Aquatic Fulvic Acids: Chemical Characteristics and Complexation with Copper (II)

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ABSTRACT


In this work we determined the quantity of fulvic acid functional groups and their interactions with copper(II) ions. The fulvic acids used were extracted from water collected from Itapanhau River, around the city of Cubatão, on the south coast of São Paulo state, southeast Brazil. The samples were characterized by Elemental Analysis and Infrared Spectroscopy (FTIR) and the results indicated the major presence of carboxylic and phenolic groups. Determination of the quantity of carboxylic and phenolic groups was performed by potentiometric titration using a modified Gran's method and BEST7 software. With the BEST7 software, it was possible to determine, quantitatively (meq g⁻¹), two classes of carboxylic groups (carboxylic and phenol) and two classes of phenolic groups (phenol and catechol), and the combination of these groups (salicylic), as well as the protonation and complexation constants.

ADDITIONAL INDEX WORDS: Humic substances, potentiometric titration, BEST7 software.

INTRODUCTION

The contamination of coastal ecosystems with metallic ions has damaged fishing and the culture of marine species around the world (CURTIS et al., 2001; LORENZO, et al, 2002). In soils and natural waters complex mixtures of organic substances including humic substances are found, that act as buffer agents diminishing the availability of metallic ions (SARGENTINI, JR. et al., 2001). For this reason, the study of the behavior of these substances is of fundamental importance for the reduction of pollution in coastal ecosystems. A knowledge of the chemical structure of humic substances and how their complexation with metallic ions occurs is very important. Through this knowledge, synthetic substances could be created in the future (with low cost) to absorb pollutants, since the humic substances present in nature are often insufficient for this purpose. The fulvic acids (FA) are a group of humic substances that interact very well with pollutants in nature, because they have a great number of functional groups (carboxyls, hydroxyls, phenols, salicylic, etc) (NIFANT’EVA et al.,1999). Very little is known about the chemical interactions of the FA and metallic ions. The major difficulty is to determine which functional groups are involved in the complexation of the ionic metals. In the literature there are a number of papers that describe the procedures for functional group analysis of humic substances (DAVIS et al.,1999; RITCHIE and PERDUE, 2003; SIERRA et al.,2001; MASINI, 1993). The best manner to study how the metals interact with FA is using analyses techniques in solution. Potentiometric titration can be very helpful to determine chemical interactions, reproducing, as closely as possible, the reality that occurs in nature. However, it is impossible to elucidate the titration curves, without the use of a mathematical method or a computational program. The objective of this paper is to show how BEST7 and SPE software can elucidate the titration curves of the FA and copper (II) ion complexation determining various functional groups (their quantities) and the specific complexation sites.

MATERIALS AND METHODS

Fulvic Acids

The FA were extracted from surface water from the Itapanhau River, which flows around the city of Cubatão, on the south coast of São Paulo state, southeast Brazil. This area has been protected from polluting substances by environmental law since 1972. The surrounding area is covered with Atlantic Forest. We chose this river because it has a very high concentration of natural organic matter, facilitating the obtention of the FA. The samples were extracted and purified in an Amberlite XAD-8 resin using the international standards set by the International Humic Substances Society (IHSS).

Elemental Analysis

Elemental analyses were run for C, N, H, O and S on an Elemental Analyser CHNS-EA1110 (Fisons Instruments). Oxygen was determined, separately, using the VTF-900 accessory.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were collected with KBr pellets (1.0 mg FA in 100 mg dried KBr) from 4,000 to 650 cm⁻¹ on a Perkin-Elmer, Paragon 1.000 Infrared Spectrometer.

