$]/[MCat][Cat]	9.80 (05)	14.18 (08)
[M(Cat)(Sal)]/[M(Cat)][Sal]	8.59 (28)	8.44 (25)
[M(Cat)(Pht)]/[M(Cat)][Pht]	3.71 (02)	-
[M(OH)(Cat)$_2$][H$^+$]/[M(Cat)$_2$]	-8.91 (12)	-

*The number in parentheses is the average deviation of the measurement.

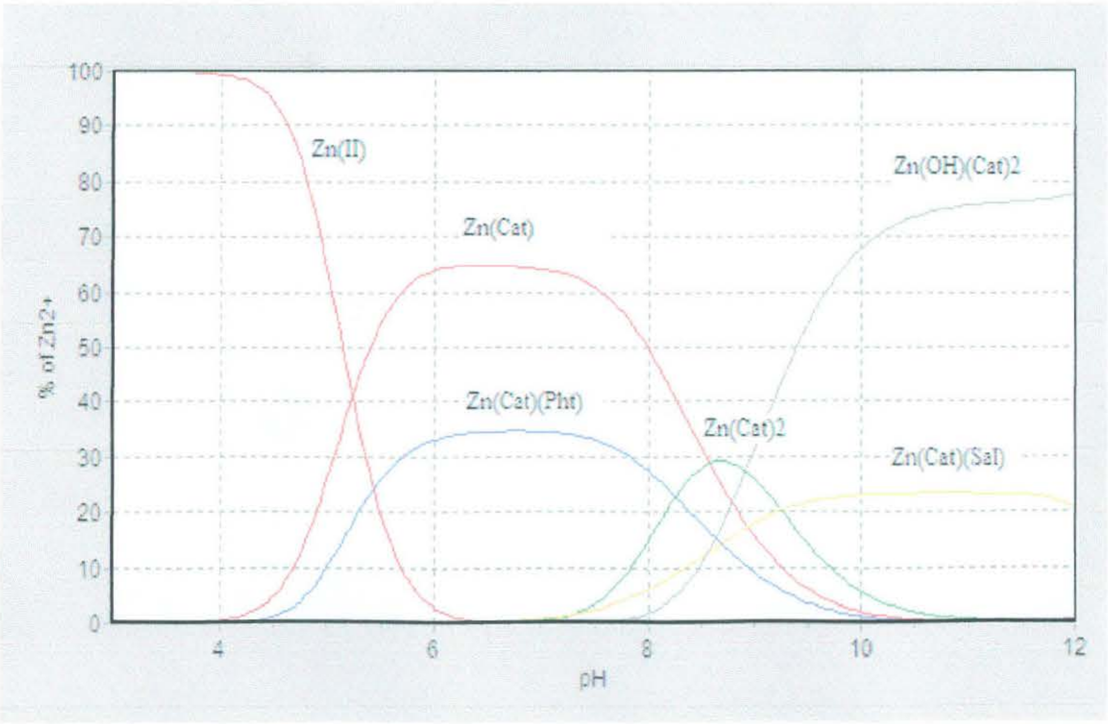

Figure 2 – Distribution curves of coordinated groups with Zn(II) ion.

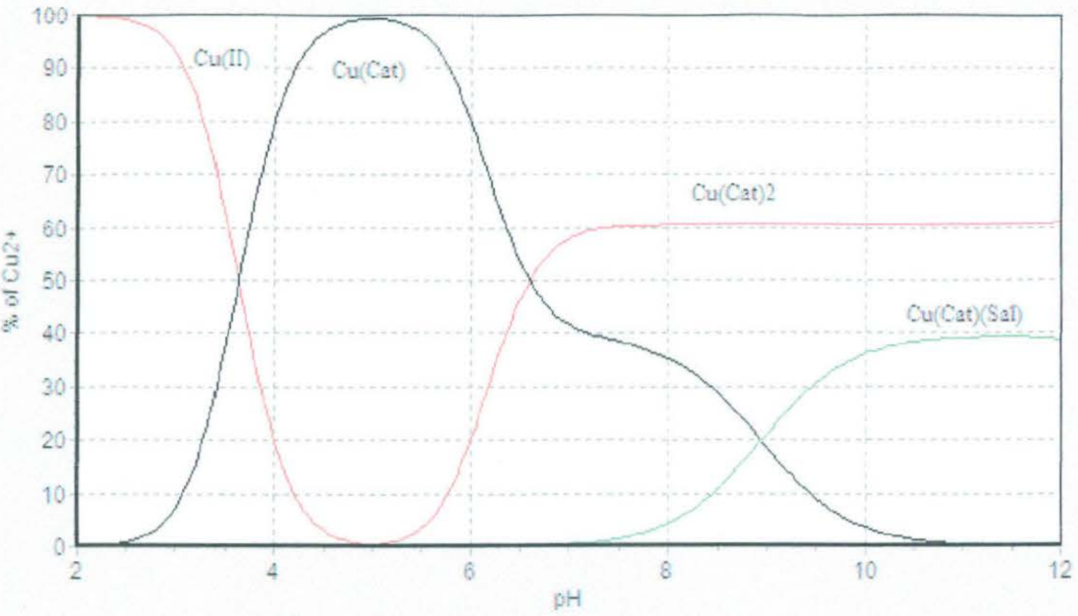

Figure 3 – Distribution curves of coordinated groups with Cu(II) ion.

