

## Studies on copper(II)- and zinc(II)-mixed ligand complexes of humic acid

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Received 10 October 2005; received in revised form 16 December 2005; accepted 20 December 2005

Available online 8 February 2006

### Abstract

Interactions between humic acid (HA), extracted from Brazilian peat soil, and cations of copper(II) and zinc(II) have been examined by infrared spectroscopy, and electrochemical and thermogravimetric analyses. Spectral studies revealed that the interaction with metals occurred mainly at the carboxylic acid groups of HA. The stability constants of HA complexes formed with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were found, by square wave voltammetry and application of the Lingane model, to be  $8.93 \times 10^{10}$  and  $2.92 \times 10^2$ , respectively. Thermal analysis indicated that the stability of HA was increased by the presence of divalent cations of copper and zinc.

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*Keywords:* Humic acid; Thermal decomposition; Stability constants

### 1. Introduction

Humic substances are natural macromolecules produced by biological and geochemical processes derived from plant and animal debris, and are present in both soluble and insoluble forms in soil, water and sediments [1]. Humic substances may thus be considered as natural polyelectrolytes. The high content of acidic functional groups is responsible for the ability of humic acids (HAs) to interact with inorganic and organic contaminants in soils and natural waters [2]. Furthermore, the interactions of HAs with inorganic and organic contaminants are entropically favoured by virtue of the typical chelate effect [3].

The complexation of trace metal ions with HAs may lead to a decrease in metal toxicity (as is the case for copper) or to an increase in solubility (as for iron) thus making the metal ion more available for plant uptake. Hence, a detailed knowledge of the properties of the organic ligands present on HA, together with information concerning their capacities for the complexation of metal ions, is of paramount importance in understanding the bioavailability, mobility and distribution of heavy metals in natural ecosystems [4]. However, the full elucidation of the

adsorption equilibria between metal ions and HAs presents a difficult problem owing, in part, to the chemical complexity of the heterogeneous macromolecules involved [5]. The aim of the present study was to follow the interactions between HAs and divalent cations of Cu and Zn using electrochemical and thermal techniques in order to gain further insight into the nature of HA–cation interactions.

### 2. Materials and methods

#### 2.1. Preparation of samples of HA

Samples of HA were obtained from peat soil fractions collected at the margins of the Mogi Guaçu river ( $47^{\circ}9'W/21^{\circ}5'S$ ) in the town of Luiz Antonio (São Paulo, Brazil) [6]. The crude material was stored in polyethylene bags prior to air drying for 10 days at 298 K [6]. The extraction and purification of HAs followed the recommendations of the International Humic Substances Society (IHSS) [7].

#### 2.2. Characterisation of HAs

The percentage values of carbon, nitrogen, hydrogen and oxygen in samples of HA were determined by elemental analysis

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using a Fisons CHNS-O elemental analyser. The total acidity, and the proportions of phenolic and carboxylic acids, of HA samples were assayed as described before [8].

$^{13}\text{C}$ -NMR spectra of solid HA samples were determined on a Varian Mercury Plus 300 spectrometer operated at room temperature as detailed described before [9].

### 2.3. Characterisation of HA–metal ion complexes

#### 2.3.1. Infrared spectroscopy

Samples of HA (10.0 mg) were suspended in aqueous solutions (20.0 cm<sup>3</sup>) of metal ion (Cu<sup>2+</sup> or Zn<sup>2+</sup>; 100.0 mg/dm<sup>3</sup>). The suspensions were mechanically stirred for 24 h at 298 K and the solid materials (subsequently referred to as HA–Cu and HA–Zn, respectively) separated by filtration and lyophilised. The infrared spectra of HA, HA–Cu and HA–Zn samples were measured in KBr pellets using a MB-Bomem FTIR spectrophotometer in the region 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> through the accumulation 32 scans for each sample.

