

Article

Potentiometric Equilibrium Constants for Complexes of Nitrosalicylic Acids and Mg(II), Mn(II), Cu(II) and Zn(II)

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As constantes de equilíbrio para os sistemas dos ácidos 3-nitrossalicílico (3-NSA), 5-nitrossalicílico (5-NSA) e 3,5-dinitrossalicílico (3,5-DNSA) com os metais Mg(II), Mn(II), Cu(II) e Zn(II) foram determinadas por potenciometria. Esses resultados, cujas espécies formadas foram também investigadas por espectroscopia de UV-Vis, são mostrados na forma de diagramas de distribuição das espécies em relação ao p[H]. Estes resultados foram comparados aos obtidos com o ácido salicílico e os mesmos íons metálicos. Este estudo mostrou que apesar dos ligantes não serem complexos, fornecem uma visão completa da habilidade de complexação dos constituintes derivados do ácido salicílico (SALA) das substâncias nitro-húmicas (NHS), um produto obtido da nitrificação em laboratório das substâncias húmicas (HS). Os resultados mostraram que os modelos empregados derivados dos ácidos nitrossalicílicos são ligantes mais eficazes em relação aos íons metálicos divalentes estudados, que o ácido salicílico nos valores normais de p[H] dos solos.

Uma tentativa de se determinar os sítios ácidos de uma fração solúvel de NHS já caracterizada por Espectroscopia de Ressonância Paramagnética Eletrônica (EPR) na literatura¹, revelou quatro grupos de sítios ácidos principais. Desses quatro, três foram atribuídos a derivados de catecolatos, de ftalatos e de salicilatos.

Equilibrium constants for the systems of 3-nitrosalicylic (3-NSA), 5-nitrosalicylic (5-NSA) and 3,5-dinitrosalicylic (3,5-DNSA) acids and Mg(II), Mn(II), Cu(II) and Zn(II) metal ions were determined by potentiometry. The values are reported for all major complexes formed, and also investigated by UV-Vis spectroscopy, and the results are presented in the form of distribution diagrams. These results were compared to those from with salicylic acid (SALA) and the same metal ions. This study shows that although the ligands are not bulky, they can provide an insight into the complexing ability of the aromatic dicarboxylic constituent of the nitrohumic substances (NHS), a laboratory derivative product of humic substances (HS). These results show that the nitrosalicylic acid model compounds employed are more effective in complexing the divalent metal ions studied than the salicylic acid itself, at the normal p[H] value for soil.

An attempt to measure the acidic groups of a water soluble part of a NHS already characterized by Electron Paramagnetic Resonance (EPR)¹ revealed that of the four main classes of acidic groups detected, three are due to catecolate, phthalate and salicylate derivatives.

Keywords: equilibrium constants, nitrohumic acid models, divalent metal complexes, UV-Vis spectroscopy

Introduction

The benefits of organic matter in the soil regarding to crop productivity are well documented in the literature, and include the ability to be a slow-release source of N, P and S, and the capacity to binding micronutrient metal ions in the soil that would otherwise be leached out².

Humic substances (HS) refer to all heterogeneous mixtures of naturally occurring organic compounds, ubiquitous in nature and arising from the decay of plant and animal residues, and can be fractionated using a combination of acid and base extractions³. A look at its main structural constituents found in the literature^{1,4-7} reveals that there are three main classes of aromatic rings: salicylate, phthalate and catechol derivatives.

Although the models chosen in this work are simple molecules, they provide an insight into the complexation sites in the structure of nitro humic substances (NHS), and complement the data for salicylic acid derivatives that are already reported in the literature (see Results and Discussion). This work was based in the discrete ligand approach described in the literature⁸ for use with humic acids (HA). In this kind of approach it is assumed that the observed potentiometric properties are a consequence of the different acid strengths of a limited number of functional sites which constitute the HA molecule.

Using potentiometry, Kiss *et al.*⁹ have shown the complexing ability of Al(III) and catechol, as well as different derivatives of salicylic acid and 2,3-dihydroxyterephthalic acid.

In work using potentiometric titration, Gamble *et al.*¹⁰ concluded that the site-bound chelate formed by fulvic acid (FA) polymer molecules and Cu(II) was the same type that this metal ion forms with salicylic (SALA) and phthalic acids.