3.3 IR studies.

The IR studies showed the complexation of the metal ions. On the IR spectrum of HA (Figure 4) a broad peak can be seen at 3400 cm^{-1} due to the axial stretching of the carboxylic and catechol O-H groups. The peaks between 2915 cm^{-1} and 2851 cm^{-1} are due to the CH_2CH_3 stretching, and at 1680 cm^{-1} there is a peak due to the stretching of deprotonated C=O.

The metal complexation can be evidenced through the increase in the intensity of the peaks at 1680 cm^{-1}, attributed to asymmetric stretching of the COO^-. For the HA-Zn(II) system the intensity of the peak at 1680 cm^{-1} is greater at pH 7, where Zn(II) is coordinated to phtalic and catechol groups (Figure 3). At higher pH values, Zn(II) is predominantly coordinated to catechol and salicylic groups, reducing the carboxylic environment in the Zn(II) ion, since the salicylic group has only one carboxylic group while phtalic has two. The peak at 1394 cm^{-1} is narrow due to the interaction with the metal ion and catechol group. At neutral pH it can be observed that there is also complexation of the metal ion with the catechol. At alkaline pH values, the tuning of the peaks 1680cm^{-1} and 1394cm^{-1} is attributed to the complexation of catechol and salicylic groups (Figure 4).

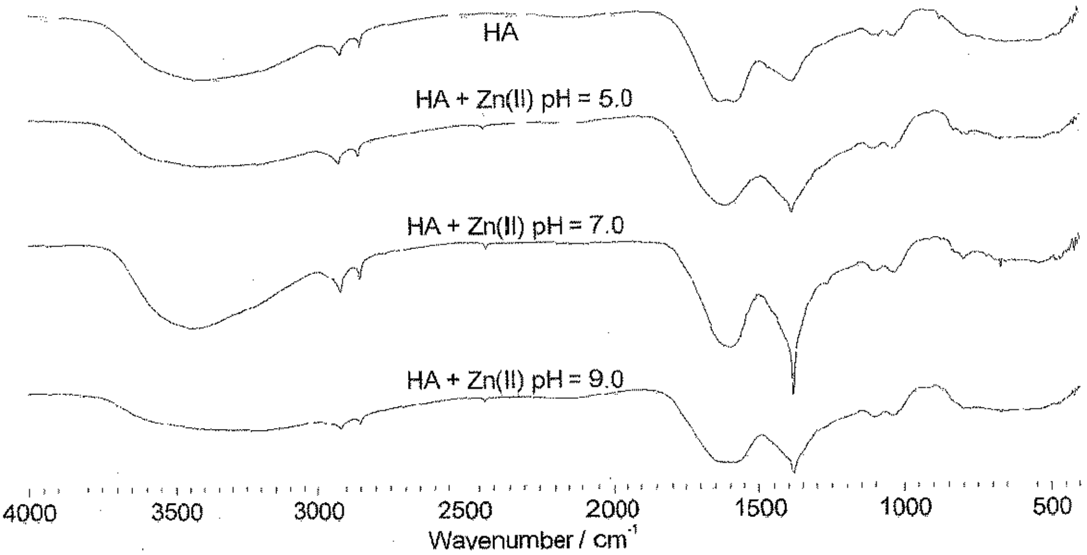

Figure 4 – IR spectra of HA-Zn(II) system.

The IR spectra of the HA-Cu(II) system is shown in Figure 5. The intensity of the peak at 1680 cm^{-1}, attributed to asymmetric stretching of the COO$^-$ group of HA remains constant at acid and neutral pH. A slight shift of this peak to a higher wave number (cm^{-1}) is observed at pH 9 (Figure 5), indicating the interaction of Cu(II) with the salicylic group, since this group has a carboxylic group. The peak at 1394 cm^{-1} is narrow due to the interaction with the metal ion and catechol group. Cu(II) is coordinated with catechol at all pH values above pH 3 (Figure 3), and in all IR spectra at pH values 5, 7 and 9 the peak at 1394 cm^{-1} is narrow, indicating that catechol is involved in the coordination sphere of Cu(II).