#### 2.3.2. Stability constants

The stability constants of the complexes formed between divalent metal ions and HAs were determined by square wave voltammetry by application of the Lingane model for complexation data [10]. Samples of HAs, varying in weight between 0 and 15 mg, were suspended in separate aliquots (15.0 cm<sup>3</sup> each) of 0.10 mol/dm<sup>3</sup> potassium chloride/hydrochloric acid buffer (pH 5) containing 100.0 mmol of metal ion (Cu<sup>2+</sup> or Zn<sup>2+</sup>). The suspensions were mechanically stirred for 24 h at 298 ± 1 K and submitted to square wave voltammetry in an EG&G 394 potentiostat using a mercury drop of 1 cm<sup>2</sup> superficial area as the working electrode, a platinum thread as the auxiliary electrode and Ag/AgCl as the reference electrode.

#### 2.3.3. Kinetics of thermal degradation

Thermogravimetric (TG) curves were obtained by heating ca. 10.0 mg samples of HA, HA–Cu or HA–Zn from room temperature up to 900 °C at a heating rate of 10 °C/min in a model TA 2960 thermogravimetric analyser under a dynamic atmosphere provided by a dry nitrogen flux. Kinetic thermal parameters were calculated by application of the Coats–Redfern equation [11].

## 3. Results and discussion

Elemental analyses of samples of HAs isolated from Brazilian peat soil showed values for carbon, nitrogen, hydrogen and oxygen of 48.30 ± 0.03, 8.72 ± 0.02, 7.01 ± 0.03 and 35.97 ± 0.08%, respectively. These values are similar to those reported for HA derived from other types of peat soil [12,13].

Since the chemical behaviour of humic acids is determined to a great extent by the acidic nature of the biopolymer, the HA samples employed in this study were assayed for total, phenolic and carboxylic acidity levels, giving values of 4.08 ± 0.03, 1.20 ± 0.05 and 2.88 ± 0.02 mmol/g of HA, respectively. More specific information concerning the structure of the HA could be obtained from  $^{13}\text{C}$ -NMR spectroscopy. The spectrum of a

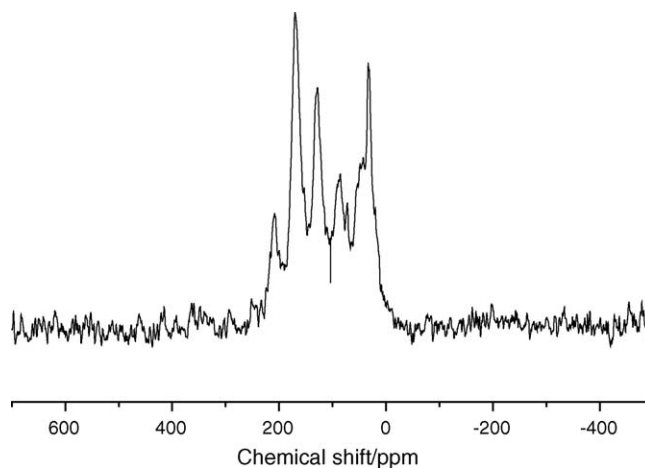


Fig. 1.  $^{13}\text{C}$ -CP/MAS-NMR solid state spectra of HA sample.

solid HA sample (Fig. 1) presented broad peaks in five distinct regions that could be assigned to: (i) CH<sub>n</sub>–C, signals in the range 0–65 ppm, (ii) CH<sub>n</sub>–OR, 65–100 ppm, (iii) C<sub>aromatic</sub>, 100–165 ppm, (iv) C<sub>carboxyl</sub>, 165–190 ppm, and (v) C<sub>ketone</sub>, 190–230 ppm [9,13].

