

## Equilibrium Studies of Al(III) and Fe(III) with Nitrosalicylic Acids – Nitrohumic Acid-like Models

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Complexos dos íons ferro e alumínio trivalentes com os ácidos 3-nitrossalicílico (3-NSA), 5-nitrossalicílico (5-NSA) e 3,5-dinitrossalicílico (3,5-DNSA) em meio aquoso, a 30 °C e com força iônica de 0,100 M (KNO<sub>3</sub>), foram caracterizados por titulação potenciométrica, tendo sido alguns diferenciados por espectrofotometria de UV-Vis. Os ácidos 3-NSA, 5-NSA e 3,5-DNSA foram escolhidos como modelos de sítios de complexação de íons metálicos do ácido nitro-húmico (NHA). São apresentados diagramas de distribuição mostrando as concentrações das espécies encontradas em função do p[H]. Os resultados obtidos com os compostos-modelo nitrados foram comparados aos do ácido salicílico (SALA), composto-modelo escolhido para o ácido húmico (HA)<sup>1</sup>. Essa comparação demonstrou que os compostos nitrados são agentes de quelação mais eficientes frente aos metais estudados em solução neutra que o composto não-nitrado. Sugere portanto – conforme possibilidade já mencionada na literatura<sup>2,3</sup> – que o NHA é melhor agente de quelação de íons metálicos no solo que o HA natural.

The complexed species of Fe(III) and Al(III) with 3-nitrosalicylic (3-NSA), 5-nitrosalicylic (5-NSA) and 3,5-dinitrosalicylic (3,5-DNSA) acids, in aqueous media, at 30 °C and with an ionic strength of 0.100 M (KNO<sub>3</sub>) were characterized by potentiometric titration and some of them were differentiated by UV-Vis spectrophotometric analysis. The 3-NSA, 5-NSA and 3,5-DNSA acids were used as models of metal ion complexation sites in nitrohumic acids (NHA). Formation constants for the complexes found are reported. Distribution diagrams for the species were drawn showing the concentrations of individual species as a function of p[H]. The results for the models of NHA were compared with those for salicylic acid (SALA), the model chosen for the Humic Acids (HA)<sup>1</sup>. The comparison has shown that the NSA studied are more acidic and more effectual chelating ligands in neutral solutions than SALA, therefore suggesting that the NHA are more effective chelating agents to metal ions in soil than the natural HA. This possibility was already stated in the literature<sup>2,3</sup>.

**Keywords:** equilibrium studies, metal complexes of nitrosalicylic acids, Fe(III) and Al(III) complexes, organic fertilizer complexation site models

### Introduction

Among the many reasons for the vital role that organic matter exercises in the soil, adequacy for plant growth is

the capacity for the complexation of essential micronutrient metal ions. HAs are broadly studied in the literature because they are the most abundant and ubiquitous class of organic matter found in the biosphere, and are the precu-

sors of fossil fuels. Their capability to sequester metallic ions plays an important role in agriculture and in the study of environmental speciation<sup>4</sup>. NHA, a kind of HA extracted by alkaline solubilization and acidic precipitation from the product of the reaction between nitric acid and organic sediments, such as peat and coal, can be used as an organic fertilizer<sup>5</sup>. The main difference between NHA and the natural HA is the greater percentage of nitrogen as nitro groups (-NO<sub>2</sub>) in the NHA structure.

Many qualitative studies concerning metal ion-HA complexation have been performed by electron paramagnetic resonance (EPR), some involving VO<sup>2+</sup> as a spectroscopic probe for the detailed quantitative determination of bonding parameters for the MHA and MNHA complexes<sup>2,3</sup>.