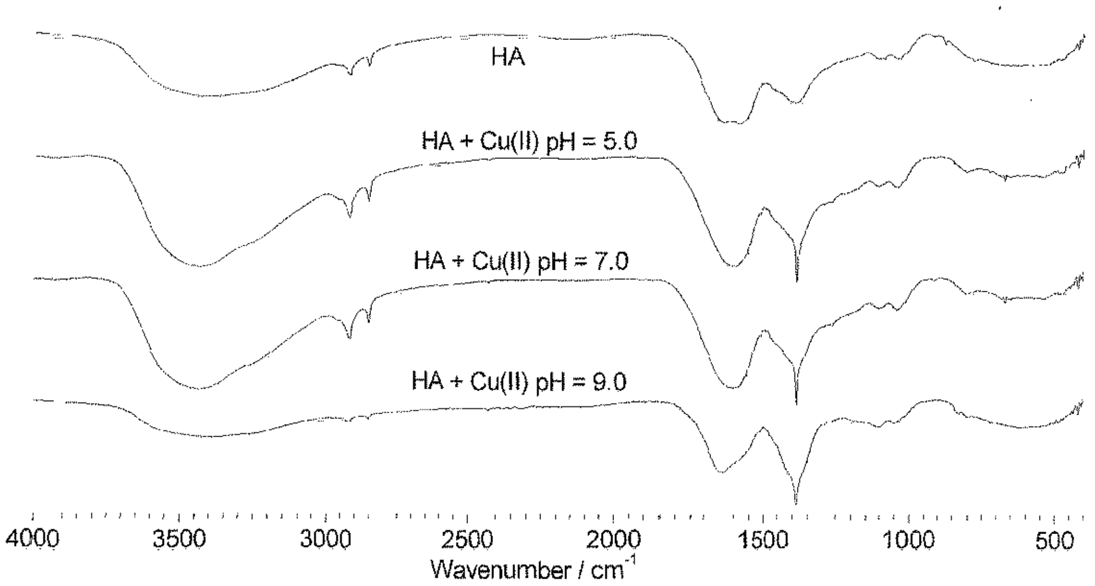

Figure 5 – IR spectra of HA-Cu(II) system.

3.4 – Fluorescence titration

Figure 6 shows the Stern-Volmer graph for the Cu(II) quenching titration of HA at 366/510.5 nm. As the amount of Cu(II) added in solution increases, the fluorescence intensity decreases due to Cu(II) binding, up to 2.1 μmol of Cu(II) per mg of HA, and further addition of Cu(II) does not affect the fluorescence intensity. At pH 9 most of the

Cu(II) ion is coordinated in a 1:2 coordinating group:metal ion ratio (Figure 3). The saturation of the coordination groups with Cu(II) occurs with this amount of Cu(II). Thus, 2.1 mmol of Cu(II)/g of HA saturate approximately 4.2 mmol of coordinating groups per gram of HA. The sum of the mmoles for all groups in Table 1 is 4.221 mmol/g of HA. This result confirms the total amount of HA groups determined by potentiometric titration.

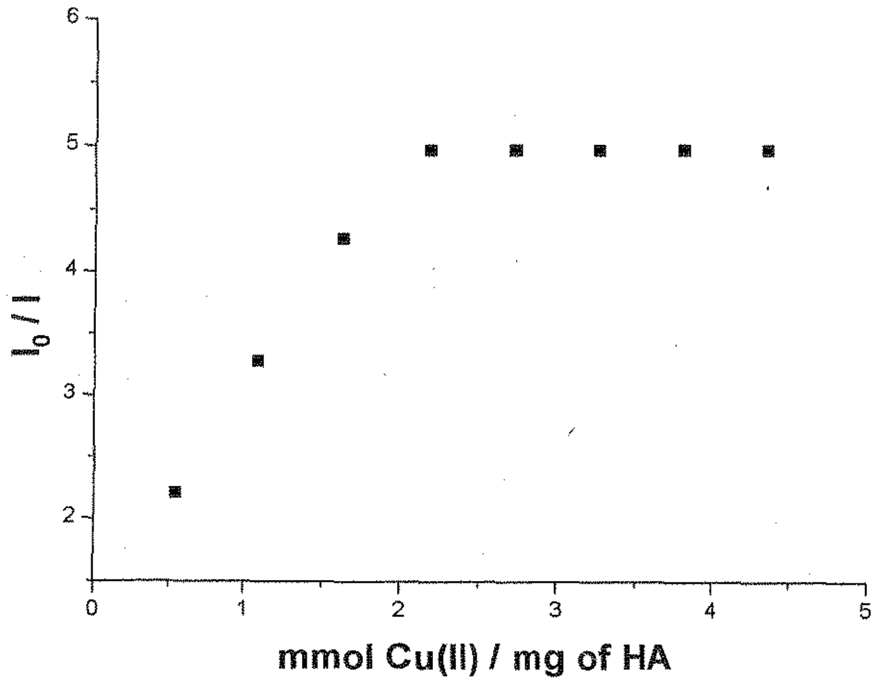

Figure 6 - Stern-Volmer graph of the HA-Cu(II) system at pH 9.

4. CONCLUSIONS

Potentiometric titration, used in conjunction with other techniques, is a powerful means to study the speciation of metals in the environment. The amount of each group present in HAs in significant quantities was determined by potentiometric titration and appropriate computer programs. Catechol, salicylic and phtalic are the major groups involved in the coordination of Zn(II) and Cu(II) and the equilibrium constants are determined for each group.

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