The biological availability of metal ions in soils is strongly influenced by complexation reactions occurring among them and the organic matter fraction.

This has been shown in the literature. Stevenson *et al.*¹¹ studied the metal ion Cu(II) and some samples of HA from Illinois, using base titrations. Marinsky *et al.*¹² also studied the interaction of Cu(II) and HA by potentiometric titration.

Nitrohumic acids (NHA) - a product obtained by the addition of concentrated nitric acid to HA - were once

suggested as potential organic fertilizers, with the extra benefit for soils of having a greater N content than HA¹³⁻¹⁶. The study of the complexation of this material alone or with metal ions is at the very beginning¹.

Equilibrium constants were determined using potentiometry in systems having the ligands 3-NSA, 5-NSA and 3,5-DNSA as NHA models (Fig. 1), as well as salicylic acid (SALA) as a model for the HA. Distribution diagrams were drawn for each system. The metal ions employed in this study are all essential to the different metabolisms of each kind of plant. The results for the essential ion Fe(III) and the phytotoxic Al(III) have been reported elsewhere¹⁷.

Each system was inspected by UV-Vis spectroscopy revealing the different species present.

A sample of NHA¹ was also inspected by potentiometry, and the stability constants found for the acidic groups were compared with data in the literature¹⁸.

Experimental

Reagents

All chemicals used were of analytical-reagent grade, and were used without further purification. All solutions were made with bi-distilled, deionized and CO₂ - free water. All ligand solutions - nitrosalicylic acids (NSA) (TCI/Japan) and salicylic acid (SALA) (Reagen/Brazil) - were made in 5% v/v ethanol (Reagen/Brazil) - water. Metal solutions were made from their nitrate salts (Carlo Erba/Brazil), and their concentrations were determined following the procedures in the literature¹⁹. The aqueous KOH (Merck/Brazil) 0.100 M, carbonate-free solution was standardized against potassium hydrogen phthalate (Carlo Erba/Brazil). KNO₃ (Baker & Adamson/USA) was the supporting electrolyte.

Apparatus

The potentiometric titrations were carried out under an inert atmosphere of water-KOH saturated nitrogen (White-Martins/Brazil) in a water-jacketed vessel maintained at 30.0 ± 0.1 °C, in samples of about 0.15 and 0.30 millimoles of ligands when in the presence of the metal ions, and 0.1 millimoles of ligands in the absence of metal ions. The pK_w was determined to be 13.63. A Metrohm manual piston microburet was used to deliver the titrant (standard CO₂ - free KOH), and the p[H] values were directly measured

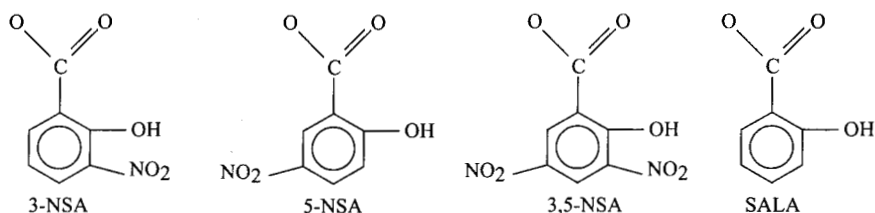


Figure 1. Structures for the NHA model compounds, 3-nitrosalicylic acid (3-NSA), 5-nitrosalicylic acid (5-NSA), 3,5-dinitrosalicylic acid (3,5-DNSA), and for the HA model compound, salicylic acid (SALA).

with a Micronal (Sao Paulo - Brazil) model B-375 pH meter fitted with Analyzer glass and calomel reference electrodes (SP - Brazil), calibrated with standard HCl and KOH solutions to read $-\log [H^+]$ directly²⁰.

At constant increments of titrant volume (0.10 ± 0.02 mL) added to the system, adjusted to a 0.100 M constant ionic strength (μ) by the addition of KNO_3 , the corresponding p[H] was read and plotted to calculate the values of the protonation and formation constants of the system. The desired ionic strength was set using the formula²¹ $\mu = 1/2 \sum m_i z_i^2$.

The aliquots analyzed by UV-Vis spectroscopy were taken at specific pH values from a second titration, specially done for this purpose.

