

Thesis of the Ph.D. dissertation

**Interaction of humic acids with magnetite nanoparticles:
from soils to magnetic fluids**

Erzsébet Illés Mrs. Nyerges

Supervisor: Dr. Etelka Tombácz
Associate professor, DSc.

University of Szeged
Department of Colloid Chemistry
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Introduction and objectives

Humic substances (HSs), such as humic and fulvic acids, formed during the physico-chemical and microbial degradation of plant and animal residues, are present in soils, surface- and groundwaters, and even atmospheric aerosols. The basic characteristics of these organic materials are the acidic feature, the chemical heterogeneity, the polydisperse size and the ability to form complex with metal ions. These natural organic materials have numerous attractive features, for example the enhancing effect on soil productivity, and nowadays the human utilization of humate-metal complexes is also known. However, humic substances, besides their advantages, can cause serious problems in aquatic systems as well: perchlorinated by-products form during the disinfection of drinking waters, and the elimination of these materials has not been solved yet. Humic substances dissolved partly in natural waters (e.g. soil solutions, lakes and rivers) increase the water-solubility of metal impurities due to the complexation reactions, which leads to their enhanced transport and significant dispersing in the environmental systems.

Soils contain not only dissolved organic matter (e.g. humic and fulvic acids) but also dispersed mineral (e.g. clay and metal oxide) particles. Among the inorganic soil constituents the magnetite is an important iron oxide due to its ferromagnetic property. The super-paramagnetic nano-sized magnetite particles with different coating (e.g. stabilizing, biocompatible) have several practical applications in the industry and electronics as sealing magnetic fluids, and also in the medical therapy and diagnosis as hyperthermal and contrasting agents. The magnetic fluids contain small (5-10 nm) magnetic particles with a protecting layer on their surface, which preserves the colloidal stability of particles and protects against particle aggregation and incidental environmental and biological effects.

In soils the mineral particles can be found not in specimen form, their surfaces are weathered and coated by exposure to the soil solution, in which humic substances are dissolved. The humus coating leads to the significant change of the surface charge properties and so the aggregation behavior of covered particles. The surface modification is the consequence of the combined electrostatic and chemical interactions between the mineral particles and humic substances.

In the course of the Ph.D. studies I aimed to know the natural processes in soils, especially the interaction between magnetite and humic acids. Based on my experimental results I examined the possibility of the preparation of a water-based, humate-stabilized magnetic fluid.

Experimental (materials and methods)

Humic acids were obtained from brown coal and peat by traditional alkaline extraction and in accordance with the instructions of IHSS. Synthetic magnetite (Fe_3O_4) nanoparticles were prepared by alkaline hydrolysis of iron(II)- and iron(III)-salts. The chemicals were of analytical grade product of Reanal (Hungary). All experiments were performed at room temperature (25 ± 1 °C) and under atmospheric pressure.

The pH and ionic strength-dependent dissociation of humic acids obtained from brown coal and peat samples, and their interaction with Cu^{2+} and Fe^{2+} ions were characterized by potentiometric acid-base titration. The equilibrium constants and the pH-dependent speciation for the dissociation of humic acids and for their interaction with metal ions were determined by FITEQL software using the titration data. The interaction of humic acids with Cu^{2+} and cethyl-trimethyl-ammonium(CTA^+)-ions were studied by potentiometric titration using ionselective electrodes (ISE) as well.

The synthetic magnetite product was characterized by X-Ray diffraction (XRD), N_2 -adsorption (BET) and transmission electronmicroscopy (TEM) methods. The pH-dependent surface charging of magnetite particles was examined by potentiometric acid-base titration. The hydrodynamic size and the charge state (as zeta-potential) of magnetite particles were determined by dynamic light scattering (DLS) and laser Doppler electrophoresis. The flow properties of dense iron oxide suspensions were studied by means of rheometer.

