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STUDIES ON COLLOID PROPERTIES OF THE HUMIC ACID – CLAY SYSTEMS

INTRODUCTION

Interactions between humic substances, being an amorphous polyfunctional natural polymer, and the clay colloids are of importance in studies of many environments, both natural (soils, oceanic and river waters) and technological (drilling fluids). The physico-chemical properties and reactivity of humic colloids are mostly controlled by the variety of different surface sites, such as: ion exchange sites (mostly acidic COOH and phenolic OH groups), surface functional groups active in hydrogen bonds and in formation of oxygen, nitrogen and sulphur bridges (OH, NH, COOH, SH, C=O, C-O), electron-donor and electron-acceptor sites, and also nonpolar sites responsible for hydrophobic interactions. Almost equally rich variety of active sites we can find on the clay mineral surfaces (i.e. different kinds of ion exchange centres, polarised water molecules, terminal OH groups, coordination unsaturated ions, hydrophobic sites on siloxane layers) multiply a number of possible interactions between those two groups of colloids, as it was described by many authors (Stevenson.1994; Yariv, Cross 1979; Varadachari et al. 1991; Varadachari et al. 1995; Fijał, Bytnar 1996; Tarchitzky, Chen 2002)

The main target of our researches was to recognise the influence of humic acid substances (HA) on the stability of mixed HA - clay colloid systems in water solutions, as well as to analyse the role of some chemical changes in the colloid surfaces, on binding of the HA macromolecules in dried HA-clay samples.

MATERIALS AND METHODS

Investigations have been carried out using a montmorillonite sample extracted from bentonite from “Chmielnik” deposit using sedimentation technique. Humic acid fraction has been obtained by NaOH extraction from a brown coal sample from “Bełchatów” Brown Coal Mine and subsequently purified in order to remove mineral fraction using HCl-HF mixture. Experimental procedure has been adapted basing on Tarchitzky et al. 1993.

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RESULTS AND DISCUSSION

When mixing different amounts of sodium humate with the dispersions containing 1g samples of different clay minerals (montmorillonite, saponite, kaolinite, illite) one can see that with the increase in the concentrations of HA in water solutions, the critical coagulation concentration of electrolyte increase too. The co-

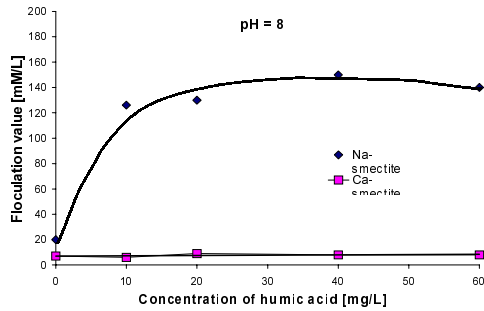


Fig. 1. The flocculation value of Na- and Ca-montmorillonite as a function of HA concentration at pH = 8.

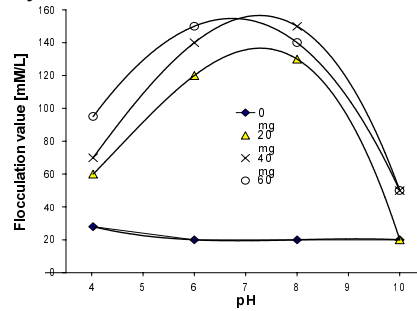


Fig. 2. The flocculation value of Na-montmorillonite as a function of various HA concentrations.

agulation values, measured for HA-montmorillonite system (Fig. 1), shows that at the concentrations of HA above 30 mg/dm³ the stability of the colloid mineral particles increased by about 7 times, compared to initial montmorillonite sample (the result for pH = 8). It proves that some kind of bonding of HA molecules on the external surfaces of clay particles takes place. Judging from the results of the series

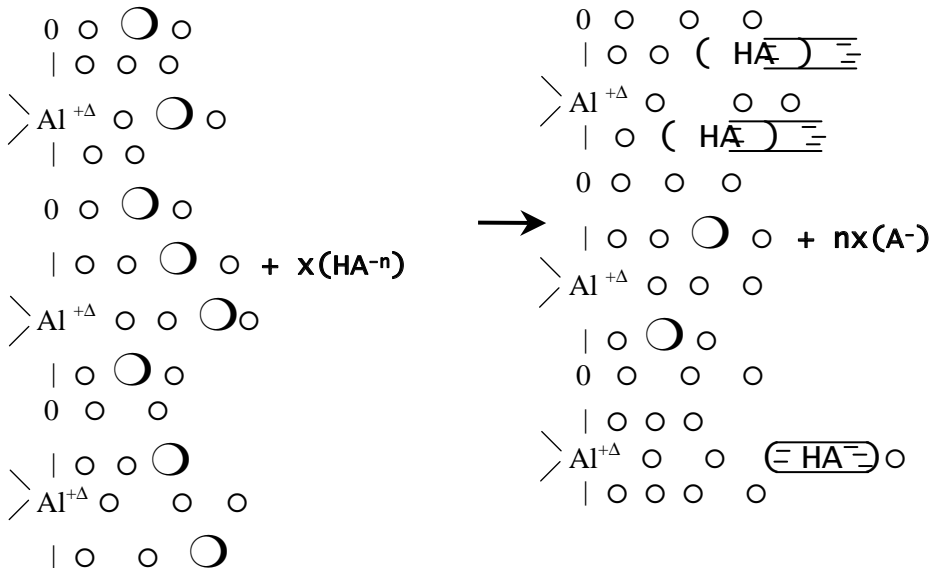


Fig. 3. Schematic representation of non-specific anion exchange adsorption of humic acid molecules (HA⁻ⁿ) within the diffuse double layer, in the region clay minerals crystal edges.

○ – H₂O, ○ – simple anions (Cl⁻, OH⁻, SO₄²⁻), $\overline{\text{HA}^-}$ – humic acid poly-anions

of chemical experiments on the influence of the pH and HA concentrations, on the stability of clay mineral colloids (Fig. 2), one can confirm that the efficiency of bonding reactions depends mostly on both chemical character of the pH-depending clay active sites and the stadium of conformation of humic acid molecules. It has been found that, in the pH range 5-9, the HA macromolecules could enter the diffuse double layer, due to non-specific anion exchange adsorption reactions (Fig. 3).

CONCLUSIONS

The mechanism of mutual interactions between clay mineral surfaces and humic acid colloids is controlled by many factors, such as:

- structure and chemical composition of clay crystallites
- chemistry and a structure of the crystal edges
- the kind of the exchangeable cations
- pH of the reaction environments
- delamination of the clay crystallites

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