The UV-Vis spectra were taken with a Hewlett - Packard model 8450A (USA) - Diode array spectrophotometer from 260 to 600 nm, in aliquots of the ratio solutions of 1:3 metal to ligand, using 1.000 cm quartz cells at a controlled room temperature of 25.0 °C, with air as the reference. The p[H] values of the experimental solutions were adjusted by adding small volumes of 0.100 M KOH with a Metrohm microburet attached to the vessel.

An aliquot of fulvic acid (FA) extracted by water for 24 h of a nitrated coal material previously used by Mangrich and Vugman¹ was titrated with KOH 0.047 M with the ionic strength (μ), maintained at 0.100 M with the proper addition of KNO_3 .

Data treatment

The protonation constants of all ligands used have been previously reported¹⁸. They were determined again for the experimental conditions employed in this work in order to calculate the formation constants of the equilibria involving metals.

All computations of the equilibrium constants were done with the aid of the BEST program²⁰. Best was designed to solve for the set of equilibrium constants corresponding to the model selected, and also makes it possible to explore all aspects and variations of the model.

The model selected involved the choice of chemical species based on known chemistry concepts, those species shown to be present by spectrophotometric evidence and those that can be justified on the basis of established principles of coordination chemistry in solution^{20,22}.

Best utilizes the number of millimoles of each component, the titration variables, the initial estimates of the equilibrium constants of each species thought to be present in the solution, the protonation constants of the ligand, the hydrolysis constants for the metal ion used, and the experimentally determined profiles of p[H] versus solution composition.

The program sets up mass balance equations for all species present at each increment of base added, and solves for the concentration of each one of the species.

Each species concentration consists of a product of the overall stability constant (β) and individual component concentrations raised to the power of its stoichiometric coefficient. The calculation of values continues until no further minimization of the standard deviation (σ) in pH units is obtained. The overall stability constant can be defined as Eq. 1, where brackets indicate concentration:

$$M^{2+} + nL^{2-} = ML_n^{+2-2n} \quad \beta_n = \frac{[ML_n^{+2-2n}]}{[M^{2+}] \cdot [L^{2-}]^n} \quad (1)$$

The species distribution curves were drawn with the SPE microcomputer program²⁰. On average, three titrations were made, one with the ligand alone, and two others with metal to ligand ratios of 1:1.5 and 1:3 millimole.

Titration of NHA

A 25 mL aqueous extract of a nitrated coal was titrated with KOH 0.047 M, as previously described in the literature¹. The p[H] values were plotted against the volume (mL) of base added. The Best program²⁰ was used for the first time to calculate the protonation constants of its acidic groups, as well as the total H^+ ion contents.

Results and Discussion

The protonation constants, defined by Eqs. 2 and 3, of SALA, 3-NSA, 5-NSA and 3,5-DNSA (Fig. 1) were determined and compared with the values reported in the literature¹⁸ (Table 1).

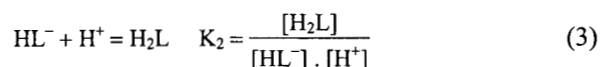
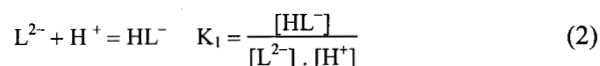


Table 1. Protonation constants of the ligands salicylic acid, 3-nitrosalicylic acid, 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid; $\mu = 0.100M$ (KNO_3), $T = 30.0 \pm 0.1$ °C.

log K	HL/H.L	H ₂ L/H.HL
SALA	13.66 ^b 13.4 ^a	2.84 ^b 2.8 ^a
3-NSA	9.87 ^c 9.87 ^a	1.76 ^c 1.73 ^a
5-NSA	9.83 ^c 9.8 ^a	1.91 ^c 1.94 ^a
3,5-DNSA	7.08 ^d 7.22 ^a	0 ^e 0.26 ^a

^a Reference 18; ^b standard deviation (ϕ) = ± 0.02 ; ^c this work, ϕ = ± 0.02 ;

^d this work, ϕ = ± 0.03 ; ^e non-determined.

When compared with similar constants for SALA these values are nearly 4 log units smaller for 3-NSA and 5-NSA, and about 7 log units smaller for 3,5-DNSA. This behavior may be attributed to the nitro- group attached to the aromatic ring of 3-NSA and 5-NSA. This effect is bigger in the case of 3,5-DNSA due to the two nitro- groups present in the structure of the ligand, as was expected. It was not possible to measure the protonation constant for the carboxylic substituent in the 3,5-DNSA molecule due to its extreme acidity imposed by these two nitro- groups¹⁷.