Potentiometric Titrations

All the reagents used were analytical grade materials and were used without further purification. All the solutions were prepared with twice-distilled, CO₂-free water. KCl (potassium chloride) (Synth) was used, in all titrations, as a supporting electrolyte to adjust the ionic strength (µ = 0.1 mol L⁻¹). As the titration agent carbonate-free solutions of 0.1mol L⁻¹ KOH (potassium hydroxide) were used, prepared from 1.0 mol L⁻¹ KOH Dilut-it ampoules (J.T.Baker Co.) and standardized by titration with potassium acid phthalate (Merck). Solutions of FA (80 mg L⁻¹) were prepared directly in the titration cell, dissolving a known weight of FA in water, adding 8 mL HCl (hydrochloric acid) (Merck) 0.01 mol L⁻¹ (µ = 0.1 mol L⁻¹) and completing the volume with water to 50 mL. The stock solution of 0.01 mol L⁻¹ CuCl₂,2H₂O (copper (II) chloride) (Vetec Ltd.) was standardized by titration with EDTA (Merck) (ethylenediaminetetraacetic acid) using murexide (Merck) as the indicator. The titrations were carried out in a thermostated sealed cell at 25 ± 0.05°C, in an inert atmosphere (using argon gas), in the absence and presence of Cu(II). Each experimental solution was titrated at least three times, and the average was calculated. Prior to the titrations the electrode was calibrated with dilute HCl solutions to read directly -log[H⁺], here represented by pH. The pH values of the titrations were read with a pH meter (Corning 350) equipped with glass and reference electrodes (filled with KCl 4 mol L⁻¹) (Thomas Co.).
was performed utilizing the same mathematical algorithm as formed during the titration. With this the computation the species diagrams, that indicate the percentage of the species strong acid titrated with a strong base (titration agent). The titration equilibriums of weak monoprotic acid mixtures and a humic substances, and consists of linear equations that describe the groups into weak acid groups and strong acid groups. This humic substances using the modified Gran's method, dividing the quantities found are listed. As one can see, the major quantity of phenol, carboxyl, cathecol, phthalic and salicylic. In Table 2 the major category found is cathecol groups (1.39 meq g\(^{-1}\)) the functional groups (logK) of the titration data, using the BEST7 software. The samples were analyzed by elemental analysis and the results are in the range of other fulvic acids from the literature. O (47.8%) and C (45.14%) were the major constituents, H (3.9%), N (2.1%) and S (1.1%) were detected (composition calculated on an ash-free basis). The FTIR spectra indicated the major bands at 3.420 cm\(^{-1}\) (OH deformation and C-O stretching of phenolic OH) and 1.220 cm\(^{-1}\) (C-O stretching of esters, ethers and OH deformation of carboxylic acids). The results are in agreement with the results from other authors (E., 1996; Davis et al., 1999). The FTIR spectra indicated the major presence of carboxyl and phenolic groups. The principal band for the carboxylic acids at 1.720 cm\(^{-1}\) is less intense than that for the phenolic group.

Table 2. Oxygenated species found in aquatic FA (Itapanhau River) (meq g\(^{-1}\)) calculated by BEST7.

<table>
<thead>
<tr>
<th>Oxygenated species</th>
<th>quantities (meq g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic</td>
<td>0.76</td>
</tr>
<tr>
<td>Carboxylic</td>
<td>0.30</td>
</tr>
<tr>
<td>Cathecol</td>
<td>1.39</td>
</tr>
<tr>
<td>Phthalic</td>
<td>0.59</td>
</tr>
<tr>
<td>Salicylic</td>
<td>1.03</td>
</tr>
</tbody>
</table>

modified Gran's method is applied to the titration curve data values. Seymour simplified the representative titration equation of an acid mixture eliminating some mathematical constants and making some approximations, assuming that at the beginning of the titrations (shorter pH region values) the weak acids are totally protonated. The limitation of this method is that it can be used only for two distinct groups. In this work, we use it only to calculate the quantities of the phenolic and carboxylic groups.

RESULTS AND DISCUSSION

Elemental Analysis

The samples were analyzed by elemental analysis and the results are in the range of other fulvic acids from the literature. O (47.8%) and C (45.14%) were the major constituents, H (3.9%), N (2.1%) and S (1.1%) were detected (composition calculated on an ash-free basis). On the basis of the atomic ratios (C/N (21.34), H/C (1.03) and O/C (0.08) it is possible to make a hypothesis of the organic matter source, as well as the structure of FA. The C/N values are high probably due to the consumption of nitrogen by the ecosystem plants, resulting the FA being poor in N (2.1%). The ratio 0.08 O/C can indicate low COOH content. The ratio 1.03 H/C can indicate that this FA sample shows high aromaticity, confirming the hypothesis of its origin from the vegetation around the river, because aromaticity is related to a lignin source (Sargentini et al., 2001).

Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups corresponding to the respective wavenumbers are: 3.435 cm\(^{-1}\) (hydrogen-bonded phenolic OH groups); 1.720 cm\(^{-1}\) (C-O stretching of carboxylic acids); 1.626 cm\(^{-1}\) (asymmetric stretching of COO ions); 1.402 cm\(^{-1}\) (OH deformation and C-O stretching of phenolic OH) and 1.220 cm\(^{-1}\) (C-O stretching of esters, ethers and OH deformation of carboxylic acids). The results are in agreement with the results from other authors (El-Sayed et al., 1996; Davis et al., 1999). The aquatic FA have a considerable aromaticity and some methyllic groups. The FTIR spectra indicated the major presence of carboxyl and phenolic groups. The principal band for the carboxylic acids at 1.720 cm\(^{-1}\) is less intense than that for the phenolic group.

