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Potentiometric studies on the complexation of copper(II) by phenolic acids as discrete ligand models of humic substances

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Abstract

Studies on the complexation of copper(II) by phenolic acids, as ligand models of humic substances were done by potentiometry. The acids under study were: 3,4-dihydroxyhydrocinnamic acid or hydrocaffeic acid (1), 3,4-dihydroxyphenylacetic acid (2) and 3,4-dihydroxybenzoic acid or protocatechuic acid (3). Acidity constants of the ligands and the formation constants of metal–ligand complexes were evaluated by computer programs. The carboxylic group of the phenolic acids has different pK_{a1} values, being the dissociation constants intrinsically related with the distance between the function and the aromatic nucleus. The results obtained allow concluding that acidity constants of the catechol moiety of the compounds are similar with pK_{a2} and pK_{a3} values between 9.47–9.41 and 11.55–11.70. The complexation properties of the three ligands towards copper(II) ion are quite similar, being the species found not different either in nature or stability. Although the model ligands have some structural differences no significant differences were found in their complexation properties towards copper(II). So, it can be postulated that complexation process is intrinsically related with the presence of a catechol group.

Keywords: Phenolic acids; Dissociation constants; Complexation properties; Copper(II); Humic substances

1. Introduction

Most of the organic matter present in the soil and water systems is made up of humic substances (HSs) [1,2]. These substances are characterised as a mixture of macromolecules composed of fulvic acids, humic acids and humin, which differ in size, structure and solubility [2–5]. The chemical structure of HSs is very complex and it is strongly related to its biological origin. Despite of the continuous investigations on the humic material, the exact structure of the different HSs fractions has not been well defined. HSs exhibit similar functional groups, mainly of carboxylic and phenolic types, and are characterised by their exceptional complexation capabilities towards metal ions [2–5]. Besides the capacity of complexation of metal ions, namely of free copper, HSs can also decrease the toxicity of metal ions and/or increase its biological availability [6–10].

Several authors have described the detoxification of copper by HSs and other ligands [1,11]. The behaviour of metals towards these ill-defined natural compounds is complicated because of the large number of possible interactions. The complexation phenomena of HSs have recently been the subject of several studies [12–17]. However, a consensus about the species formed and the formation constant values have not been reached yet. The interpretation of the data is complex because of two fundamental problems: (1) the great chemical diversity and heterogeneity of HSs and the poor knowledge of their structure; and (2) the lack of analytical methods of speciation, sensitive enough to enable determination of complexing properties of HSs without altering natural conditions. Several mathematics models, which consider the

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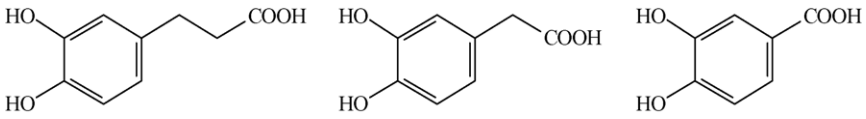

Fig. 1. Chemical structures of phenolic acids studied: 3,4-dihydroxyhydrocinnamic acid (1); 3,4-dihydroxyphenylacetic acid (2); 3,4-dihydroxybenzoic acid (3).

functional heterogeneity and their polyelectrolyte nature have been, reported [18–20]. Because the heterogeneous structure and high molecular of HSs, the stability of the HSs–metal complexes is very difficult to evaluate.

In an effort to understand and quantify humic–metal interactions, some discrete ligand models (such as citric, salicylic, tricarballylic, malic, phthalic and glycylaspartic acids) have been used in the study of complexation properties of humic substances [14].