Table 2 shows the values of the formation constants following Eq. 1, found for complexes with Mg^{2+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} ions, respectively, compared with the values found in the literature¹⁸.

A glance at the logarithm values of the formation constants of the complexes found the constants to be smaller for the nitro- compounds compared with those of SALA, as expected. The nitro compounds have a smaller driving force towards forming the complexed species with the metal ions than the non-nitro model compound, SALA. However, the ability of the nitro- groups to delocalize negative charges of the negatively net charged complexes, ML_2 and ML_3 , has allowed the formation of species having three molecules of ligand, in spite of the bulky size of the complex formed, overcoming the effect of possible steric hindrance.

The species ML , ML_2 and ML_3 (L = ligand; M = metal ion) were observed for the four ligands and Mn^{2+} , and with three ligands and Mg^{2+} . The latter metal ion did not form complexed species with 3,5-DNSA. This was attributed to the smaller basicity of the phenolic substituent in this

ligand, and to the weak driving force towards forming complexes exhibited by the metal ion Mg^{2+} .

Manganese(II) shows small values (it binds more weakly than zinc(II)) for the formation constants, suggesting that the complexes are probably of the outsphere type, being binded *via* water molecules (Table 2).

Two sharp inflexions for the potentiometric profiles of Cu^{2+} and the ligands (Fig. 2 - Cu^{2+} and 5-NSA) show that only the ML and MHL species were present. Formation of insoluble products in the Cu^{2+} systems at $p[H]$ values above 6.0 for 3-NSA and 5-NSA, and at $p[H]$ values near 3.0 for 3,5-DNSA, prevented further investigations, and may also explain the high standard deviation value for the formation constant of the 1:1 of 3,5-DNSA and Cu^{2+} species found in this study (Table 2). The formation constants show that

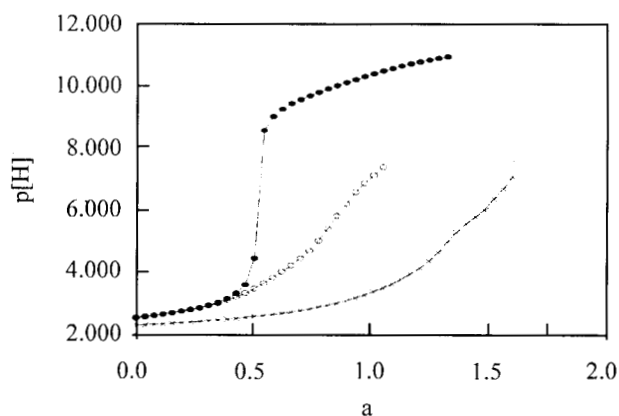


Figure 2. Potentiometric $p[H]$ profiles for solutions containing $\bullet = 3.75 \times 10^{-3}$ M 5-NSA alone; $\circ = 3.75 \times 10^{-3}$ M 5-NSA and 2.5×10^{-3} M Cu^{2+} ; and $\square = 7.5 \times 10^{-3}$ M 5-NSA and 2.5×10^{-3} M Cu^{2+} ; a = moles of base added per mole of ligand; $t = 30.0 \pm 0.1$ °C, and $\mu = 0.100$ M.

Table 2. Formation constants of the complexes of salicylic acid, 3-nitrosalicylic acid, 5-nitrosalicylic acid and 3,5-dinitrosalicylic acid with the metal ions: Mg^{2+} , Mn^{2+} , Cu^{2+} and Zn^{2+} ; $\phi = 0.100$ M (KNO_3), $T = 30.0 \pm 0.1$ °C.

	log K	3-NSA	5-NSA	3,5-DNSA	SALA
Mg^{2+}	ML/M.L	3.9 ^d	4.3 ^d	-	5.8 ^d
	ML ₂ /ML.L	2.6 ^d	3.0 ^d	-	5.56 ^b
	ML ₃ /ML ₂ .L	2.4 ^d	2.5 ^d	-	4.5 ^d 4.3 ^d
Mn^{2+}	ML/M.L	4.3 ^d	4.5 ^d	3.7 ^d	5.9 ^c 3.9 ^a
	ML ₂ /ML.L	2.7 ^d	4.99 ^a	3.52 ^a	
	ML ₃ /ML ₂ .L	2.3 ^d	2.8 ^d	2.2 ^d	
Cu^{2+}	ML/M.L	8.1 ^d	8.3 ^d	7.2 ^e	10.62 ^a
	MHL/ML.H	3.7 ^d	8.42 ^a	6.85 ^a	
Zn^{2+}	ML/M.L	5.1 ^d	2.9 ^d	4.2 ^e	6.85 ^a
	ML ₂ /ML.L	4.0 ^d	5.3 ^d	3.8 ^d	
			3.9 ^d	2.7 ^d	

