

Communication



Comparative Study of the Hydrophobicity of Organo-Montmorillonite Modified with Cationic, Amphoteric and Nonionic Surfactants

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Abstract: In this work, a series of comparative studies for the effect of the nine commercially available cationic, amphoteric and nonionic surfactants on the structure and wettability of the montmorillonite based organoclays were performed. The pristine and modified clays were characterized by X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and water contact angle (CA) measurements. It has been observed that the maximum basal spacing and the hydrophobicity of the organoclays increased with the alkyl chain length and chain number of the surfactant. It was found out that this effect is most pronounced when using cationic surfactants. The maximum value of contact angle corresponded to the organoclay obtained using di(hydrogenated tallow) ammonium chloride (DDA). The outcomes of this study are important and relevant to the preparation of effective organoclays for geotechnical, petroleum and polymer nanocomposite applications.

Keywords: clay minerals; montmorillonite; surfactant; hydrophobicity; wettability

1. Introduction

A lot of technological processes and applications are based on the regulation of the surface properties of clay minerals by means of modification with surface-active substances (surfactants) [1]. In this case, the role of surfactants is reduced mostly to a decrease in hydrophilicity and surface energy of clay particles; surfactants also cause an increase in the volume of galleries due to an increase in the interlayer distance (for minerals with a laminar structure) [2]. While preparing polymer nanocomposites based on both polar and nonpolar polymers, special attention is given to the selection of the surfactants used for organomodification of clays [3,4]. The specific chemisorption of the surfactants on the surface of clay minerals allows improving the adhesive interaction at the phase boundary of the polymer matrix and inorganic filler particles. This supports a uniform distribution of clay particles in the volume of the polymer matrix, providing improved mechanical, thermal, and barrier properties of finite nanocomposites [5]. Organomodification of surfactant clays plays a very important role in oil production technologies. In particular, surfactants are used in drilling for hydrophobization of clay-bearing rocks which are components of bore hole walls [6]. This lessens the interaction of these areas with water and decreases permeability of the wellbore walls, and also inhibits clay swelling [7,8]. Technologies for soil stabilization for geotechnical purposes are based on hydrophobization of the surface of hydrophilic clay minerals with surfactants [9]. The correct choice of surfactants and processing of clays with their help ensures a change in the consistency and plasticity limits of soils, an increase in its density, and a reduction in its heaving, swelling and soaking [10,11].

Currently, immense experimental material on the interaction of clay minerals with surfactants has been accumulated [1,2,12,13]. In particular, the researchers have widely studied the effect of

various surfactants on the pore structure and adsorption characteristics of clay minerals [14,15], and their morphology [16]. They have also analyzed the structure and thermal stability of organically modified clays (organoclay) depending on the type of surfactant and the capacity of cation exchange of minerals [17–19]. At the same time, the base regularities of the influence of surfactants on the wettability of clay minerals by water have been established only for individual substances [20–22]. Yet, systematic comparative studies of the hydrophobic action of surfactants of various kinds have not been carried out. That is why the purpose of this work is to study the regularities of the modifying action (in terms of hydrophobicity) of various commercially available cationic, amphoteric, and nonionic surfactants toward clay minerals of the smectite group and to characterize their structure.

2. Experimental Section

2.1. Materials

In this study, homoionic sodium forms of montmorillonite SWy-2 from Wyoming (Na⁺-Mt) were used as clay materials. Na⁺-Mt was purchased from the Source Clays Repository of the Clay Minerals Society (Purdue University, USA) and was used without pretreatment. 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 [23]. The crystallochemical formula of this sample is (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 [23]. The cation exchange capacity (CEC) of the Na⁺-Mt is 85 meq/100 g [24]. Nine types of surfactants (including of cationic, amphoteric and nonionic ones) were purchased from Scientific Manufacturing Enterprise "ENPAV" (Volgodonsk, Russia). The chemical structures of these surfactants are shown in Figure 1. A brief description of surfactants used in this study are provided in Table 1.



Figure 1. Chemical structures of the used surfactants.

