

Protolytic Properties of Alkoxysilylated versus Natural Humic Materials Aimed at Use as Stabilizers for Magnetic Fluids

Sorkina T.^{a*}, Goldt A.^b, Polyakov A.^b, Dubov A.^b, Toth I.^c, Hajdu A.^c, Goodilin E.^b, Tombacz E.^c, Perminova I.^a

^aDepartment of Chemistry, Lomonosov MSU, Leninskie Gory 1-3, 119991, Moscow, Russia;

^bDepartment of Material Science, Lomonosov MSU, Leninskie Gory 1-3, 119991, Moscow, Russia; ^cDepartment of Colloidal Chemistry, Univ. of Szeged, Aradi Vt. 1, Szeged H-6720

E-mail: sorkina@org.chem.msu.ru

1. Introduction

Biocompatible magnetic fluids (MF) receive currently a lot of attention due to broad applications in biomedical technologies such as hyperthermia, drug delivery, tomography, and others. Magnetic fluids of this note are water based colloidal suspensions composed of ferromagnetic or superparamagnetic nanoparticles. The main problem to solve is aggregation of nanoparticles in aqueous solutions under physiological conditions. The main requirements to modifiers are non-toxicity and ability to form stable coating on magnetic nanoparticles. In this regard, of particular advantage can be a use of humic substances (HS). Application of HS as stabilizing agent for magnetic fluid has been previously reported [1]. However, the humic coating obtained was very sensitive to changes in pH and salinity. In this work, the protolytic properties were investigated of native HS against the specifically modified HS with incorporated alkoxysilyl-groups providing high affinity of these humic materials for mineral surfaces. It was hypothesized that these humic derivatives will form stable coating on the surface of iron oxide particles due to formation of Si–O–Fe linkages. The selected magnetic nanoparticles were superparamagnetic γ -Fe₂O₃ and ferromagnetic δ -FeOOH. The magnetic nanoparticles possessed different morphology, which will be stable at physiological conditions after appropriate coating and possess reliable magnetic properties.

Thus the goal of the research was to evaluate stabilizing properties of alkoxysilylated humic derivative versus natural non-modified HS with respect to magnetic nanoparticles of different micromorphology presented by γ -Fe₂O₃ and δ -FeOOH, and to conclude on their applicability for producing biocompatible MF suited for biomedical applications.

2. Materials and methods

Four samples of HS from different sources were studied as stabilizing agents for MF. Two IHSS samples of aquatic SR FA and SR NOM, one sample of natural leonardite humic acids (CHA-Pow), extracted from Powhumus (Humintech, Germany) and one sample of modified

leonardite HA (CHA-APTS-20) were tested as stabilizing agent for biocompatible MF. The CHA-APTS-20 was obtained as described in [2] using modification of parent humic materials with organosilane 3-aminopropyltriethoxysilane (APTS) in DMF solution. Maghemite γ -Fe₂O₃ nanoparticles were obtained in microspheres using aerosol spray pyrolysis and in nanotubes: 200-300 nm long and ~ 10-15 nm thick. Ferrihydrite δ -FeOOH was synthesized in the form of spheres with average diameter of ~ 30-40 nm associated into aggregates (~ 200–300 nm).

Humic based MF were obtained by dispersion of iron oxide dry powder in water solution of humic samples with pH 7.0–7.15 as described in [3]. The pH-dependent surface charge state of HS was determined from acid-base titration under CO₂-free condition using background electrolytes (NaCl) to maintain the constant ionic strength of 0.01 M as described in [4].

The two IHSS samples were dissolved in MQ water; the leonardite samples were converted to suspensions using technique described in [5]. Equilibrium titration was performed by means of a self-developed titration system (GIMET1) with 665 Dosimat (Metrohm) burets, nitrogen bubbling, magnetic stirrer, and high-performance potentiometer. Powder sample was added to 0.01 M NaCl solution equilibrated with electrolyte to reach a starting pH 3.5. After nitrogen purging for 15 min suspensions were titrated by standard NaOH solution up to pH 10.5 and then by standard acid solution down to pH 3.5.

3. Results and discussions

The set of humic materials used in this study included the samples of aquatic FA and NOM with low aromaticity and significant content of aliphatic oxidized structures and the sample of leonardite humic acid (CHA-Pow-05) with the highest content of aromatic fragments and lowest – of carbohydrate groups and directly modified leonardite humic acid (CHA-APTS-20) with 20% modified carboxylic groups. Direct modification of humic backbone using APTS increases the affinity of humic materials for mineral surfaces by incorporation of methoxysilyl groups into their structure. The latter produce covalent bonds with hydroxyl carrying surfaces of silica and metal oxides. Conversion of carboxyl groups into amides can lead to significant changes in the acidic properties of HS.

Furthermore, complexing properties of HS depend on carboxyl groups content. Interaction between humic acids and iron oxides occurs via hydroxyl group on the surface of iron oxide and acidic groups on HS, so one of the most important parameters is the acidic groups content. To characterize acid-base properties of the humic samples used in this study, the

method of direct potentiometric titration was used. The pH-dependent net proton surface excess curves calculated from acid-base titration data are presented in the Fig. 1.

