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Comparison of complexation properties of humic acids and simple organic ligands

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Abstract

Simple organic compounds as citric acid, phthalic acid, salicylic acid, EDTA, hydroquinone and pyrocatechol were used as structural models of active sites of humic acids. Combination of high resolution ultrasound spectrometry with potentiometry, conductometry and UV/VIS spectrometry were utilized for complexation of copper (II) ions by humic acids and model compounds. Changes in the slope of measured quantities were used to find the saturation of binding. Ultrasound spectrometry showed follow changes of hydration of interacting species. The differences observed for individual model compounds show that there are active centres not only with various strength and stability of formed complexes but also with their various rigidity and ability of conformational changes.

Keywords: Humic acid, copper ions, high resolution ultrasound spectrometry, potentiometry, UV/VIS spectrometry, conductometry

Introduction

Several simple organic (hydroxy)acids as models of principal functional moieties of lignite humic acids and the copper ion as a model ion to investigate metal–humic interactions were studied by four various methods. The models were chosen for their. similarity with the active sites in the structure of humic acids and high affinity to metal ions, e.g. salicylic acid is frequently considered as the most suitable coordination site in structure of humic acids (Saar and Weber 1980). No significant differences in the complexation properties of various phenolic acids as the ligand models of humic acids towards Cu^{2+} ions were observed. Because all these acids contained the catechol group, authors postulated that the complexation process is intrinsically related with its presence (Borges et al. 2005).

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Many authors reported that there are four possibilities of humic binding with metal ions: 1) chelation between carboxylic and phenolic groups, 2) chelation between two carboxylic groups, 3) complexation with carboxyl group and 4) binding with phenols or phenolic ethers (Baker and Khalili 2003; Pandey et al. 1999).

A model of fulvic acids based on randomized positioning of the functional groups and aromatic rings showed that the predominant bidentate sites are likely to be phthalate- and salicylate-type sites with a significant proportion of the aromatic carboxylic and phenolic groups not participating in the chelating sites (Murray and Linder 1984). The model was then applied to both humic and fulvic acids and several models included the nitrogen atom were added (Bryan et al. 1997). The important role of N content in the affinity of humic substances towards copper was predicated also by other authors (Gregor et al. 1989).

The method of ultrasound spectrometry is newly utilized in study of the humic complexation in this work. The method is based on observing interactions of the ultrasound wave with the studied system. The ultrasound velocity reflects the local elasticity and density of the material, which are determined by the molecular arrangements, conformation and the solvation shell. Due the high resolution the method is sensitive to, e.g., details of the molecular organization or the solvating state. Applications thus may cover the study of micellization or aggregation, ligand-ligate binding, metal ion-(bio)polymer interaction, conformation changes etc.

Materials and methods

Ultrasonic spectrometer with high resolution HR–US 102 (Ultrasonic Scientific, Ireland), was utilized for measurement of basic ultrasonic parameters at three various frequencies (5110, 8220 and 12 200 kHz). No changes of ultrasonic velocity (ΔU) on applied frequency were occurred and presented results are the average values of these three determinations. The device consists of two independent cells tempered at 25°C. Both cells were filled by the same model compound or humic acids solution (1 cm^3). Sample in cell 1 was titrated by $CuCl_2$ (1 $mmol.dm^{-3}$) up to saturation of acidic group. The conductometric and potentiometric titrations were carried out with the same solutions to investigate complexation of humic acids and model compounds in detail. The solutions of model compounds or humic acids (50 cm^3) were titrated by $CuCl_2$ (1 $mmol.dm^{-3}$) up to saturation of acidic group as in previous case. The combined pH/conducto-meter (Mettler Toledo S47 SevenMulti™) was used for monitoring pH values and conductivity after each addition of titrant.

Results and Discussion

In Fig 1 we can see that titration of EDTA causes gradually the increase of ultrasound velocity (ΔU) but the concentration dependence is not linear. The decrease in slope between 0,3 and 0,7 value of Cu/H (ratio between added Cu^{2+} ions and amount of acidic groups of model) corresponding with saturation of model active sites was observed. Measured pH–values confirmed that no H^+ ions are splitted off for Cu/H > 0,7. Titration of humic acids by $CuCl_2$ showed minimum of ΔU at Cu/H ratio slightly above 0,5. It corresponds which hypothesis that the bivalent ions are bonded by two acidic functional groups.

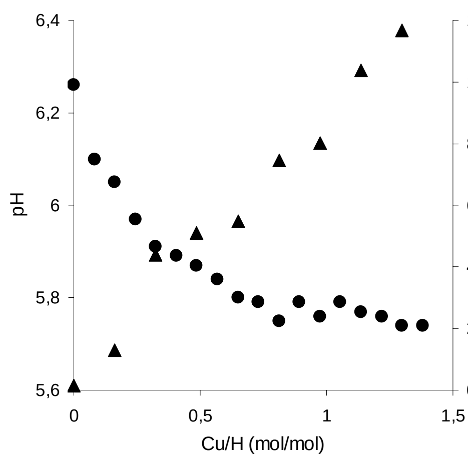

Figure 1: Comparison of results obtained by potentiometry and ultrasound spectrometry for titration of EDTA by $CuCl_2$

The ΔU-value obtained for complexation of humic acids decreases with the addition of Cu^{2+} ions and the obtained concentration dependence has a relatively marked minimum (in contrast to the used model compounds). The formation of Cu-humic complexes results in the initial decrease of ΔU. It is caused by the release of hydration water from the coordination shell of copper and atomic groups of humic acids. The compressibility of water in the hydration shells of the ligand is less than that of bulk water therefore transferring of hydration water into the bulk water increases the total compressibility of the solution, thus reducing the ΔU-value. When all available sites are occupied the curve levels off. The electrostatically neutralised humic molecules begin to form the aggregates tt higher concentrations of copper, which could cause the increase of ΔU at this stage.

Conclusion

The interaction of humic compounds with metal ions is complex problem, studied by various methods to understand better their principles and effects on their function in nature. The differences

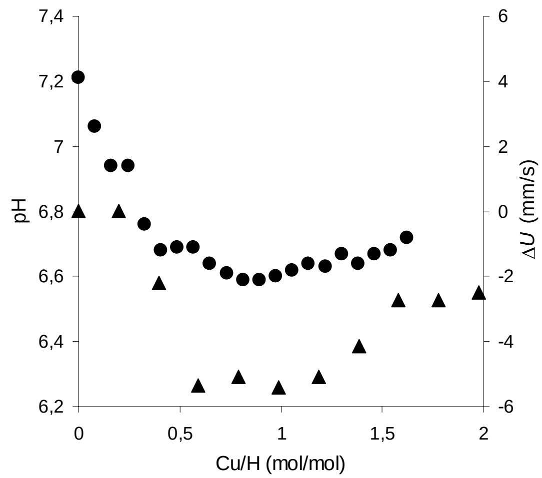

Figure 2: Comparison of results obtained by potentiometry and ultrasound spectrometry for titration of humic acids by $CuCl_2$

observed for individual model compounds show that there are active centers not only with various strength and stability of formed complexes but also with their various rigidity and ability of conformational changes.

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