^a Reference 18 and references therein; $T = 25$ °C; $\mu = \pm 0.1$ M; ^b Reference 18 and references therein; $T = 37$ °C; $\mu = \pm 0.15$ M;

^c Reference 18 and references therein; $T = 20$ °C; $\mu = \pm 0.1$ M; ^{d,e} this work ^d $\phi = \pm 0.1$ and ^e $\phi = \pm 0.3$.

copper formed the most stable complexes among those studied here.

Zn^{2+} only formed the ML and ML_2 species with 3-NSA, 5-NSA, 3,5-DNSA and SALA, probably due a tetrahedral symmetry, although the complexes are second in strength after Cu^{2+} .

The determined equilibrium constants permitted the build up of distribution curves for all of the species present in these systems. In all of the distribution curves the metal concentration, 2.5×10^{-3} M, was set at 100%. Inspecting these curves for the metal ion Cu^{2+} and SALA, 3-NSA, 5-NSA and 3,5-DNSA (Figs. 3 to 6), it can be seen that in general, the greater numbers of species, for the nitro-compounds are found near p[H] value of 7.5, whereas for the non-nitro model SALA the p[H] values for this greater number of species are above 8.0. Another interesting feature is that there was a delay in the formation of the hydroxo species in the systems with the metal ions zinc(II) (Figs. 7 to 10 for Zn^{2+} and SALA, 3-NSA, 5-NSA and 3,5-DNSA,

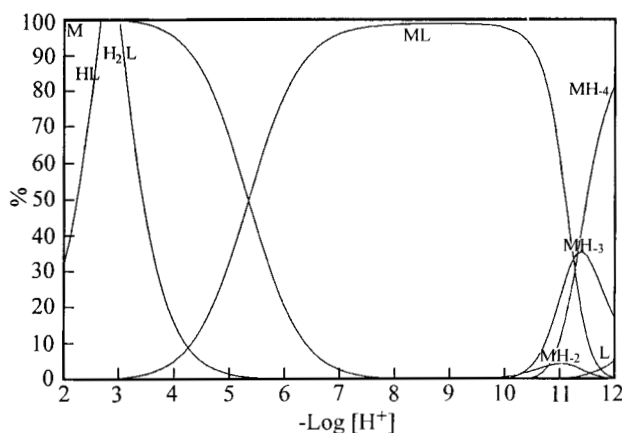


Figure 3. Species distributions for Cu^{2+} (M) 2.5×10^{-3} M and the ligand SALA (L) 7.5×10^{-3} M from p[H] 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

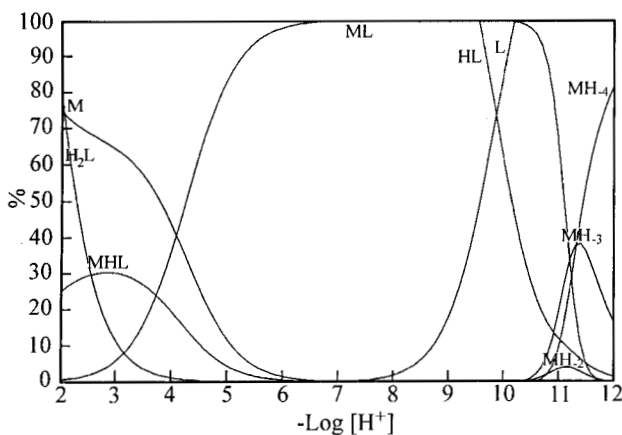


Figure 4. Species distributions for Cu^{2+} (M) 2.5×10^{-3} M and the ligand 3-NSA (L) 7.5×10^{-3} M from p[H] 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

respectively) and manganese(II), where any of the studied NSA ligands was the chelating agent. With the ligand SALA the metal ions present hydroxo species at lower p[H] values than with the ligands NSA. This characteristic was less observed for copper(II) and magnesium(II) metal ions.