The bond parameter values and spectroscopic data suggested that the spectroscopic probe, VO<sup>2+</sup>, in both HA and NHA, is at complexation sites with C<sub>4v</sub> symmetry having o-hydroxycarboxylic aromatic (salicylic) acids as equatorial ligands. It is well known that phenol groups activate aromatic rings towards nitration in *ortho* and *para* positions<sup>6</sup>. The addition of one or two electron withdrawing (-NO<sub>2</sub>) groups to the aromatic ring, in the *ortho* and/or *para* position in relation to the phenol group of the salicylic acid (SALA) structure, is predicted to significantly lower the phenol protonation constants and the metal complexation strength of the salicylate ligand. The bonding parameters encountered suggested that the metal-NHA complexes are thermodynamically more stable than the metal-HA complexes. These results were unclear, and maybe the stability of the complexes was dominated by the total structure of the humic substances and not only by the ligand groups on the complexation sites. The knowledge of the complexation behavior of the free ligand group is critical for the understanding of the effect of the structure of the humic substances on the chelation of metal ions.

A detailed investigation of Fe(III) and Al(III) ion coordination chemistry with 3-NSA, 5-NSA and 3,5-DNSA is reported which covers all possibilities of nitration of the original salicylic ligand group of the organic sediment submitted to the nitric acid action.

## Experimental

### Materials

All reagents were of analytical grade and were used without prior purification but were dried. The solutions were made with distilled, deionized and boiled water and maintained at 0.100 M ionic strength with KNO<sub>3</sub> (Carlo Erba). A stream of nitrogen (White-Martins) passing through the reaction system maintained the required inert atmosphere for the potentiometric titrations. All NSA (TCI), 3-nitrosalicylic acid (3-NSA), 5-nitrosalicylic acid (5-NSA) and 3,5-dinitrosalicylic acid (3,5-DNSA) solu-

tions were made in 5% v/v ethanol-water, and the metal ion (Carlo Erba) solutions were made from the nitrate salts in 0.03 M HCl. The Al(III) and Fe(III) content and the concentration of H<sup>+</sup> were determined following the literature<sup>7-8</sup>. The aqueous KOH 0.1 M solution was made from Titrisol (Merck) and standardized by titration against potassium hydrogen phthalate<sup>8</sup> (Baker).

### Potentiometric equilibrium measurements

The potentiometric titrations were carried out under an inert nitrogen atmosphere in a water-jacketed vessel maintained at 30.0 ± 0.1 °C. A Metrohm manual piston burette was used to deliver the titrant (aqueous KOH), and the p[H] values were measured using a Micronal pHmeter B-375 model – results up to 0.001 – with an Analyser reference calomel electrode and a glass one. The system was previously calibrated following the methodology found in the literature<sup>8</sup>. At constant increments of volume of titrant (0.10 ± 0.02 mL), the corresponding pH was read and plotted *vs. a* (number of moles of KOH per number of moles of ligand)<sup>9</sup> to calculate the values of the protonation and formation constants of the system with the aid of the BEST program<sup>8</sup>. The input for the BEST program consists of millimoles of each component, the titration variables, the initial equilibrium constant estimates of each species thought to be formed from the solution components and the experimentally determined profiles of p[H] *vs.* base added. The program also employs the formation constants of the metal hydroxo species<sup>10</sup>. Further details have been described elsewhere<sup>8</sup>.

The solutions of the ligands were approximately one tenth the concentration of the titrant, and when with the metal, two titrations were carried out: the first with a concentration ratio of 1:1.5, metal to ligand, and the second 1:3, metal to ligand. All of the solutions were maintained at 0.100 M ionic strength with KNO<sub>3</sub>.

### UV-Visible spectra

The UV-Visible spectra were recorded on a Hewlett-Packard model 8450A-diode array spectrophotometer in the range of 260 to 600 nm. Aliquots of about 3.0 mL of a separate titration in the ratio of 1:3 metal to ligand were done to obtain the UV-Vis spectra. Quartz cells of a 1.000 cm path length were used, and air was the reference.