Phenolic acids are a well-known family of natural compounds, which have as general chemical structure an aromatic nucleus and phenolic and carboxylic functions. Phenolic acids are present in fruits and plants, and represent a large fraction of the chemical structure of humic substances. Studies reveal that the amount of phenolic acids in HSs is evaluated to be up to 35%, depending of the humus origin [1,21,22]. This class of compounds may play an important role in the metal complexation by HSs. Detailed investigations of humic substances have confirmed that different dihydroxyaromatic acid moieties (catechol-type groups) have an essential function as structural building blocks [22–26]. The information obtained using this type of compounds, as ligand models can be helpful in the difficult task of evaluation of the nature and strength of donor sites in HSs.

The acids under study were 3,4-dihydroxyhydrocinnamic acid or hydrocaffeic acid (1), 3,4-dihydroxyphenylacetic acid (2) and 3,4-dihydroxybenzoic acid or protocatechuic acid (3) (Fig. 1). Acidity and formation constants with the copper(II) of three ligands (phenolic acids) were evaluated by potentiometry. A detailed examination of the complexation species formed in copper(II)/phenolic acid systems is presented, together with their respective formation constant values.

2. Experimental section

2.1. Reagents

All the chemicals employed were of analytical grade purity and purchased from Aldrich (copper(II) nitrate and the phenolic acids) and Riedel (nitric acid, sodium hydroxide and potassium nitrate). The water used was double deonized water (conductivity less than 0.1 $\mu S\,cm^{-1}$).

2.2. Potentiometric measurements

Potentiometric measurements were carried out with a Crison 2002 pH meter and 2031 burette controlled by a personal computer, which was also used for data store and manipulation. The electrode assembly was made up of an Orion 900029/4 AgCl/Ag reference electrode and a Russell SWL glass electrode. System calibration was performed according to the Gran method [27] in terms of hydrogen ion concentration using strong acid/strong base titrations [HNO_3 (1.00 mM)/NaOH (≈0.02 M)] with solutions having adjusted ionic strengths (0.1 M with KNO_3). Titrations were always carried out under a nitrogen atmosphere at 25.0 ± 0.1 °C in a double-walled glass cell.

2.3. Determination of acidity and stability constants

Acidity constants were obtained by titrating 20 mL of acidified solutions (1 mM HNO_3) of the phenolic acids (0.8–1 mM) with NaOH (≈2.00 mM). Stability constants of copper(II)–ligand complexes were determined by titrating 20 mL of aqueous solutions of the phenolic ligands, nitric acid (1 mM) and copper(II) nitrate (1 mM) with sodium hydroxide (≈0.02 M)]. For all solutions the ionic strength was adjusted to 0.1 M with KNO_3 [28]. System calibration was performed before each determination. The evaluation of acidity constants of the ligands and of formation constants of metal–ligand complexes were performed with data obtained from at least six independent titrations, each with more than 30 points. The experimental titration data were analysed using the computer program Superquad [29]. The reported errors were calculated by the method of Albert and Serjeant [30], as the maximum difference between the logarithm of the average of the antilogarithms of the calculated pK_a values and their individual values.

In this work different concentration ratios of metal–ligand were used in the complexation studies (1:2; 1:1; 2:1).

3. Results and discussion

In order to contribute for a better knowledge of the organic–metal interactions of humic substances the study of

Table 1
Acidity constants of the phenolic acids: 3,4-dihydroxyhydrocinnamic acid (1), 3,4-dihydroxyphenylacetic acid (2) and 3,4-dihydroxybenzoic acid (3)

Phenolic acids	pK_{a1}	pK_{a2}	pK_{a3}
(1)	4.45 ± 0.02	9.41 ± 0.05	11.70 ± 0.10
(2)	4.18 ± 0.03	9.42 ± 0.05	11.65 ± 0.10
(3)	3.86 ± 0.03	9.47 ± 0.02	11.55 ± 0.09

the complexation properties of copper(II)–phenolic acids, as ligand models, was performed. The three phenolic acids under study (Fig. 1) have in common oxygen functional groups (COOH and OH), i.e. a catecholic moiety and a carboxylic acid function which is in para position to a phenolic group. The compounds are homologous and differ from each other by the distance between the –COOH function and the aromatic nucleus.