### 3.1. Evidence of complexation from infrared spectroscopy

The infrared spectra obtained for HA, HA–Cu and HA–Zn samples are presented in Fig. 2. In all of the spectra, signals characteristic of humic acids are clearly present as detailed described before [9]. On the other hand, differences between the spectra are observable in the region between 1750 and 1550 cm<sup>-1</sup>. In the spectrum of HA a well-defined peak appears at around 1720 cm<sup>-1</sup>, which is the C=O stretching frequency associated with COOH and CONH<sub>2</sub> groups [9]. This peak is, however, absent from the spectra of HA–Cu and HA–Zn because the hydrogen atoms of the COOH groups have been substituted by divalent cations producing COO<sup>-</sup> groups that exhibit a characteristic peak at around 1660 cm<sup>-1</sup>. Further evidence of interaction between the metal ions and COOH groups is provided by the reduction of intensity in the spectra of HA–Cu and HA–Zn of

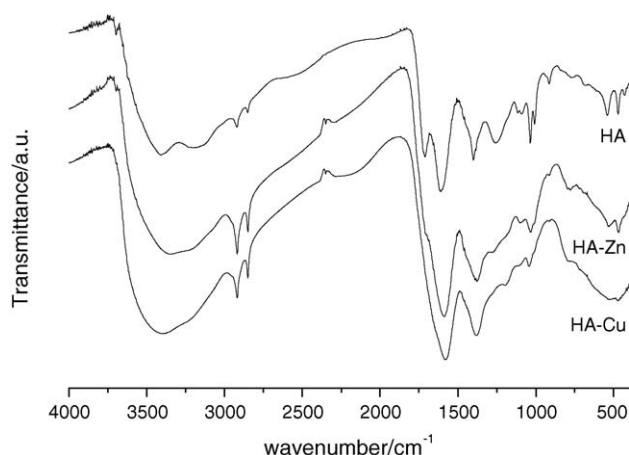


Fig. 2. Infrared spectra of HA, HA–Cu and HA–Zn samples.

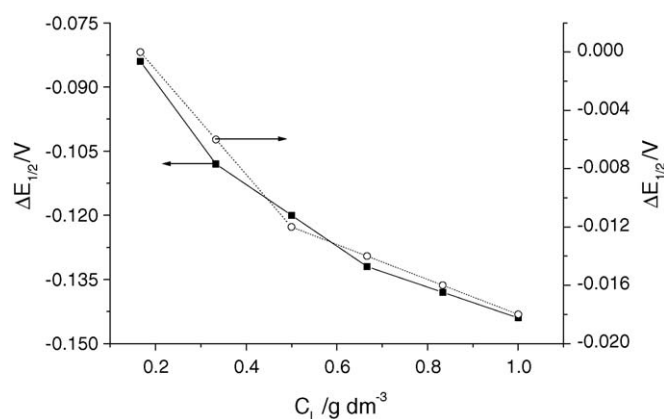


Fig. 3. Influence of HA concentration on half-wave potential at 298 K in the presence of  $\text{Cu}^{2+}$  (■) and  $\text{Zn}^{2+}$  (○).

the band at  $1250\text{ cm}^{-1}$  associated with  $\text{COOH}$ , and the increase of intensity of the peak at  $1660\text{ cm}^{-1}$  attributed to asymmetric stretching in  $\text{COO}^-$  groups.

### 3.2. Determination of stability constants

The stability constant ( $K_S$ ) of each HA–metal ion complex was determined by direct application of the Lingane equation [10]:

$$\Delta E_{1/2} = -\frac{RT}{nF} \ln K_S - j \frac{RT}{nF} \ln C_L \quad (1)$$

where  $\Delta E_{1/2}$  is the change of half-wave potential,  $C_L$  the ligand concentration,  $R$  the universal gas constant,  $T$  the temperature,  $n$  the number of electrons involved in the transfer,  $F$  the Faraday number, and  $j$  is the number of bonds formed during complexation. The voltammetric behaviour of HA in the presence of various amounts of each of the divalent metal ions was examined, from which changes in the half-wave potential caused by increasing concentrations of ligand could be derived. Plots of  $\Delta E_{1/2}$  versus  $C_L$  (Fig. 3) show that the increase in humic acid concentration had a direct effect on the half-wave potential. The complex formed between copper and humic acid presented a calculated value for  $K_S$  of  $8.93 \times 10^{10}$ , while that for the complex formed between zinc and humic acid was  $2.92 \times 10^2$ . Voltammetric studies thus demonstrate that humic acid interacts more effectively with  $\text{Cu}^{2+}$  than with  $\text{Zn}^{2+}$ , a finding that is in accord with previously reported data from thermodynamic studies showing that such interactions are spontaneous in nature [6]. Although, these interactions present endothermic behaviour in terms of enthalpy, they are entropically driven by virtue of the chelate effect [3,6].