Abbreviation	Full Name	Impurities	Molecular Weight (g/mol)	CAS Number	
DA	Didecyl dimethyl ammonium chloride 30% ethanol 362.1		362.1	7173-51-5	
DDA	Di(hydrogenated tallow) dimethylammonium chloride	25% isopropanol	558.4	61789-80-8	
CTA	Cetrimonium chloride	50% ethanol	320.0	112-02-7	
ATA	Alkyl trimethyl ammonium chloride	50% ethanol	N.R.	61788-78-1	
ADBA	Alkyl dimethyl benzyl ammonium chloride	50% ethanol	311.9	63449-41-2	
LMB	Lauryl myristyl betaine	70% water	271.4	66455-29-6	
CPB	Cocamidopropyl betaine	63% water	342.5	61789-40-0	
OPB	Oleylamidopropyl betaine	70% water	424.7	6436555	
ADA	Alkyl dimethylamine oxide	70% water	271.5	68955-55-5	

Table 1. The properties of used surfactants.

N.R. = none reported.

2.2. Preparation of Samples

The samples of surfactant-modified clays were prepared as described by Lazorenko et al. [20]. First, the non-pretreatment Na⁺-Mt (10 g) was dispersed in 1000 mL of deionized water under continuous stirring at 25 °C for 12 h. Then, modifying agent (1.0 CEC of montmorillonite) was gradually added and the mixture was stirred at 1200 rpm for 24 h at 60 °C until the modification was accomplished. After that, the mixture was centrifuged at 15,000 rpm for 5 min and washed by deionized water five times to remove excess surfactant. The sediment of organically modified clay was dried at 60 °C for 12 h and ground in an agate mortar. The dried organoclays were stored in a desiccator before analysis. The different samples (clay and organoclays) prepared in this work were ten in total.

2.3. Characterization

The X-ray diffraction (XRD) patterns of pristine and surfactant-modified clays were obtained with X-ray diffractometer D/Max-2200 (Rigaku, Tokyo, Japan) using CuK α radiation (n = 1.5418 Å). Operating mode: current 30 mA, voltage 40 kV, scan range 0.8°-10° 2theta, scanning step 0.01° 2theta, divergence slit 0.25°, anti-scatter slit 0.25°, exposure 20 s at a point, scintillation counter, graphite monochromator. Samples were prepared from dry powders by punching into cuvettes using pressure to obtain relatively oriented preparations. XRD data of the samples were used to analyze the change of basal spacings (d_{001}) before and after modification. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the samples were recorded with an ALPHA-E spectrometer with a zinc selenide (ZnSe) crystal cell (Bruker Optik GmbH, Ettlingen, Germany) used in [25]. All spectra were obtained by averaging 50 scans at 2 cm⁻¹ resolution over the mid-infrared spectral range of $500-4000 \text{ cm}^{-1}$. Contact angle (CA, θ) measurements were conducted by using a sessile drop method in order to determine the wettability of the samples. For static CA measurements, a droplet of deionized water was placed on the top surface of pelletized powder sample pressed at a pressure of 300 kg/cm² in a cylindrical form of stainless steel (5 mm in thickness, \emptyset 20 mm) and θ was measured in 2–3 min after the drop of water was deposited. The droplet parameters were measured using a stereoscopic microscope MBS-10 (Lytkarino Optical Glass Factory, Moscow, Russia). A series of 3 measurements was taken for each test sample.

