

# Conductimetric behaviour of humic acids with Cu(II) ions

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Humic substances play an important role in the behaviour of Cu(II) in natural environments, due to the formation of complexes which can modify the mobility of these ion. A study of the interaction between Cu(II) ions and a lignite humic acids in different metal - ligand ratios has been made by conductimetric techniques. The results are interpreted using an excess function which relates the conductivity of the mixture and of the separated components. Its variation with concentration and with pH in absence of heavy metal cations is discussed. The capacity of complexation of the lignite humic acids enables them to be used in environmental sites polluted by heavy metals such as copper.

## Introduction

Humic substances play an important role in the behaviour of heavy metals in natural environments, due to the formation of complexes which can modify the mobility of these ions [1-3]. The complexation process depends on the nature of the heavy metal and on the humic substance (humic or fulvic acid). Thermodynamic, kinetic and structural studies using of different experimental techniques are needed to gain relevant information on global processes [4].

Because relevant conclusions are reached using experimental conditions which are similar to those of natural ecosystems, in particular without the addition of species which could disturb the free equilibria, conductimetric techniques have been used to study the behaviour of humic substances both in absence and presence of complexing heavy metals [5-9]. On the other hand, theoretical work has been done to build mathematical equations which could be used to explain the experimental results [10]. Nevertheless, as far as we know, there are no studies of the influence of humic substances on the conductimetric behaviour of heavy metal/humic substance solutions. Here, we report the conductivity analysis of mixtures of a coal humic acid and Cu(II) ions.

## Experimental

All reagents were purchased at analytical grade and were used without further purification. We used deionised water with resistivity  $\geq 14 \text{ M}\Omega \text{ cm}$ .

The sample of humic acid was extracted from a lignite coal from Candiota mines (Rio Grande do Sul, Brazil) using Tyurin's procedure as described by Kononova [11]. 150 mL of NaOH 0.1 M were added to 10 g of coal sample, shaken in a closed flask during 24 hours and centrifuged (3000 rpm) during 30 min. The solid phase was discarded. The supernatant was acidified with  $\text{H}_2\text{SO}_4$  (pH  $\sim 2$ ) then centrifuged 30 min at 8000 rpm. The precipitate (humic acids) was separated from fulvic acids by filtration, dissolved in 0.1 M NaOH then dialysed against water (pore diameter 20 Å). The final humic acid solution was then freeze-dried to obtain a brown powder.

Cu(II) and NaOH stock solutions were prepared by dissolving solid  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and NaOH respectively in free- $\text{CO}_2$  water. Humic acid solutions were obtained by dissolving the appropriate amount of solid in water then stored under  $\text{N}_2$  atmosphere.

A Metrohm 660 conductometer, equipped with a platinum cell (nominal constant 0.7) and calibrated with 0.1000 M KCl solution, was used to measure the conductivity of Cu(II)/humic acid solutions. pH was measured with a Metrohm 6.0216.100 electrode fitted to a Methrom 654 pH-meter and calibrated by strong acid/strong base titration [12].

All experiments were performed with a Methrom double-walled glass cell at constant temperature ( $298.0 \pm 0.2\text{K}$ ) with water from a Landa refrigerated circulator bath. For each titration, 50 mL of a mixture of humic acid (20, 40, 60, and 80  $\text{mg L}^{-1}$ ) and Cu(II) solution (0 to  $1.9 \cdot 10^{-4} \text{ M}$ ) were equilibrated during 12 hours, transferred in to the cell then, after thermal equilibrium was reached, titrated with 0.011 M NaOH solution (Methrom 665 Dosimat burette). Prior and during titration,  $\text{N}_2$  was bubbled into the solution while stirring using a Methrom 649 magnetic stirrer. Mean conductivity values of three replicates give variations of less than  $0.2 \mu\text{S cm}^{-1}$ .

Results and discussion

The conductance measurement of a solution of humic acids and metallic salt, is the sum of the contributions of all ions, namely polyion, adsorbed and free counterions, and complex ions. In order to distinguish these ionic contributions, a conductivity excess ( $\Delta k$ ) has been defined as the difference between the specific conductivity of humic substance/metallic ion mixtures and the sum of the values recorded for the separated solutions [13,14]. A positive value of this function is usually obtained. It indicates the complexation of humic substances with metallic ions [15]. Here, the slope value of the  $\Delta k$  versus metal ion concentration indicates the association degree of the metal ions with humic acids.

Figure 1 shows conductimetric curves for mixtures of humic acid and Cu(II) during the titration with sodium hydroxide. First, we observe an increase of conductivity with Cu(II) concentration ( $< 0.4$  mL NaOH). It is due both to the presence of heavy metal cation and counterion, and to the release of protons induced by the complexation of copper ions with humic acid. Secondly, two main facts appear at high Cu concentrations. On one hand, the existence of a plateau which has been previously described for metal hydroxides [9]. This phenomenon can be attributed to the enhanced association degree of divalent metal cations with humic acids, induced by the deprotonation of ligand sites due to the presence of growing quantities of Cu(II). On the other hand, the decrease of conductivity values with Cu con-