### 3.3. Evidence of complexation from thermal analyses

The thermogravimetric (TG) curves obtained for HA, HA–Cu and HA–Zn samples are presented in Fig. 4, and the corresponding mass loss ( $\Delta m$ ) values, decomposition temperature range, and differential TG peak temperatures ( $T_s$ ) are listed in Table 1. All samples showed a single characteristic decomposition stage

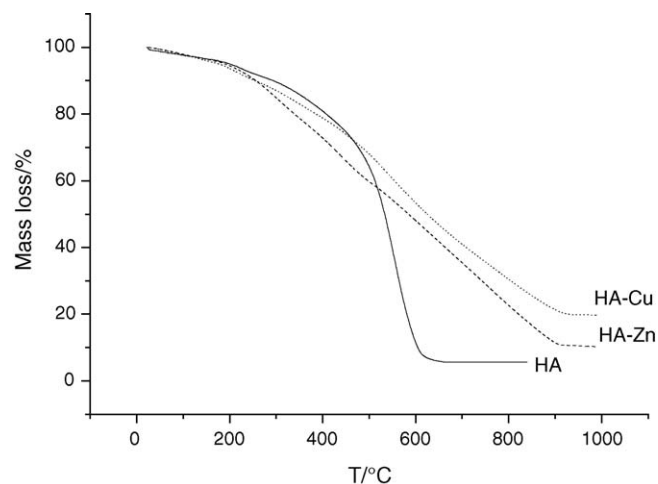


Fig. 4. Thermogravimetric curves of HA, HA–Cu and HA–Zn samples.

starting at around  $160\text{ }^\circ\text{C}$ , which is assigned to the decomposition of the chain end-groups of HA (including carboxylic acid, aldehyde, amide, amine, alcohol, and phenol groups), leading finally to the total decomposition of the organic matter of HA [14]. HA samples presented an abrupt loss of organic mass leaving a residue of 5.3% corresponding to the oxides of the metallic impurities typically present in the biopolymer. In contrast, the decompositions of HA–Cu and HA–Zn samples occurred gradually up to a temperature of  $900\text{ }^\circ\text{C}$  indicating that complexation with metal results in additional thermal stability of HA. From TG residual data, the residues that remained following loss of organic mass from HA–Cu and HA–Zn samples were determined as 19.6 and 10.2%, respectively. Assuming that these residues were made up of oxides of the corresponding divalent metal and of the metallic impurities originally present in the biopolymer, it could be calculated that 1.70 mmol of Cu was absorbed per gram of HA, while Zn complexation was less efficient leading to the absorption of only 0.60 mmol/g of HA.

The data embodied in the TG curves were used to explore the mechanism of the decomposition stage of HA, HA–Cu and HA–Zn. The thermal decomposition studies have been extensively used in order to characterize materials and their properties. Considering the kinetics of decomposition, the integral function of conversion ( $g(\alpha)$ ) is given by the Coats–Redfern equation [11,15]:

$$\log \left[ \frac{g(\alpha)}{T^2} \right] = \log \left[ \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.303RT} \quad (2)$$

Table 1

Percentage mass loss ( $\Delta m$ ), respective temperature range ( $T$ ) and differential thermogravimetric analysis peak temperatures ( $T_s$ ) determined for HA, HA–Cu and HA–Zn samples

Sample	$\Delta m$ (%)	$T$ ( $^\circ\text{C}$ )	$T_s$ ( $^\circ\text{C}$ )
HA	94.7	160–690	555
HA–Cu	80.4	165–950	550
HA–Zn	89.8	160–930	660