Functional Group Analysis

At first we used a modified Gran's method to calculate the total oxygenated groups, divided into two classes of groups: phenolics and carboxylics. The results listed in Table 1 were obtained from the average of three titrations and are in agreement with the results of the Elemental Analysis and FTIR, indicating less carboxylic, in relation to the phenolic groups. With the help of the BEST7 software we then divide the quantity of the two classes of functional groups into five categories: phenol, carboxyl, cathecol, phthalic and salicylic. In Table 2 the quantities found are listed. As one can see, the major quantity of any category found is cathecol groups (1.39 meq g\(^{-1}\)).
second is salicylic groups (1.03 meq g⁻¹) and the third is phenolic
groups (0.76 meq g⁻¹).

Using the titration curve data (pH V (mL), we
obtained, with the help of the BEST7 the equilibrium
constants (log K) for each oxygenated species. Table 3 shows
the values for protonation of the functional groups of the
FA represented by the equilibrium quotients [H L]/[HL][H]
and [HL]/[H][L], and the metal binding is shown by
expressions: [ML]/[M][L] and [ML₂]/[M][2L]. The
experimental values and those of the literature for the simple
ligand with these functional groups, are very close. The
equilibrium constants for the binding of Cu(II) with fulvic acid
molecules represented by the interactions of binding groups
are shown in Table 3, and they are compared with values reported
for simple molecules of groups like cathecol and salicylic acid.
The average constants for the binding of the cathecol and
salicylic groups of FA molecules with Cu(II) ions are slightly
higher compared with the values for the simple molecule. This
slight increase may be due to FA binding groups being less
solvated compared to cathecol and salicylic acid molecules. The
lesser solvation reflects slightly in the increase in binding
constant values (MARTELL and HANCOCK, 1996).

The greater differences that occur in the protonation
constants for the stronger acid groups (carboxylic and phthalic)
can be explained by the hydrogen bondings, polar, steric, and
resonance effects that are present with these groups in the fulvic
acid structures. Carboxylic groups close to each other can form
clusters that elevate the potentiometric constants (log K) (LU
and JOHNSON, 1997). The species distribution diagrams for
aquatic FA and the complexation with Cu(II) ions are presented
in Figure 2. The cathecol group (C) the major group of this
fulvic acid (Table 2) is set at 100% in Figure 2 (upper diagram).
The diprotonated form (H₂C) predominates up to near p[H] 9.0.
Above p[H] 9.8 the monoprotonated species (HC) predominates
reaching a maximum at p[H] 11.2, decreasing at higher
p[H] values. The second major group is salicylic (E). The
diprotonated salicylic group predominates at low p[H] values
with the monoprotonated form increasing up to p[H] 3.40 when
it predominates over H,E and continues to increase until p[H] 6
where it is completely monoprotonated, being present in the
completely deprotonated form above p[H] 11. The
monoprotonated phenolic form (HA) represents 54% up to p[H]
7.5 when it starts to diminish giving way to the deprotonated
form. The diprotonated form of the phthalic group is 40%
formed at p[H] 2.0. It diminishes at high p[H] values giving way
to the monoprotonated form reaching a maximum at p[H] 4.5
where it is 37% formed and the deprotonated form appears at
higher p[H] values being 40% formed at p[H] above 7.0. The
protonated form of the carboxylic group is 22% formed at p[H]
2.0, decreasing at p[H] values above 4.0 giving way to the
deprotonated form which reaches 22% at p[H] values above
p[H] 7.0. On the lower diagram of Figure 2, we can see that the
Cu(II) ion begins to bind FA molecules at p[H] 3.0 binding the
salicylic groups and complex CuE reaches a maximum of 48%
formed at p[H] 6.5. The phenolic group also complexes the Cu
(II) ion and at p[H] 6.5 copper is 14% complexed with this
group. At p[H] 7, 29% of the copper is complexed with the
cathecol group in a 1:1 ratio. At higher p[H] values there is a 1:2
ratio of cathecol complexation and above p[H] 9 about 60% of
the copper ions are bound in this ratio. A 1:2 copper: binding
species ratio is also observed for the salicylic group at p[H]
values higher than 10.4, where copper is 22% complexed.
Finally, hydrolysis products appear above p[H] 10 forming
Cu(OH)₂, and Cu(OH)₃⁺.
CONCLUSIONS

A new methodology to elucidate and quantify the functional groups of complex substances, such as fulvic acids, has been developed. This methodology was also very helpful to determine the sites of copper (II) ion complexation with fulvic acids. The potentiometric constants were very close to the values observed in the literature, confirming the viability of the technique. This new methodology could be useful in studies to investigate the interactions between other metals and fulvic acids.

ACKNOWLEDGEMENTS

Thanks to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for financial support and fellowships. Thanks to the FUNCITEC (Fundação de Ciência e Tecnologia) for supporting this research. We are grateful to Dr. Eduarda Regina Carvalho and Dr. Ladislau Martin Neto (Embrapa-Instrumentação Agropecuária, São Carlos, SP) for the aquatic fulvic acids supply.

LITERATURE CITED