Some species found were examined further by UV-Vis spectroscopy, when the system did not prevent taking an aliquot. This occurred when at some p[H] values the species were mixed with others, or when the system formed too many hydrolytic products.

Figures 11 and 12 show the spectra of 5-NSA alone and in the presence of Cu^{2+} , respectively. In Fig. 12, the absorption peaks of the two complexed species found can be seen at p[H] = 5.0, due to ML at 319 nm, and at p[H] = 2.5 at 313 nm due to MHL + H_2L . In Fig. 11, the absorptions of the deprotonated phenol group can be seen at wavelengths between 400 and

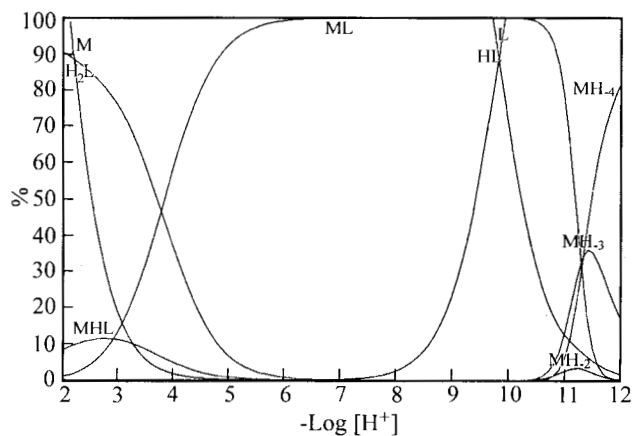


Figure 5. Species distributions for Cu^{2+} (M) 2.5×10^{-3} M and the ligand 5-NSA (L) 7.5×10^{-3} M from p[H] 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

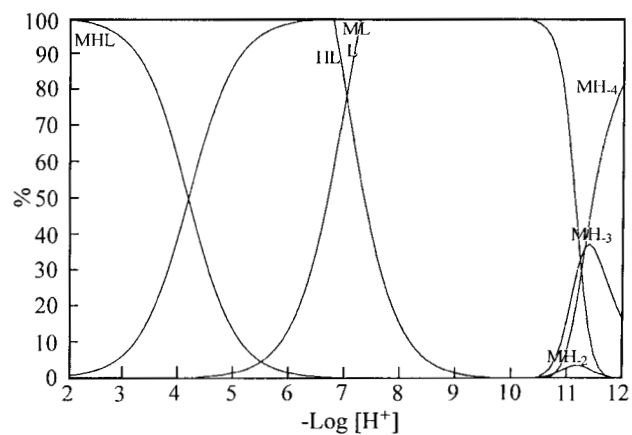


Figure 6. Species distributions for Cu^{2+} (M) 2.5×10^{-3} M and the ligand 3,5-DNSA (L) 7.5×10^{-3} M from p[H] 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

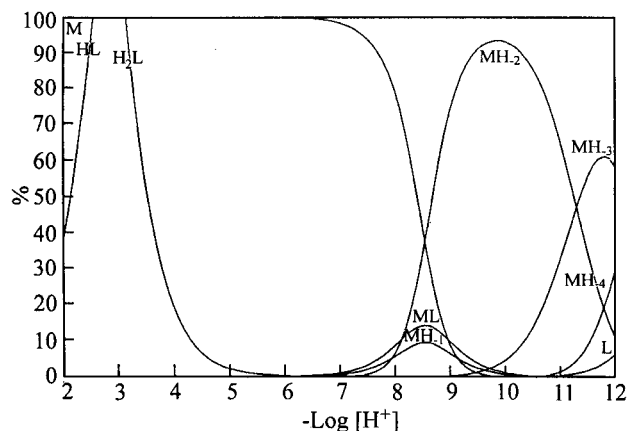


Figure 7. Species distributions for $Zn^{2+}(M) 2.5 \times 10^{-3} M$ and the ligand SALA (L) $7.5 \times 10^{-3} M$ from $p[H]$ 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