3. Results and Discussion

XRD patterns and FTIR spectra of unmodified Na⁺-Mt and organoclay prepared on its basis are presented in Figure 2. Figure 3 shows the measured average values of θ for all samples those are compared with the maximum basal spacing, as well as the lengths and amount of hydrocarbon radicals (R) in the molecules of the used surfactants. In the air-dry state, unmodified clay gives a reflection corresponding to an interlayer distance of 1.19 nm (Figure 2a) which is typical for the sodium form of Wyoming montmorillonite [26]. The asymmetric broadening of the d001 reflection indicates poor crystallinity of the mineral, swelling heterogeneity and different hydration states [27]. After modifying of montmorillonite with the surfactant, a shift of the maximum to a small-angle region is observed for all organoclay, which indicates the displacement of Na⁺ ions from exchange positions and the introduction of an organic modifier in the mineral galleries. The absence of a peak of montmorillonite at 2theta = 7.4° (1.19 nm) in the diffraction patterns of organoclay indicates the overall completion of the intercalation process. The basal (d_{001}) spacing organoclay Na⁺-Mt/CTA, Na⁺-Mt/ATA and Na⁺-Mt/ABDA intercalated with cationic surfactants with one alkyl chain (C₁₆, C_{16} - C_{18} , C_{16} - C_{18}), as well as Na⁺-Mt/DA and Na⁺-Mt/DDA ($C_{10} \times 2R$ and $C_{18-16} \times 2R$) intercalated by cationic surfactants with two alkyl chains were 1.88, 1.92, 2.05, 2.05, and 2.67 nm, respectively (Figure 2a, Figure 3). Obviously, the position of the 001 reflection goes up with increasing length and number of alkyl chains. The relationship of the number of carbons in the alkyl chain with the basal distance d_{001} was found earlier in He et al. [17], Shah et al. [22], and Açışlı et al. [28]. A similar pattern of increasing d₀₀₁ when prolonging the alkyl chain length is also observed in the case of organoclay Na⁺-Mt/LMB (C₁₂-C₁₄), Na⁺-Mt/CPB (C₈-C₁₈) and Na⁺-Mt/OPB (C₁₂-C₁₈) intercalated with amphoteric surfactants. The d-values in this case were 2.10, 4.61 and 4.65 nm, respectively (Figures 2a and 3). It can be seen that the maximum values of d₀₀₁ are obtained when short-chain hydrocarbon radicals are present in the surfactant structure along with long-chain fragments of C_{18} . Large intercalation of both CPB and OPB can be explained by the mutual repulsion of negatively charged carboxyl groups of these betaines, which, together with the relatively large size of the molecules of these surfactants, leads to a large distance between the montmorillonite layers. Similar results were also observed in the work of McLauchlin and Thomas (2008), who studied the structure of organoclays based on an amphoteric surfactant depending on the surfactant concentration and pH of the medium [26].

Based on previous studies [1], it is possible to correlate the observed d-value of organoclay and orientations of surfactant molecules in the interlayer space of montmorillonite. Basal spacing of 1.84–2.10 nm indicates lateral bilayer or pseudotrimolecular layer arrangement; that is, an alkyl chain lying parallel to the mineral layer. At the same time, the maximum basal spacing of 4.61 and 4.65 nm in the case of intercalation of betaines indicate a paraffin-type bilayer arrangement. In the case of Na⁺-Mt/CAP and Na⁺-Mt/OAP, except the intense first reflection, the second maximum appears at the diffraction pattern at $2\theta = 3.9^{\circ}$, which may be due to the presence of a lateral bilayer or pseudotrimolecular layer arrangement (Figure 2a). Basing on the results of studies by McLauchlin and Thomas (2008) [26], it can be assumed that the formation of two types of layer arrangement in organoclays prepared using betaines is connected with the nature of the hydrophilic end-groups of these surfactants. The negatively charged carboxyl groups of betaines repulse each other, resulting in a wider spacing between the montmorillonite layers. In turn, protonated carboxyl groups are more prone to associate through a hydrogen bond, leading to less significant separation of the layers.

Given the presence of two alkyl chains in the structure of the DDA molecule, the basal distance of 2.67 nm Na⁺-Mt/DDA probably corresponds to a lateral bilayer conformation turning into an inclined paraffin-type bilayer structure. Here the alkyl chains are oriented at an acute angle (less than 35°) relative to the plane of the montmorillonite layer [29]. It should be noted that a d₀₀₁ value of 1.84 nm for Na⁺-Mt/ADA (C₁₂-C₁₈) with a nonionic surfactant is significantly lower than the d-value for amphoteric surfactant-modified clays Na⁺-Mt/CPB (C₈-C₁₈) and Na⁺-Mt/OPB having hydrocarbon radicals of the same length. This is due to differences in the nature of the binding of the head-group surfactants to the Na⁺-Mt surface, conformational ordering and interlayer packing density of intercalated surfactants within the clay interlayers.



Figure 2. (a) XRD patterns and (b) attenuated total reflection-Fourier transform infrared (ATR/FTIR) spectra of sodium montmorillonite (Na⁺-Mt) and its organomodified forms with different surfactants.



Figure 3. The relationship between organoclay types, their wettability, d-spacing and alkyl chain length (number) of surfactant. Note: R—alkyl chain.