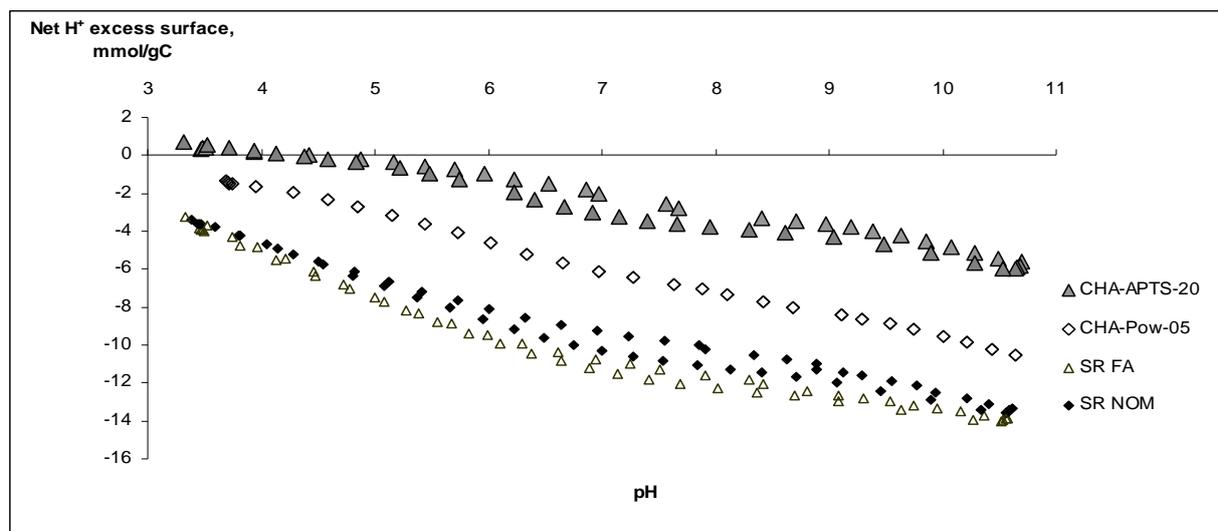


Figure 1. pH-dependent net surface H^+ excess curves for IHSS SR NOM (black rhombuses) and SR FA (small white triangles), for the natural leonardite sample CHA-Pow-05 (white rhombuses) and modified sample CHA-APTS-20 (grey triangles)

According to the obtained net proton surface excess vs. pH curves, modified humic material has acid-base properties substantially different from those of the parent humic material. The negative and positive values of net proton surface excess indicate the presence of negatively and positively charged groups such as e.g., deprotonated $-COO^-$ and protonated $-NH_3^+$ at the given pHs, respectively. In particular, this referred to the appearance of the inflection points on the titration curves as well as to the positive values of net proton surface excess. Comparing the measured points at pH~8, the given difference might be connected to the conversion of carboxyl groups into amide ones, which was caused by the undertaken modification. The modified sample had also lower water solubility as compared to the parent humic materials that indicates an increase in their hydrophobicity.

The acidic group content calculated according to Ritchie&Perdue (2003) is given in the Table 1. The results are presented as quantity of functional group in mmol per mass of carbon in samples.

Table 1: Titration results: humic substances acidic group content

Sample	-COOH, mmol/g C	-OH, mmol/gC
IHSS SR FA	11.57	3.54
IHSS SR NOM	10.25	4.48
CHA-Pow-05	6.61	3.52
CHA-APTS-20	3.32	2.88

The results of acid-base titration of the parent leonardite humic acids (CHP-Pow-05) and its derivative show substantial change in acid-base properties of the modified HS and an increase in its hydrophobicity may be caused not only by a significant decrease in –COOH content, but also by the presence of residual organic solvent (DMF) in the composition of the obtained compound.

4. Conclusions.

Natural and modified humic acids are perspective stabilizing agent for water based MF for biomedical application. The obtained iron oxides nanoparticles γ -Fe₂O₃ and δ -FeOOH possessed necessary magnetic properties and were suitable for stabilization with HS due to the presence of hydroxyl groups on their surface. As APTS modification of parent humic material leads to increasing sample's hydrophobicity and decreasing ability for complexing surface Fe-OH sites of iron oxides, efficiency of natural HS as stabilizing agents of water based MF is higher in the case of common chemisorption procedure. Directly modified humic samples can be applied for preparation of stable humic coating on mineral surfaces in solid organo-mineral sorbents. Modification of parent humic material using silicon organic compounds should to be provided in other non-toxic and less hydrophobic solvent. At present sample CHA-Pow-05 of natural humic acids from leonardite at concentration 100 mg/L have shown to be the most effective stabilizing agent against iron oxide nanoparticles in water solutions from tested samples.

Acknowledgements

Tatiana Sorkina would like to acknowledge the International Humic Substances Society for financial support of her stay in the research group of Prof. Etelka Tombacz at the University of Szeged (Hungary) within the IHSS Training Award - 2009.

References

1. Illés E., Tombácz E. 2006. The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles. *J Colloid Interface Sci.* 295:115–123.
2. Perminova, I.V., Karpouk, L.A., Shcherbina, N.S., Ponomarenko, S.A., Kalmykov, St.N. Hatfield, K. 2007. Preparation and use of humic coatings covalently bound to silica gel for Np(V) and Pu(V) sequestration. *J. Alloys Comp.*, 444–445, 512–517.
3. Chekanova A.E., Sorkina T.A., Nikiforov V.N., Davidova G.A., Selezneva I.I., Goodilin E.A., Dubov A.L., Trusov L.A., Korolev V.V., Arefev I.M., Perminova I.V., Tretyakov Y.D. 2009. New environmental nontoxic agents for the preparation of core-shell magnetic nanoparticles. *Mendeleev Commun.*, 19, 1–4.
4. Tombacz E., Szekeres M. 2001. Interfacial Acid-Base Reactions of Aluminum Oxide Dispersed in Aqueous Electrolyte Solutions. 1. Potentiometric Study on the Effect of Impurity and Dissolution of Solid Phase, *Langmuir*, 17, 1411–1419.
5. Ritchie J., Perdue M. 2003. Proton-binding study of standard and reference fulvic acids, humic acids, and natural organic matter, *Geochim.Cosmochim. Acta*, Vol. 67, No. 1, pp. 85–96.