



Research paper

Synthesis and structural characterization of betaine- and imidazoline-based organoclays

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ABSTRACT

The samples of organic-modified clays based on a Wyoming SWy-2 sodium montmorillonite (Na^+ -Mt) with the cationic surfactant hydroxyethylalkyl imidazoline (HEAI) and the amphoteric surfactant oleylamidopropyl betaine (OAPB) were synthesized via a cation exchange process. The obtained materials were characterized using XRD analysis, ATR-FTIR spectroscopy, SEM, BET and Water contact angle measurements. The potential sites of binding of OAPB and HEAI to the mineral surface were determined by the DFT calculations. For the variants of the structure of the complex, DFT calculations is performed and the interaction energy of the surfactant and clay mineral is estimated.

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1. Introduction

Organomodified clays (organoclays) obtained by modifying the surface of clay minerals with organic compounds have attracted increasing attention over the latest two decades because of their unique properties and potential for widespread use. Various new functional nanomaterials are created for the production of polymer nanocomposites [1], paints and protective coatings [2], lubricants [3], hydrocarbon-based drilling fluids [4], environmental sorbents [5] and biomedical applications [6]. In all of these applications, the physicochemical properties and behavior of the organoclays are mainly determined by the type of the organic modifier used. The most frequently used clay minerals for organomodification are cationic [7–9], anionic [10,11] and non-ionic [12,13] surface-active substances (SAS) with different length and number of alkyl chains. Along with surfactants, alcohols, aldehydes, silanes, biomolecules and other organic compounds are used for this purpose [14,15]. Depending on the requirements for the properties of the target organoclays, their composition and surface properties can vary over a wide range. The mechanisms underlying the interactions in the “clay mineral-organic modifier” system have been the subject of intensive research in recent years, and to date a great amount of theoretical and experimental material has been accumulated concerning the technologies for the synthesis of organoclays, their surface properties and structure, as well as for the conformations of molecules of the organic modifier [14–17]. It is

known that in the synthesis of polymeric nanocomposites, the modification of clay minerals by such types of cationic surfactants as, for example, trimethylammonium salts [18,19], provides a better compatibility of organoclay for nonpolar polymers. At the same time, for polar polymers more promising for these purposes are, for example, octadecylammonium salts [20]. Nonionic surfactants have proven themselves to improve the adsorption capacity and chemical stability of organoclays [21]. Modification of clay minerals by silanes facilitates the binding of silane to two adjacent mineral layers by a strong covalent bond [15], a decrease in porosity and an increase in the hydrophobicity of the mineral surface [22]. The encapsulation of biomolecules (including proteins, enzymes, amino acids, peptides, etc.) into the interlayer space of clay minerals, in view of their high hydrophilicity and chemical reactivity, promotes the formation of stable colloidal dispersions with high catalytic properties [23,24].

The influence on the structure and properties of the modified clay minerals by amphoteric surfactants has been studied to a much lesser extent. In particular, the modification process of clay minerals by betaine derivatives and imidazolines, also known as nonclassical cationic surfactants, is considered. Despite the fact that there are recently published works [25–28] concerning the study of the sorption properties of some representatives of such compounds, the potential for using betaines and imidazolines as organomodifiers of clay minerals has not been studied sufficiently. Until now, the intercalation mechanisms and microstructural features of such organoclays remain unclear.

The prospects for the use of betaines for organomodification of clay minerals are due to the stability of these compounds in hard

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water and acidic and alkaline media [29], as well as compatibility with other types of surfactants. Betaines are biodegradable and biologically safe materials, which can be of great interest in the use of organoclays synthesized on their basis in ecological applications, for example, sorption of toxic and polluting substances from ground or water media, as well as synthesis of biodegradable polymeric nanocomposites. The high thermal stability of imidazolines makes them attractive in the production of organoclays for polymer nanocomposites obtained by high-temperature treatment. In addition, the presence in the structure of both types of surfactants of various special functional groups (for example, $-\text{NH}_2$, $-\text{COOH}$, SO_3) can potentially be important in selective sorption problems and promote the appearance of specific electrochemical properties in the final organoclay.

In the present work, samples of new organoclays based on natural sodium montmorillonite were synthesized using two characteristic representatives of the above-mentioned class of surfactants, hydroxyethylalkyl imidazoline (HEAI) and oleylamidopropyl betaine (OAPB), which have a relatively low cost. The aim of this work is to study the process of modification of montmorillonite with betaine and imidazoline type surface-active substances in aqueous solution and provide a deeper understanding of the structure, properties and potential applications of this type of organoclays. The intercalation mechanism and the interlayer microstructure as well as the influence of the type of surfactant on the structure and properties of the organoclays obtained are discussed in the paper. X-ray diffraction (XRD), infrared Fourier spectroscopy (ATR-FTIR), and scanning electron microscopy (SEM) were used to study the microenvironment and packaging of the organic modifier in organoclays. To analyze the surface properties of synthesized organoclays, BET (Brewer-Emmet-Teller) data were used to analyze and measure the contact angles of wetting with drops of water. The mechanism of adsorption of the surfactants on the surface of montmorillonite have been studied by density functional theory (DFT) calculations.