## Results and Discussion

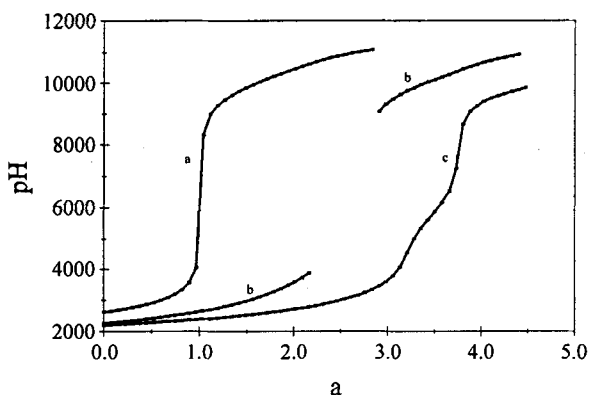
The protonation constants for SALA, 3-NSA, 5-NSA and 3,5-DNSA were determined and compared with the values reported in the literature (Table 1)<sup>11</sup>. The difference between the decimal log unit values is attributed to the different temperatures under which the systems were investigated.

**Table 1.** Logarithms of the protonation constants of the ligands SALA, 3-NSA, 5-NSA and 3,5-DNSA at 30 °C, and an ionic strength of 0.100 M (KNO<sub>3</sub>). # - values in the literature<sup>11</sup> at 25 °C and an ionic strength of 0.1 M.

log K	HL/H.L	H <sub>2</sub> L/H.HL
SALA	13.66 13.4 <sup>#</sup>	2.84 2.8 <sup>#</sup>
3-NSA	9.87 9.87 <sup>#</sup>	1.76 1.73 <sup>#</sup>
5-NSA	9.83 9.8 <sup>#</sup>	1.91 1.94 <sup>#</sup>
3,5-DNSA	7.08 7.22 <sup>#</sup>	0 0.26 <sup>#</sup>

The values were rounded to the digit in accordance with the standard deviation,  $\sigma_{fit}$ , supplied by the results of the calculations with BEST.

Potentiometric equilibrium curves of the ligands 3-NSA, 5-NSA and 3,5-DNSA alone and in the presence of 0.15 and 0.30 millimoles of metal ion were determined by the potentiometric titrations described in the Experimental section. Figure 1 shows the results for 3-NSA and Fe<sup>+3</sup>. The generalized interpretation of the data for the curves are as follows. Each curve was plotted representing a separate experiment. By analyzing the shape of a given curve, qualitative information concerning solution stoichiometry and the possible species present can be obtained. Figure 1 curve a) shows a sharp inflection at  $a = 1.0$  for the ligand ( $a =$  number of moles of titrant per number of moles of ligand). The same kind of inflection for curves b) and c) appears at  $a = 2.5$  and  $a = 3.0$  when in the presence of Fe<sup>+3</sup>, the latter two curves being lower than that of the ligand alone, with no coincidence. Curve b) breaks abruptly from near p[H] 4.0 until near 9.0 due to insoluble products formed in the system. For p[H] values above 9.0 those



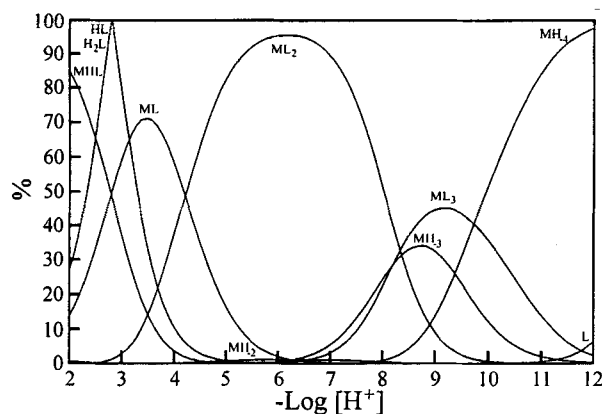
**Figure 1.** Potentiometric p[H] profiles for solutions containing a) 3-NSA, 0.15 millimoles, and 3-NSA and Fe<sup>+3</sup> in the ratios b) 1.5:1 (0.15 and 0.10 millimoles) and c) 3:1 (0.30 and 0.10 millimoles) respectively.  $t = 30.0 \pm 0.1$  °C and  $\mu = 0.100$  M.

insoluble products became soluble and the titration was carried out again.