An analysis of these features is possible by the position $-CH_2$ stretching (3000–2800 cm⁻¹), bending (1480–1450 cm⁻¹), and rocking (740–710 cm⁻¹) modes (Table 2) appearing on the FTIR spectra of modified clays (Figure 2b). On the whole, the IR spectrum of the obtained sodium form of Wyoming

montmorillonite corresponds to the structure described in previous research [30]. The intercalated chains of ADA, as well as short-chain DA, form a more disordered liquid-like structure due to an increase in gauche/trans conformer ratio. This is indicated by the shift of antisymmetric CH_2 stretching mode to the high-frequency region of the spectrum up to 2927 cm⁻¹ (Figure 2b, Table 2) [31,32].

	Wavenumber (cm ⁻¹)								
Assignment	Na ⁺ -Mt/ DA	Na ⁺ -Mt/ DDA	Na ⁺ -Mt/ CTA	Na ⁺ -Mt/ ATA	Na ⁺ -Mt/ ABDA	Na ⁺ -Mt/ ADA	Na ⁺ -Mt/ LMB	Na ⁺ -Mt/ CPB	Na ⁺ -Mt/ OPB
Antisymmetric CH ₂ stretching	2927	2922	2925	2925	2923	2927	2924	2923	2923
Symmetric CH ₂ stretching	2851	2850	2847	2848	2850	2851	2850	2853	2853
COO ⁻ stretching	-	-	-	-	-	-	1634	1364	1634
CH ₂ bending	1467	1467	1471	1471	1468	1471	1470	1468	1463
CH ₂ rocking	728	720	727	727	730	726	723	721	721

Table 2. Assignment of the main absorption bands in FTIR spectra of organoclays.

"-" = No absorption bands.

With increasing chain length, the $v_{as}CH_2$ band shifts toward lower wave numbers, which indicates a decrease in the number of disordered (gauche) conformation and the formation of ordered (all-trans) conformation. Reducing the number of gauche conformations with a curved spatial configuration of the chain contributes to the growth of interlayer packing density [1]. From the data given in Table 2, it can be seen that the highest ordering of the structure and packing density of intercalated surfactants corresponds to Na⁺-Mt/DDA. The position of the $v_{as}CH_2$ band most sensitive to conformational changes in the IR spectra of Na⁺-Mt/DDA is shifted to 2922 cm⁻¹. A similar tendency to shift to lower wave numbers in the spectrum of Na⁺-Mt/DDA is also observed for CH₂ rocking deformation and symmetric CH₂ stretching oscillations. This observation correlates with the measured values of the contact angles, where Na⁺-Mt/DDA showed the highest hydrophobicity (θ ~100°) (Figure 3).

The hydrophobic activity of DDA is also visible by the decrease in the intensity of the interlayer water bands 3401 (vOH) and 1635 cm⁻¹ (δ OH) (Figure 2b) which is associated with the penetration of the modifier molecules into the Na⁺-Mt galleries. This feature is also observed on the spectra of other organoclays. In case of Na⁺-Mt/LMP, Na⁺-Mt/CAP and Na⁺-Mt/OAP, the OH bending band of water molecules is close to the COO-stretching band of head-group amphoteric surfactants (1634 cm⁻¹).

When the Na⁺ -Mt surface is wetted by deionized water, an increase in the contact angles is observed with an extension in the length of the alkyl chain and d-value. Moreover, surfactants with two alkyl chains provide hydrophobization of the surface more effectively than surfactants with one chain. It is seen that cationic surfactants having the best ability for chemisorption on the electronegative surface of clay have the greatest hydrophobizing effect. Amphoteric and nonionic surfactants do not show specificity in relation to Na⁺-Mt in the hydrophobic action. Both types of surfactants cause comparable hydrophobization of the surface of montmorillonite.

4. Conclusions

The hydrophobizing effect of cationic, amphoteric, and nonionic surfactants on organoclay based on sodium montmorillonite was studied. It was demonstrated that in all cases an increase in the water contact angle was observed, and the degree of hydrophobization depended both on the nature of the surfactant and on the length and number of alkyl chains in their structure. It was found out that this effect is most pronounced when using cationic surfactants. The maximum value of θ (~100°) corresponded to the organoclay obtained using di (hydrogenated tallow) ammonium chloride, which can probably be achieved by a high packing density and ordering of DDA molecules in the interparticle or interlayer space of the clay. The outcomes of this study are important and relevant to the preparation of effective organo-modified clays for geotechnical, petroleum and polymer nanocomposite applications.

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