The binding of humic acids on magnetite and the adsorptive fractionation were investigated by UV-VIS and fluorescence spectroscopy, and by size exclusion chromatography (HPLC-SEC). The surface modification effect of adsorbed humate on the magnetite particles, and the change in the charge state and the aggregation behavior of iron oxide particles were examined by laser Doppler electrophoresis and dynamic light scattering.

New scientific results

1. Humic acids obtained from brown coal and peat have negative charge due to their polyanionic character. The dissociation of humic macroions is enhanced by the increasing pH and ionic strength of aqueous medium. Assuming two dissociation steps, the charge formation is related to the strong (L_1 : carboxyl) and weak (L_2 : phenolic hydroxyl) acidic groups. The net proton surface excess–pH functions (calculated from the material balance of H^+ and OH^-) and their evaluation (based on two pKs and diffuse double layer model) showed that the sample obtained from peat is stronger acid (acidity is 5.5 mmol/g) than the brown coal one (acidity is 3.9 mmol/g). At low pHs carboxylate and undissociated hydroxyl groups are dominant in the solution of both humic acids, while an increase in pH induces the deprotonation of hydroxyl groups from pH~6.
2. The evaluation of titration data using the hydrolysis model revealed that only the presence of Cu^{2+} and $Cu(OH)_2$, and Fe^{2+} , $FeOH^+$ and $Fe(OH)_2$ species has to be assumed in the hydrolysis processes of Cu^{2+} and Fe^{2+} ions. Supposing non-stoichiometric complex formation (MeL_1 and MeL_2), the equilibrium constants and the pH-dependent distribution of different ionic forms were determined for the interaction of humic acids with metal ions. The logK values obtained from the numerical-fitting were higher for hydroxyl-complexes of Cu^{2+} ions ($Cu(L_2)$), while the carboxylate ones were larger in the case of Fe^{2+} ions ($Fe(L_1)$) for both humic acids. The presence of humic acids essentially influences the hydrolysis and the pH-dependent speciation of hydroxo-complexes of these metal ions, in the case of Fe^{2+} ions the large amount of humic acid inhibits the precipitation of $Fe(OH)_2$ as well.
3. The Cu^{2+} -ISE measurements showed that the humate anions form complexes with more metal ions at higher pHs up to ~7. The amounts of functional groups being equivalent to the average complexation capacities are significantly smaller than that of dissociated acidic groups (i.e. acidity) at given pHs. It can be stated that this method leads to a parameter (complexation capacity), which can be used for the quantitative characterization of the interaction between humic acids and copper-ions, but it does not agree with the total amount of acidic functional groups of humic acids, i.e. with their total acidities.

4. The CTA^+ -ISE measurements showed that the specific surfactant amount corresponding to the intersection point (CIP: common intersection point) of the titration curves measured at different NaCl concentrations is in quantitative agreement with the dissociated proportion of functional groups of humic acids. Small organic molecules (salicylic acid, glycine, oxalic acid) added to the titration sample do not influence the ion-pair formation between humate anions and surfactant cations. This titration method measuring the amount of dissociated functional groups of polyanions is suitable for the quantitative determination of dissolved macromolecular organic acids in nature.
5. The pH of the point of zero charge (PZC) of amphoteric magnetite nanoparticles determined by potentiometric acid-base titration is 7.9 ± 0.1 on the basis of the pH-dependent net proton surface excess functions, which are proportional to the surface charge of magnetite, if the total H^+/OH^- consumption of magnetite sol is corrected by that of equilibrium medium. At pHs lower than the PZC, the surface charge is positive, while oxide particles are negatively charged above it. The pH of isoelectric point (IEP) determined by zeta-potential measurements is ~ 8 in good agreement with the pH of PZC. Dynamic light scattering measurements proved that in diluted aqueous systems, magnetite nanoparticles aggregate around $\text{pH} \sim 8$ as expected from the particle charge state characterization, while sols are in stable colloidal state at pHs far from the PZC. In harmony with these, the rheological investigation of dense suspensions revealed that liquid-like Newtonian behavior was characteristic of the well-stabilized systems (structure formation does not take place due to the repulsion between the particles), however, plastic feature appeared in the aggregated samples due to the formation of particle network.
6. A decrease in pH and an increase in ionic strength promote the adsorption of humic acid molecules on magnetite, in which iron oxide takes part as a high affinity partner. At pH of PZC and above it, the binding of humates on the magnetite is a ligand-exchange process on surface sites, while at pHs lower than the PZC the electrostatic attraction between the positively charged iron oxide surface and humate anions contributes in a large degree. The adsorption of humic acids on the charged oxide surface shows both chemical and electrostatic character. The adsorption kinetics measurements revealed that binding of organic molecules is fast, the adsorption equilibrium is reached in ~ 120 minutes.