The first protonation constant involves the phenol group and the second constant involves the carboxyl group of the ligands studied. Both of the protonation constants are lower for NSA than for SALA. For the phenol groups this result is expected due to the more extended  $\pi$  network available to stabilize the anionic charge produced upon deprotonation (resonant effect). The lower value of the second protonation constants (carboxyl groups) of NSA when compared to SALA is a consequence of the decrease in the negative charge on the carboxylate, resulting from the electron-withdrawing action of the nitro- groups of NSA (inductive effect). Both of the effects on the two protonation constants for 3,5-DNSA are increased as a consequence of the action of the two nitro- groups. The second protonation constant for this ligand, 3,5-DNSA, having such a low value that it was not possible to measure it.

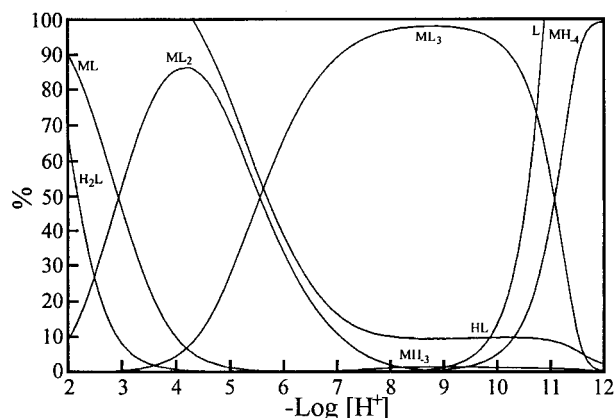
The values of the logarithms of the formation constants for the complexed species are shown in Table 2, along with the values stated in the literature<sup>11</sup>.

The complexation of both Fe<sup>+3</sup> and Al<sup>+3</sup> by NSA is less effective than by the SALA, looking at the formation constants, 3,5-DNSA being the lowest of them. The complexes of this last ligand are probably steric hindered by the two nitro- groups reducing the effectiveness of complexation with Fe<sup>+3</sup>. Normally, the decrease in the protonation constant is accompanied by a decrease in the metal-ligand binding constant.



**Figure 2.** Species distribution curves of the SALA system and the metal ion Fe<sup>+3</sup> as a function of  $-\log [H^+]$ , for a solution initially containing  $7.5 \times 10^{-3}$  M SALA and  $2.5 \times 10^{-3}$  M metal ion.  $t = 30.0 \pm 0.1$  °C and  $\mu = 0.100$  M (KNO<sub>3</sub>). % is the percentage of a species present, with the concentration of the metal set at 100%. L = totally deprotonated species; HL<sup>-</sup> and H<sub>2</sub>L are mono- and diprotonated species; M = non-hydrolyzed metal; ML, ML<sub>2</sub> and ML<sub>3</sub> are the complexed species with one, two and three ligand molecules; MHL is the protonated complex species with one ligand molecule; MH<sub>x</sub> = hydrolysis product of the metal with x OH<sup>-</sup> ions.

Figure 2 depicts the distribution diagrams of the species found in equilibrium between SALA and  $\text{Fe}^{+3}$ . Figure 3 shows the equilibrium between  $\text{Fe}^{+3}$  and 3-NSA. The distribution diagrams were drawn in the titration where the ligand to metal ratio was 3:1. They were obtained with the aid of the SPE program<sup>8</sup> and the concentration of total metal ion present,  $2.5 \times 10^{-3}$  M set at 100%.



**Figure 3.** Species distribution curves for the 3-NSA system and the metal ion  $\text{Fe}^{+3}$  as a function of  $-\log [\text{H}^+]$ , for a solution initially containing  $7.5 \times 10^{-3}$  M 3,5-DNSA and  $2.5 \times 10^{-3}$  M metal ion.