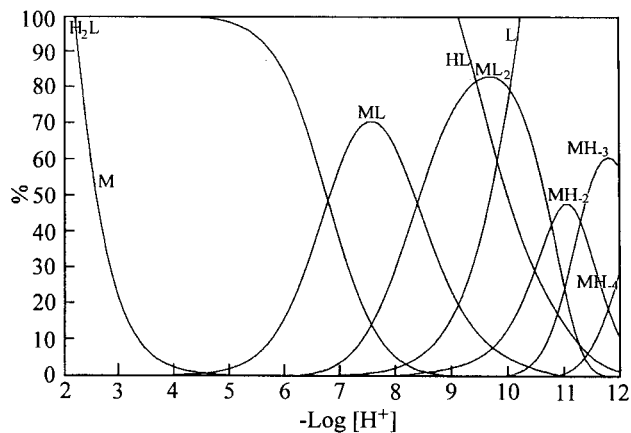


Figure 9. Species distributions for $Zn^{2+}(M) 2.5 \times 10^{-3} M$ and the ligand 5-NSA (L) $7.5 \times 10^{-3} M$ from $p[H]$ 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

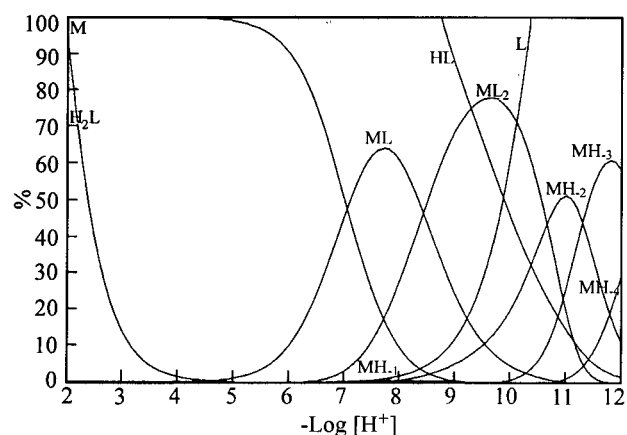


Figure 8. Species distributions for $Zn^{2+}(M) 2.5 \times 10^{-3} M$ and the ligand 3-NSA (L) $7.5 \times 10^{-3} M$ from $p[H]$ 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

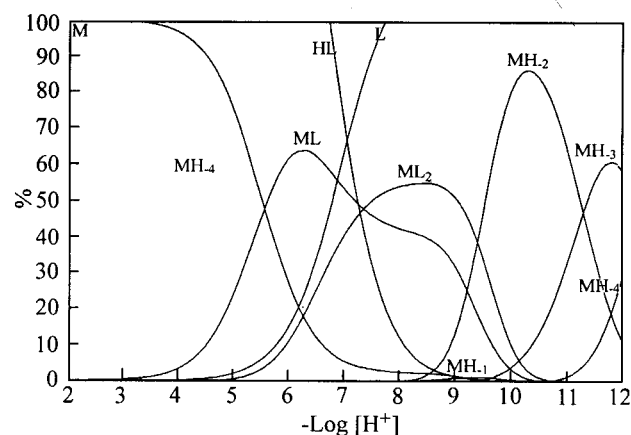


Figure 10. Species distributions for $Zn^{2+}(M) 2.5 \times 10^{-3} M$ and the ligand 3,5-DNSA (L) $7.5 \times 10^{-3} M$ from $p[H]$ 2.0 to 12.0. % is percentage of a species present, with the metal concentration set at 100%. H_x represents $(OH)_x^-$.

420 nm, due to the totally deprotonated ligand, L^{2-} at $p[H] = 10.1$, HL^- , 315 nm at $p[H] = 5.1$ and H_2L at $p[H] = 1.9$, 311 nm.

The other spectra obtained showed maximum absorbances differing by significant values of wavelengths to give support to the proposed species.

The results obtained with the NHA titration show that a total of 0.0550 millimoles of H^+ ions were present. From this total, 0.0192 millimoles were due to an acid group with an average $-\log K_a = 4.29$, 0.0284 millimoles of the total were due to an average $-\log K_a = 8.83$, and 0.0043 millimoles of the total H^+ ions were due to an average $-\log K_a = 10.82$. The difference, 0.0030, were millimoles of acid groups with $-\log K_a < 2.0$.

Inspecting the literature¹⁸, the acid groups found are suggested for values below 2.0, due to nitrosalicylates and nitrophthalates, for values ranging around 4.3, due to

nitrophthalates, and for values near 10.8, due to nitrosalicylates and nitrocatecholates.