2. Materials and methods

2.1. Materials

The organic compounds used for the synthesis of the organoclays were: oleylamidopropyl betaine (pH in 5% water solution = 6.0–8.0; main substance content = 28.0–32.0%; mass fraction of chlorides in terms of NaCl = 3.8–4.4%; free amine content = 0.5%) and hydroxyethylalkyl imidazoline (density = 0.85–0.95 g/cm³; content of active substance – 99.0%; total amine content = 2.6–2.8 mg-eqv/g) was provided by Scientific Manufacturing Enterprise «NIIPAV» (Volgodonsk, Russia). The chemical structures of surfactants are shown in Fig. 1. The clay used in this work was a natural sodium montmorillonite SWy-2 (Na⁺-Mt) obtained from Crook County, Wyoming, USA. Clay was purchased from the Source Clays Repository of The Clay Minerals Society and was used in their natural states without prior treatment. The chemical composition of

Na⁺-Mt is (wt.%): SiO₂ – 61.46; Al₂O₃ – 22.05; Fe₂O₃ – 4.37; TiO₂ – 0.09; MgO – 2.94; CaO – 1.18; Na₂O – 1.47; K₂O – 0.20 [30]. The structural formula of the Na⁺-Mt is reported as (Ca_{0.12}Na_{0.32}K_{0.05}) [Al_{3.01}Fe(III)_{0.41}Mn_{0.01}Mg_{0.54}Ti_{0.02}][Si_{7.98}Al_{0.02}]O₂₀(OH)₄ [30]. The cation exchange capacity (CEC) of the Na⁺-Mt is 85 meq/100 g [31].

2.2. Synthesis of organoclays

The synthesis of organoclays was performed as follows: 10 g of Na⁺-Mt was initially dispersed in 1000 mL of deionized water with a ULAB US-1500S magnetic stirrer at about a rotating speed of 900 rpm at 25 °C for 12 h. Surfactants were added slowly to the slurry of clay at 60 ± 1 °C. Slow introduction of surfactant is related to the prevention of a sharp change in viscosity and maintaining the homogeneity of the montmorillonite suspension. The chosen temperature of the ion exchange reaction is due to a sufficient degree of solubility of the surfactant and a low ability of micelle formation. The concentrations of surfactants were equivalent to CEC = 1.0. Then the mixture was stirred at 1200 rpm for 24 h until the modification was accomplished. After stirring the organoclay aggregates were precipitated by centrifugation at 15,000 rpm for 5 min, washed five times with water for remove excess surfactant and centrifuged again. This was repeated five times for each sample. Then the washed material dried further in an oven (at 60 °C) for 12 h. The dried organoclays were ground in an agate mortar. The products are designated: Na⁺-Mt/OAPB, Na⁺-Mt/HEAI.

2.3. Characterization of organoclays

2.3.1. X-ray diffraction

X-ray diffraction analysis of powdered preparations of synthesized organoclays was carried out using an X-ray diffractometer D/Max-2200 from Rigaku, Japan (Operator: V.V. Krupskaya, Belov Laboratory of Mineral Crystallochemistry, Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Science). Operating mode – 40 kV-30 mA, copper radiation, graphite monochromator, measuring range – 0.8–10° 2θ, step on scanning angle 0.1° 2θ, exposure – 20 s at a point, fixed system of focusing slots, scintillation counter. Samples were prepared from dry powders by punching into cuvettes using pressure to obtain relatively oriented preparations.

2.3.2. Fourier-transform infrared spectroscopy

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the organoclays were obtained using an ALPHA-E spectrometer produced by Bruker Optics (Bruker Optik GmbH, Germany). Spectra over the middle infrared region 4000–500 cm⁻¹ range were obtained by the 50 scans with a resolution of 2 cm⁻¹. The powder samples were placed onto the surface of ZnSe crystal and pressed with a micrometer-controlled compression clamp. Good contact between the samples and ZnSe is needed to obtain high-quality spectra. The area of contact was 19.6 mm². Spectral analysis was performed using the OPUS software package.

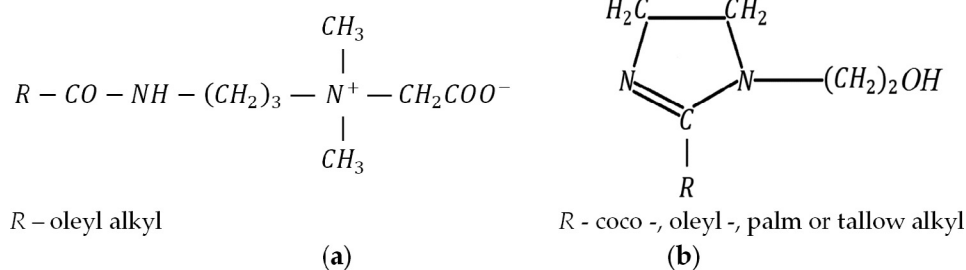


Fig. 1. Chemical structures of surfactants: (a) oleylamidopropyl betaine (OAPB) and (b) hydroxyethylalkyl imidazoline (HEAI).

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