3.1. Acidity constants

Table 1 summarises the values of the pK_a evaluated for each ligand. Results are presented as means ± S.D. of at least 6 independent experiments.

As expected, the carboxylic groups exhibit different acidic strengths. Is could be related to the different chemical structure of the ligands, i.e. in which concerns the distance between the function and the aromatic nucleus. From the values obtained for pK_{a1}, corresponding to acidity constants of carboxylic group, one can conclude that they are controlled by the electronic effects of substituent groups. The pK_{a1} value of 3,4-dihydroxybenzoic acid (3) is lower because the –COOH group is connected to the aromatic moiety, which inductively pulls the electron density.

Results have shown that acidity constants (pK_a) of the catechol moiety of the ligands are similar with pK_{a2} and pK_{a3} values between 9.47–9.41 and 11.55–11.70. Acidity exhibited by the phenolic groups of the ligands under the study, is a consequence of the sum of the electronic influences of the substituents, such as: dipolar field/inductive properties, π-electron delocalisation, and polarizability effects. According with the pattern of substitution of aromatic nucleus acidity of *para*-OH is higher than *meta*-OH which is in agreement with the pattern of substitution of the aromatic nucleus, type and position of the substituents [31]. The introduction of methylene unit (CH_2) as spacer in the side chain that contains the carboxylic acid does not led to a significant variation on the values of acidity constants of phenolic groups, which have pK_{a2} and pK_{a3} values between 9.47–9.41 and 11.55–11.70.

Allowing for the variation in ionic strength and background medium, the differences between the values of acidity constants found for 3,4-dihydroxyhydrocinnamic acid (1) and those referred in the literature can be considered acceptable ($pK_{a1} = 4.56$; $pK_{a2} = 9.36$; $pK_{a3} = 11.6$, determined at 25 °C, $I = 0.1$ M $NaClO_4$) [26].

Table 2
Equilibrium constants ($\log \beta$) calculated for copper(II)/phenolic acids in aqueous solution

p	*q*	*r*	Species	(1)	(2)	(3)	pH range
1	1	−1	$[CuLH_2]^{+1}$	2.06	2.12	2.72	3.5–7.0
1	1	−3	$[CuL]^{-1}$	13.1	13.0	11.7	4.6–8.0
2	1	−5	$[CuL_2H]^{-3}$	21.1	21.1	19.3	5.0–8.0
2	1	−6	$[CuL_2]^{-4}$	29.5	29.8	27.9	7.0–8.0
2	2	−5	$[Cu_2L_2H]^{-1}$	16.9	17.1	14.7	5.3–7.5
2	2	−6	$[Cu_2L_2]^{-2}$	22.8	21.6	20.3	5.4–8.0
2	3	−6	$[Cu_3L_2]$	19.6	21.0	17.9	5.3–7.8

All constants were calculated with the programs Superquad (23) from data obtained potentiometrically, at 25 °C and $I = 01$ M KNO_3. The symbols *p*, *q* and *r* are used in the programs to indicate the stoichiometric coefficients associated with the possible equilibria in solution: *p*, coefficient for ligand; *q*, for copper(II); and *r*, for protons (note that HO^- binding in this convention contributes-1 to the global *r* value).

3.2. Formation constants

The formation constants [($\log \beta$) ± S.D.] obtained for the binary systems copper(II)/3,4-dihydroxyhydrocinnamic acid (1), copper(II)/3,4-dihydroxyphenylacetic acid (2) and copper(II)/3,4-dihydroxybenzoic acid (3) are presented in Table 2. The pH range used in data acquisition is also included in this table.

Different concentration ratios of metal–ligand were used in the complexation studies of the ligands. From the results obtained it must be pointed out that for all ligands the formation constant values determined were independent of the concentration ratio of metal–ligand used.