$t = 30.0 \pm 0.1$  °C and  $\mu = 0.100$  M ( $\text{KNO}_3$ ). % is the percentage of a species present, with the concentration of the metal set at 100%. L = totally deprotonated species; HL<sup>-</sup> and  $\text{H}_2\text{L}^{2-}$  are mono- and diprotonated species; M = non-hydrolyzed metal; ML,  $\text{ML}_2$  and  $\text{ML}_3$  are the complexed species with one, two and three ligand molecules;  $\text{MH}_x$  = hydrolysis product of the metal with  $x$   $\text{OH}^-$  ions.

It is well known that for any weak acid ligand, as protonation constants decrease the concentration of free ligand species necessary for metal binding at  $\text{p}[\text{H}] = 7$  increases, producing a more effective chelating agent at a lower  $\text{p}[\text{H}]$ .

For the ferric complexes with NSA ligands, even though the nitro- groups in the NSA play the role of backpulling electrons, the effectiveness of complexation when compared to SALA is observed in the region ranging from  $\text{p}[\text{H}]$  values of 7.0, whereas with SALA, this same kind of complexation happens to be at a  $\text{p}[\text{H}]$  value above 7.0. Another result contributing to this effectiveness of NSA ligands is that the net negatively charged formed in the complexed species  $\text{FeL}_2^-$  and  $\text{FeL}_3^{3-}$  (which is also the same for  $\text{AlL}_2^-$  and  $\text{AlL}_3^{3-}$ ) are better delocalized due to this same ability to backpull electrons by the nitro- groups, as cited above for the deprotonated free ligand. In the case of the 3,5-DNSA complexes, where the effect of steric hindrance is expected to be maximum, it was not evident, as the complexes  $\text{ML}_2$  and  $\text{ML}_3$  were formed (Table 2).

In Fig. 2 the protonated one mole metal to one mole ligand ratio complex between the equilibrium of SALA and  $\text{Fe}^{+3}$ , depicted as MHL, exists from a  $\text{p}[\text{H}]$  below 2.0 until a  $\text{p}[\text{H}]$  near 4.0. The complex one mole metal to one mole ligand, ML, reaches its maximum (70%) at  $\text{p}[\text{H}]$  3.5, and a minimum at a  $\text{p}[\text{H}]$  near 6.0. The complex species  $\text{ML}_2$ , starts to be formed at  $\text{p}[\text{H}]$  3.0, reaches a maximum (90%) at  $\text{p}[\text{H}]$  6.1, and the species represented by  $\text{ML}_3$ , three

**Table 2.** Logarithms of the formation constants of the complexes formed by the ligands SALA, 3-NSA, 5-NSA and 3,5-DNSA and the metal ions  $\text{Fe}^{+3}$  and  $\text{Al}^{+3}$  at 30 °C and an ionic strength of 0.100 M ( $\text{KNO}_3$ ). # - values in the literature<sup>11</sup> at 25 °C and ionic strength 0.1 M.