Table 2  
Kinetic parameters for the thermal decomposition of HA, HA–Cu and HA–Zn samples

	$E$ (kJ/mol)	$A/s$	$\Delta^\ddagger S$ (J/mol K)	$\Delta^\ddagger H$ (kJ/mol)	$\Delta^\ddagger G$ (kJ/mol)
HA	142.27	$5.48 \times 10^6$	–113	135.40	228.50
HA–Cu	38.82	$9.42 \times 10^{-1}$	–255	30.81	276.50
HA–Zn	30.08	$2.16 \times 10^{-1}$	–267	23.27	240.71

where  $T$  is the temperature,  $A$  the pre-exponential factor,  $R$  the gas constant,  $\phi$  the heating rate, and  $E$  is the activation energy of the reaction. The assignment of the mechanism of thermal decomposition was based on the assumption that the form of  $g(\alpha)$  depends on the reaction mechanism. Nine algebraic expressions for  $g(\alpha)$  encompassing the most frequently used mechanisms in solid state processes [15] were considered, and correlation coefficients, indicating correspondence with the determined kinetic data, were calculated in order to obtain the best form of  $g(\alpha)$  to determine the possible reaction mechanism. For the thermal decompositions of HA, HA–Cu and HA–Zn, the best correlation was obtained using the deceleration function  $g(\alpha) = -\ln(1 - \alpha)$ , which corresponds to a mechanism involving random nucleation with one nucleus on the individual particle [16].

The activation entropy ( $A$ ) was determined from the equation [15]:

$$A = \frac{kT_s}{h e^{\Delta^\ddagger S/R}} \quad (3)$$

where  $k$  is the Boltzmann constant,  $h$  the Planck's constant and  $T_s$  the temperature related to the differential TG peak maximum value (see Table 1). The enthalpy ( $E$ ) was obtained from  $E = \Delta^\ddagger H - RT_s$  and Gibbs energy of activation ( $\Delta^\ddagger G$ ) was calculated from  $\Delta^\ddagger G = \Delta^\ddagger H - T_s \Delta^\ddagger S$ . All of the kinetic thermal degradation parameters shown in Table 2 were calculated from data obtained from thermogravimetric curves (Fig. 4).

Kinetic thermal analysis indicates that the values of  $E$  and  $\Delta^\ddagger H$  for the decomposition of HA are much higher than those for the decompositions of HA–Cu and HA–Zn. However, regarding the HA–metal ion complexes, the entropic contributions are greater than they are for HA, thus resulting in a final  $\Delta^\ddagger G$  that is more endergonic for HA–Cu and HA–Zn than for HA. Indeed, complexation of HA with metal ions leads to an increase in the stability of this material according to  $\Delta^\ddagger G$  data, a finding that is in accord with the results of the voltammetric study. The increased stability of the HA–metal ion complexes is confirmed from the large decrease in entropy observed in the degradation of HA that is bonded to metal ions. Furthermore, HA–Cu presents a  $\Delta^\ddagger G$  value of degradation that is more endergonic than that of HA–Zn showing that interaction between HA and  $\text{Cu}^{2+}$  is more efficient than that between HA and  $\text{Zn}^{2+}$ , a finding that is in complete agreement with the observed electrochemical data.

## 4. Conclusion

Interactions between humic acids and the divalent metal ions  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  have been confirmed by infrared spectroscopy in which decreases in the intensity of the peak at the stretching frequency of C=O in COOH groups were observed following complex formation. These findings were corroborated by the determination of changes in the half-wave potentials, indicating the formation of chemical bonds between metal ions and HA. Evaluation of the thermodynamic properties of the complexes signify that HAs gain stability when bonded to metal ions.

## Acknowledgements

The authors wish to thank FUNPE/UnB and FINATEC for financial support. The authors are indebted to the CNPq and CAPEs for fellowships.

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