For all the binary systems Cu(II)/ligand under study, the best overall fitting of the data assumes the occurrence of equilibria in solution that correspond to formation of the following species: $[CuLH_2]^{+1}$, $[CuL]^{-1}$, $[CuL_2H]^{-3}$, $[CuL_2]^{-4}$, $[Cu_2L_2H]^{-1}$, $[Cu_2L_2]^{-2}$, $[Cu_3L_2]$. In these formulas L^{3-} represents the fully deprotonated form of the phenolic acids; in all subsequent discussions complex charges were omitted for simplicity.

It was found that complexation properties of the three ligands towards copper(II) ion are quite similar, since the species are not so different either in nature or stability. The formation constants obtained were $K^{Cu}_{CuL} = 12.46$ and $K^{Cu}_{CuL_2} = 21.62$ for 3,4-dihydroxyhydrocinnamic acid (1), $K^{Cu}_{CuL} = 12.25$ and $K^{Cu}_{CuL_2} = 21.20$ for 3,4-dihydroxyphenylacetic acid (2) and $K^{Cu}_{CuL} = 13.12$ and $K^{Cu}_{CuL_2} = 21.84$ for 3,4-dihydroxybenzoic acid (3), respectively.

The value of the formation constant related to CuL complex in protocatechuic acid is slightly higher, which could be related with the absence in this compound of the alkyl side chain as a spacer between the carboxylic function and the aromatic moiety.

Formation constants values calculated for 3,4-dihydroxyhydrocinnamic acid (1) in these work ($K^{Cu}_{CuL} = 12.46$ and $K^{Cu}_{CuL_2} = 21.62$) are in good agreement with those reported in literature ($K^{Cu}_{CuL} = 12.7$ and

$K^{Cu}_{CuL_2} = 22.4$ determined at 30 °C, $I = 0.1$ M $NaClO_4$) [32]. The differences between the values can be related with different concentrations ratio of metal and ligand and different ionic strength adjusters used. For the other two ligands no formation constants values were found in the literature.

In [CuL] complexes the copper ion is probably bound to the oxygen atom of the deprotonated carboxylic group of the ligands, an observation that stems from the fact that the appearance of the species occur at pH values in which the phenolic groups of the catechol are protonated. In [CuL_2] complexes the phenolic compounds act probably as bidentate ligands, through the catechol moiety, thus forming five membered chelate rings. In these complexes both phenolic anions (catechol group) are bound equatorially to the metal ion as bidentate ligands yielding a square-planar copper(II) moiety, to which two water molecules may weakly coordinate the axial positions.

The results obtained suggest that the introduction of an alkyl side chain spacer between the carboxylic function and the aromatic moiety of the structurally related phenolic acids studied does not led to a significant change on the formation constants. Indeed acidity constants of catechol group and $K^{Cu}_{CuL_2}$ values are similar for the three ligands.

3.3. Concluding remarks

HSs contain a large number of diverse chemical functionalities and there is no single analytical method to evaluate its physico-chemical properties. Thus, all analytical approaches applied to the investigation of the chemical character and properties of HS contain more or less pitfalls resulting in many kinds of disagreements.

Thus, the knowledge of the stability constants of each type of chemical component is nowadays though to be very important either for the prediction of complexation properties of HS or for the explanation of the transport of metal ions in the environment [33]. This type of studies indicates the formation and quantification constants based on certain universal one-way precursor–product relationship, which is an oversimplification of a complex process. After tracing the complexation properties of discrete ligands towards different metals it is also more easy to correlate the data to the origin of humic matter.

As phenolic acids are a significant part of the chemical structure of humic substances it can be postulated, from the data obtained, that they can have an important role in their complexation properties, mainly due to the presence of a catechol group. To note that the discrete ligands used in previous studies only possess a carboxylic and a phenolic function, usually in a *ortho*-position.

From the results obtained one can propose this type of structures corresponds to suitable discrete ligands, and mimetic models, for HSs. Owning to their natural origin, phenolic acids could be also proposed, as the stability constants were found to be rather high, as remediation agents for decontamination of polluted soils and waste waters.

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