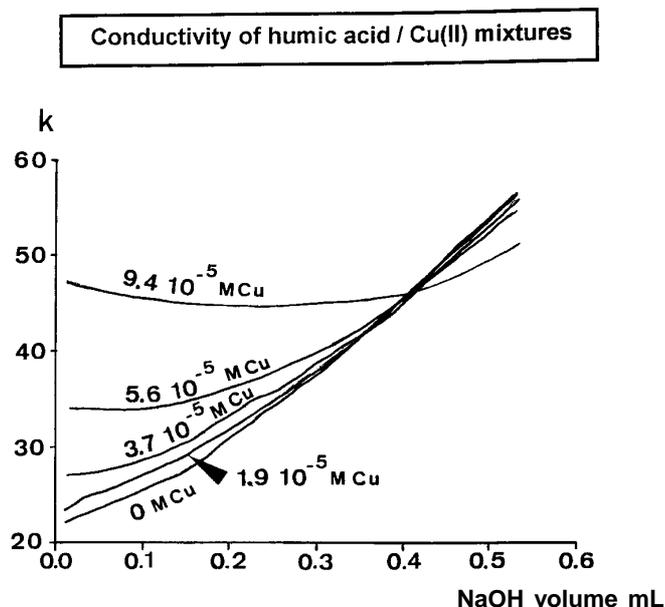


Figure 1. Conductivity values of humic acid/Cu(II) mixtures during titrate ion with NaOH  $\approx 0.011$  M.

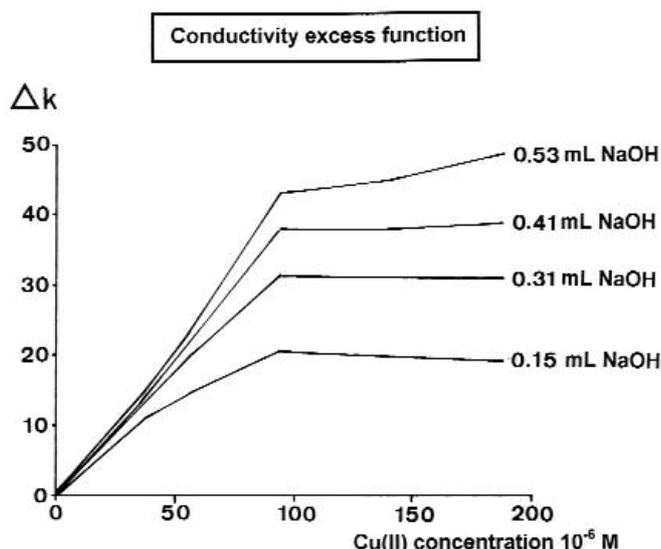


Figure 2. Plot of the conductivity excess function ( $\Delta k$ ) versus Cu(II) concentration. [Humic acid] = 60 mg/L.

centrations at NaOH  $> 0.4$  mL has not been previously cited in the literature, although similar results were obtained for fulvic and prefulvic acid titrations in absence of heavy metals [9].

In figure 2, several typical plots of the variation of the  $\Delta k$  function when Cu(II) concentration changes are presented. This type of behaviour was obtained for 40, 60 and 80 mg  $L^{-1}$  humic acid concentration. At 20 mg  $L^{-1}$  the plots (not shown here) have negative values at the lowest metal concentration. This anomalous result could be attributed to the non-additivity of polyelectrolyte/salt systems [16]. It is apparent when the complex concentration is at its lowest values (low humic acid versus metal ratios). For higher concentrations (Fig. 2),  $\Delta k$  increased both with NaOH volume and with Cu concentration, thus showing the formation of complexes. At higher Cu concentrations,  $\Delta k$  remains constant, this result is due to the saturation of humic acid groups by copper ions.

Figure 3 shows the initial slopes from figure 2 curves at various humic acid concentrations versus pH of the humic acid solution (no Cu ion, same ionisation degrees). Four behaviours are observed: an initial increase at low pH, then a plateau, then a markedly increase between pH 7.5 to 9 and finally a new plateau. In all case slope values at constant pH are proportional to humic acid concentration.

Conclusion

The whole of the results, presented here, show that the formation of copper complexes [lignite HA/Cu(II)] have an

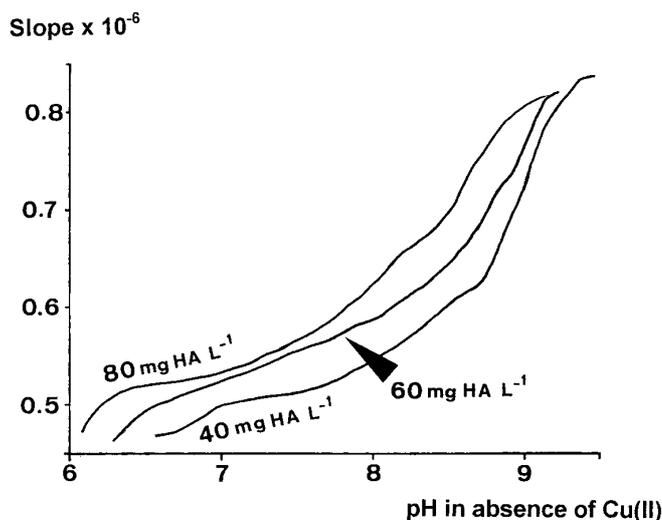


Figure 3.  $\Delta k$  slopes plot against pH of humic acid solutions (no Cu).

important contribution of ion-specific chemical association enhanced by the humic acid - cation concentration ratio growth.

The capacity of complexation of the lignite humic acids enables them to be used in environmental sites polluted by heavy metals such as copper.

### Acknowledgements

FR acknowledges to Xunta de Galicia (Spain) the concession of a grant to visit Toulouse.

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