7. Based on HPLC-SEC analysis, UV-VIS and fluorescence spectra, it can be established that all the present humic acid molecules bind to the magnetite surface at limited surface coverage over the high affinity region of adsorption, however, the smaller HA molecules probable enriched in acidic functional groups adsorb preferentially with increasing equilibrium HA concentration; so the size-preference, which is common in polymer adsorption, does not prevail in HA adsorption. The adsorption kinetics measurements revealed that no changes (displacement, rearrangement) can be observed in the adsorption layer after the development of adsorption equilibrium.
8. ICP measurements revealed that with increasing HA concentration, an increasing amount of dissolved Fe(III)-ions moves into the aqueous phase from the surface of magnetite due to the ligand exchange reactions between humic acids and the surface sites of iron oxide. Comparing the specific absorbance ($SUVA_{254}$), E_3/E_4 and E_4/E_6 values calculated from UV-VIS spectra, in addition the fluorescence emission of the humic acid solutions before and after adsorption, as well as in the absence and the presence of various trace amounts of Fe(III)-ions proved that the adsorptive fractionation of humic acids by both chemical feature and size, and the adsorptive dissolution of magnetite due to the humate complexation take place in parallel during the adsorption of humic acids on magnetite, and these processes cannot be separated from each other.
9. It was confirmed that humic acid adsorption modifies the surface charge properties of magnetite depending on the amount of adsorbed polyanions. The particle surface is covered partially or completely with increasing HA concentration, therefore the positive charges of magnetite are neutralized then recharged at pHs lower than the PZC of oxide surface. The existence of remaining positive charges on the surface and the development of negative particle charge even below PZC were proved by electrokinetic measurements. It was revealed that in the presence of humic acids the aggregation behavior of magnetite nanoparticle covered by humates in different degree changes significantly in accordance with the particle charge state characterization. The aggregation zone shifts to lower pHs with increasing amount of added polyanions in harmony with the shifting pH of charge reversal (IEP). In the presence of trace amount of humic acid, electrostatic attraction takes place between the positive and negative patches existing on the partially coated magnetite surface, which leads to the destabilization of sample, i.e. promotes the

aggregation of magnetite particles. In the samples containing larger amount of HA than its adsorption capacity, an increase in the average size of magnetite particles covered by humate was measured, which shows that the organic matter stabilizes the iron oxide particles not only in electrostatic, but also in a steric way. The pH stability and electrolyte resistance of magnetite sols increased significantly in these cases due to the combined electrosteric stabilization.

Possible applications

1. The quantitative determination of dissolved humic substances is possible by measuring the amount of dissociated functional groups via ion-pair formation between humate anions and CTA^+ -ions by means of surfactant ion selective electrode at different ionic strengths (filtration, dilution, salt addition are needed depending on the sample origin).
2. The elimination of humic substances dissolved in drinking water is probable by a combined adsorption-magnetic separation method before the chlorination (pH, ionic strength and the required amount of magnetite can be planned on the basis of the high affinity region of the adsorption isotherms).
3. Considering the composition of stabilized magnetite dispersions (pH, electrolyte concentration, the quality and quantity of humic acid and magnetite) a novel water-based magnetic fluid with good stability under physiological condition can be prepared.

Publications

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