For the average value of 8.8 no evidence was found in the literature for further speculation.

The results indicate that the NHA-like models chosen - 3-NSA, 5-NSA and 3,5-DNSA - are better chelating agents than the model for HA - SALA, at physiological $p[H]$ values near 7.0. Although the values of the formation constants for the complexes of the former ligands are smaller than those with SALA, the majority of these species are formed in the $p[H]$ range that is of interest in the soil studies, and form more quickly than the SALA can form under the same conditions. The smaller values for the formation and protonation constants are expected due to a reduction in the Lewis acidity of the nitrated ligands, due to a resonant effect of the nitro- groups. This drawback effect is compensated for when complexes with large nega-

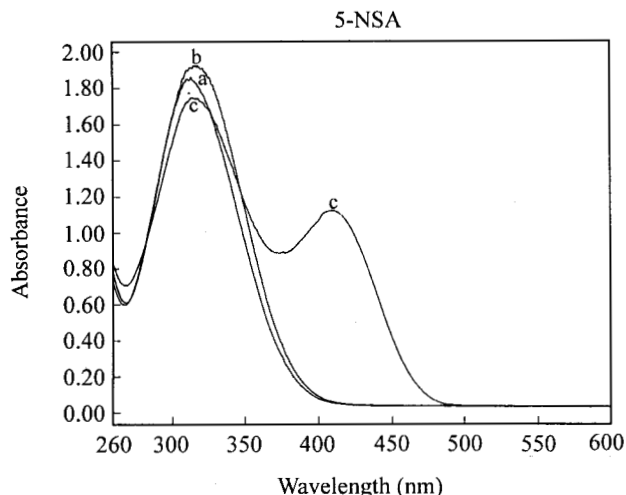


Figure 11. UV-Vis spectra of 7.5×10^{-3} M 5-NSA (L). a)- H_2L , $p[H] = 1.9$, $\lambda_{max} = 311$ nm; b)- HL^- , $p[H] = 5.1$, $\lambda_{max} = 315$ nm; c)- L^{2-} , $p[H] = 10.1$, $\lambda_{max} = 408$ nm and a shoulder at 313 nm; $t = 25$ °C and $\mu = 0.100$ M (KNO_3).

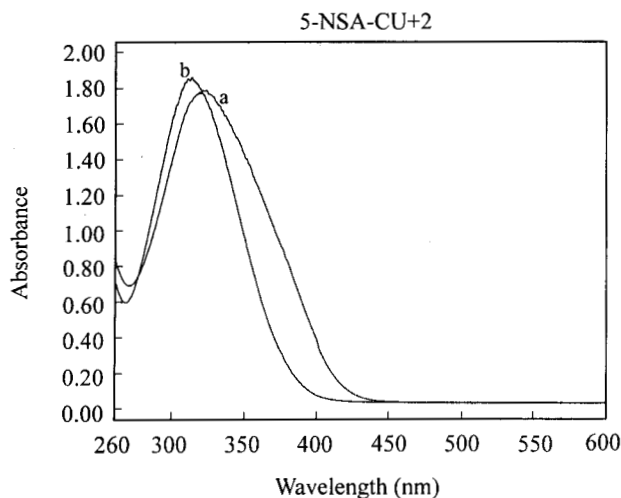


Figure 12. UV-Vis spectra of 7.5×10^{-3} M 5-NSA (L) and 2.5×10^{-3} M Cu^{2+} (M); a)- ML, $p[H] = 5.0$, $\lambda_{max} = 319$ nm; b)- MHL + H_2L , $p[H] = 2.5$, $\lambda_{max} = 313$ nm; $t = 25$ °C and $\mu = 0.100$ M (KNO_3).

tive charges are formed. Large negative charges can be better stabilized by this same resonant effect, leaving a more stable complex, in spite of the SALA ligand which does not present this possibility. Hence, the lower values of the protonation constants have left the nitrated ligands deprotonated at lower $p[H]$ values than with SALA, bringing the formation of the complexed species to a lower $p[H]$ value. The complexes are stabilized by a delocalization of the negative net charge in the network when the ligand has one or more nitro- groups.

Nitro humic acid needs to be further investigated, but there is a possibility of it being a slow-release fertilizer. The metal ions strongly bound to NHA could be released during the slow mineralization of NHS, making them available to plants in poor or very acidic soils.

Acknowledgments

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