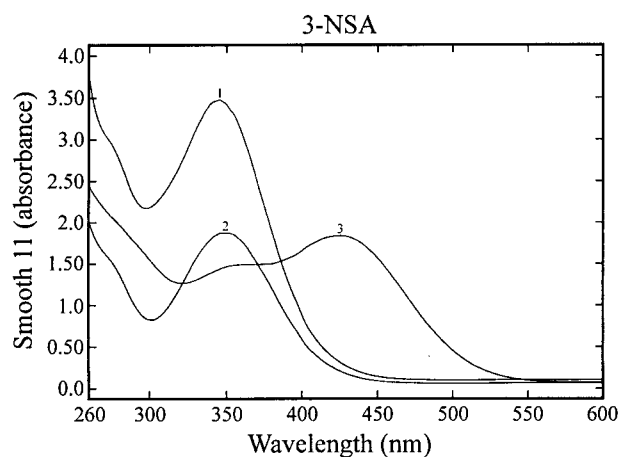
	Metal Ion	ML/M.L	MHL/ML.H	$\text{ML}_2/\text{ML.L}$	$\text{ML}_3/\text{ML}_2.\text{L}$	$\text{MHL}_3/\text{ML}_3.\text{H}$
SALA	$\text{Al}^{+3}$	—	—	—	—	—
	$\text{Fe}^{+3}$	12.9 <sup>#</sup>	—	10.3 <sup>#</sup>	6.6 <sup>#</sup>	—
3-NSA	$\text{Al}^{+3}$	—	—	—	—	—
	$\text{Fe}^{+3}$	16.3 <sup>#</sup>	2.81 <sup>#</sup>	11.9 <sup>#</sup>	7.8 <sup>#</sup>	—
	$\text{Fe}^{+3}$	13.44	—	9.5	7.3	—
5-NSA	$\text{Al}^{+3}$	10.22	—	7.98	6.87	6.56
	$\text{Fe}^{+3}$	13.7 <sup>#</sup>	—	—	—	—
	$\text{Fe}^{+3}$	13.88	—	10.2	8.3	—
3,5-DNSA	$\text{Al}^{+3}$	10.91	—	8.76	5.36	6.24
	$\text{Fe}^{+3}$	13.1 <sup>#</sup>	—	—	—	—
	$\text{Fe}^{+3}$	13.88	—	10.2	8.3	—
3,5-DNSA	$\text{Al}^{+3}$	7.53	—	5.71	4.24	—
	$\text{Fe}^{+3}$	9.81	—	7.4	3.1	—
	$\text{Fe}^{+3}$	9.8 <sup>#</sup>	—	—	—	—

moles of ligand to one of metal, reaches a maximum of 45% at p[H] 9.2.

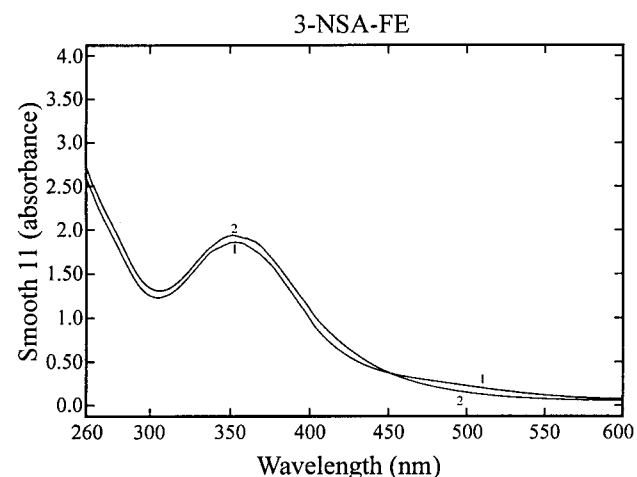
In Fig. 3 the species ML for the system 3-NSA and metal ion Fe(III) reaches a maximum of 71% at p[H] 2.0. The second species  $ML_2$ , reaches a maximum of 86% at p[H] 4.2 and  $ML_3$ , the complex species in the ratio of 3 moles of ligand to one mole metal, presents a maximum of 97.8% near p[H] 8.6.

The hydroxo species of the equilibrium involving SALA and  $Fe^{+3}$  (Fig. 2) starts to be formed at lower p[H] values when compared to those formed in a 3-NSA- $Fe^{+3}$  equilibrium (Fig. 3).

The distribution diagrams obtained for all equilibria studied, which have presented results similar to those depicted in Figs. 2 and 3, have shown the massive presence of the species formed in equilibrium with every ligand but SALA, near the region of p[H] 7.5. Also the metal ions start the formation of hydroxo species with SALA at p[H] values



**Figure 4.** UV-Vis spectra of a solution containing  $7.5 \times 10^{-3}$  M 3-NSA at the following p[H] values: 1 - 1.9 ( $H_2L$ ); 2 - 5.1 ( $HL^-$ ); 3 - 11.0 ( $L^{2-}$ ).



**Figure 5.** UV-Vis spectra of a solution containing  $7.5 \times 10^{-3}$  M 3-NSA and  $2.5 \times 10^{-3}$  M  $Fe^{+3}$  at the following p[H] values: 1 - 5.2 ( $ML_2 + HL$ ); 2 - 8.3 ( $ML_3$ ).

lower than those with the nitrocompounds, for all equilibria studied.

The UV-Vis spectra of 3-NSA in the absence (Fig. 4) and presence of the metal ion Fe(III) (Fig. 5) are presented. They were not intended to show any deep structural studies. The main feature observed in the UV-Vis curves, as well as in the other cases, is that the spectra of ligands in the presence of metal ions differ in general shape and have absorption peaks differing by significant absorption wavelength values<sup>9,12</sup> when compared to the UV-Vis spectra of the species of the ligands alone. These differences suggest different species.

The family of absorbance curves in Fig. 4 presents characteristic absorptions of deprotonated phenol groups (species  $L^{2-}$ , curve 3, 426 nm, 361 nm, with a shoulder at 285 nm), and different ones for species  $HL^-$ , curve 2, 349 nm, and a shoulder at 273 nm) and  $H_2L$ , curve 1, 345 nm, a shoulder at 285 nm).

Figure 5 shows the differences among the absorbance values found for this system in the presence of  $Fe^{+3}$ . Curve 1 is mainly due to  $ML_2$ , the complex species formed at a p[H] value near 5.0 and where the species  $HL^-$  is less. Curve 2 is due to  $ML_3$ . For both species the absorbances are at 351, with a shoulder at 270 nm. There is an isosbestic point at 451 nm. All of the systems in the presence of metal ions presented more than one species mixed in the p[H] range investigated.

## Conclusions

The 3-NSA, 5-NSA and 3,5-DNSA complexes with  $Fe^{+3}$  and  $Al^{+3}$  were characterized by potentiometric and UV-Vis spectrophotometric studies. The species distribution of these systems have shown that as the complexes with NSA compounds begin their formation in a region of p[H] values near 7.0, the same can occur with SALA only above those p[H] values. So, a greater quantity of metal ion is chelated to the nitro compounds, which represents an extra advantage for the possible use of NHA in soils as a slow release fertilizer.

Also the hydroxo species, being formed at higher p[H] values for the nitro compounds than in the systems with SALA, presents an advantage due to the possibility of delaying the precipitation of the metal ion, making it more available, in soil for plants.

These results make the nitrohumic substances into better chelating agents than humic substances in natural soil p[H] values, as previous studies indicated with the whole HA and NHA<sup>2,5</sup>.

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## References

1. Schulten, H.-R.; Schnitzer, M.; *Naturwissenschaften* **1993**, *80*, 29.
2. Mangrich, A.S.; Vugman, N.V.; *Sci. Total Environ.* **1988**, *75*, 235.
3. Mangrich, A.S.; Vugman, N.V.; *Fuel* **1990**, *69*, 925.
4. Mangrich, A.S.; Tese para concurso de professor titular (DQ/UFPR, Brazil, 1993).
5. Moliner, R.; Ruiz, C.; Uliaque, C.; Gavilan, J.; *Fuel* **1983**, *62*, 1369.
6. Green, J.B.; Manahan, S.E.; *Anal. Chem.* **1979**, *51*(8), 1126.
7. Schwarzenbach, G.; Flaschka, H.; *Complexometric Titrations*; Methuen & Co.; UK, 1969; p 192, 185.
8. Martell, A.E.; Motekaitis, R.J.; *The Determination and Use of Stability Constants*; VCH; N.Y., 2nd ed., 1992.
9. Szpoganicz, B.; Motekaitis, R.; Martell, A.E.; *Inorg. Chem.* **1990**, *29*, 1467.
10. Baes Jr., C.F.; Mesmer, R.E.; *The Hydrolysis of Cations*; Wiley-Interscience; N.Y., 1976; p 122, 235.
11. Martell, A.E.; Smith, R.M.; *NIST Critical Stability Constants of Metal Complexes*; NIST Database 46; Gaithersburg, MD, USA; 1994 (and references therein).
12. Rosso, N.D.; Szpoganicz, B.; Motekaitis, R.J.; Martell, A.E.; *Inorg. Chim. Acta* **1994**, *227*, 49.