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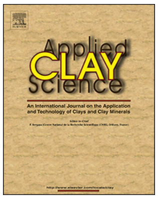

Research paper

Gemini surfactant modified clays: Effect of surfactant loading and spacer length

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ABSTRACT

Aromatic-containing gemini ammonium bromide surfactants with different spacer length and variable amounts were used to modify Na^+-montmorillonite via ion exchange reaction. The resulting organoclays (OMt) were characterized in terms of composition and morphology using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The thermal stability of OMt was determined by thermogravimetric analysis (TGA). The results indicated that gemini surfactants exhibit a good efficiency to modify clay mineral. Surfactant concentration and the length of the spacer connecting the ammonium heads were found to be key parameters governing the thermal stability and the structure of the corresponding OMt. Increasing surfactant concentration and lengthening of the spacer act favorably for the achievement of higher expended interlayer clay structures with better thermal stability. Different configurations of surfactant molecules within Mt interlayers were proposed based on *d*(001) basal spacing.

1. Introduction

Montmorillonite (Mt) have attracted much attention due to their outstanding properties such as high cation exchange capacity (CEC) and swelling ability, large specific surface areas that induce strong adsorption capacities, plastic behavior when wet, catalytic abilities, and low permeabilities (Bailey et al., 1999; Xi et al., 2005; Nie et al., 2012). These characteristics enabled preparation of several hybrid materials for a wide range of advanced application areas such as pharmacy, biotechnology, cosmetics, textile industry, catalysis, flame retardants, food packaging and environment for waste remediation (Beall, 2003; Tang et al., 2003; Avella et al., 2005; Gao and Xu, 2006; Choy et al., 2007; Carretero and Pozo, 2009; Rhim et al., 2015).

In particular, the use of nanoclays as fillers or additives of polymers to prepare clay polymer nanocomposites (CPN), have been extensively studied (Uddin, 2008). A preliminary step of chemical modification of clays is often essential to ensure compatibility between natural clay minerals and polymers. The surface modification is usually accomplished through replacing the alkali cations present in the interlayer space with host molecules particularly cationic molecules as alkylammonium and alkylphosphonium surfactants by cation exchange reactions (Zhou et al., 2009; Xue et al., 2013; Liu et al., 2014; Yang et al., 2016). In this context, gemini surfactants have been much less studies probably due to the difficulties in their preparation and purification. In comparison with conventional surfactants, gemini surfactants are known to be much more efficient in reducing the surface tension of water and the interfacial tension of the oil-water interface (Sikiri et al., 2005; In and Zana, 2007). Besides, they exhibit extremely lower CMC values, better water solubility, unusual micelle structures and aggregation behavior, and interesting rheological properties (Kamal, 2016; Patel et al., 2017).

Although there are some works focusing on the use of gemini surfactant modified clays as adsorbents for organic and inorganic pollutant remediation (Zhu et al., 1997; Boyd et al., 1988; Zhou et al., 2008; Park et al., 2013), little information are available on the effect of structural parameters, i.e. nature and length of the spacer group and the hydrophobic chain, on the arrangement of surfactant molecules into the interlayer space. A better understanding of the adsorption mechanism of gemini surfactants on silicate layered materials and the morphology of the resulting intercalated clay is still highly desired especially for the development of highly efficient catalytic materials and clay polymer nanocomposites.

Li and Rosen (2000) studied the adsorption of a series of gemini surfactants, $[C_nH_{2n+1}N^+(CH_3)_2\text{-}CH_2CH_2]_2$, $2Br^-$ where $n = 10, 12, 14$, and 16, on sodium montmorillonite and demonstrated that only one ammonium group is adsorbed onto the clay surface while the second

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one is oriented toward the aqueous phase. This conformation renders the clay surface more hydrophilic in comparison with that of organoclay obtained from monomeric cationic surfactants. Qi et al. (2007) showed that [ethanediyl α,β-bis(cetyldimethylammonium bromide)] gemini surfactant is more efficient than corresponding conventional surfactant at achieving the maximum adsorption on swelling Mt and non-swelling kaolinite layer silicates. Although cationic exchange governed the adsorption process, the higher hydrophobic nature of gemini surfactant may enhance its adsorption on the surface of clay. Similar results were obtained for organoclays prepared by modification of Mt with three gemini cationic surfactants under microwave irradiation (Liu et al., 2011). It was reported that the increase of the amount of the surfactants and the hydrophobic chain length affect positively the arrangement of the intercalary surfactant. This feature has been exploited for the efficient adsorption of methyl orange dye.

In this work, new organomontmorillonites were prepared with three quaternary ammonium gemini surfactants of the general formula C_8H_{17}-Ph-$NHCOCH_2N^+(CH_3)_2$-$(CH_2)_s$-$N^+(CH_3)_2CH_2CONH$-Ph-C_8H_{17} (with s = 2, 4, 6). Their structure and morphology were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). Special attention was focused on the effect of surfactant concentration and spacer length on the arrangement of surfactant molecules inside Mt interlayer spaces.

2. Experimental

2.1. Materials

The sodium montmorillonite (Mt), Cloisite® Na$^+$ (lot 11F14GBX006) with a cation exchange capacity (CEC) of 92.6 meq/100 g, used in this study was kindly provided from Southern Clay Products, Inc. (USA). It was used without further purification. Gemini surfactants bearing octyloxy hydrophobic terminal chains and ethyl, butyl or hexyl spacer as represented in Fig. 1, named Gem 8-2-8, Gem 8-4-8 and Gem 8-6-8, respectively were prepared as reported previously (Taleb et al., 2017). Deionized water was used in all experiments.

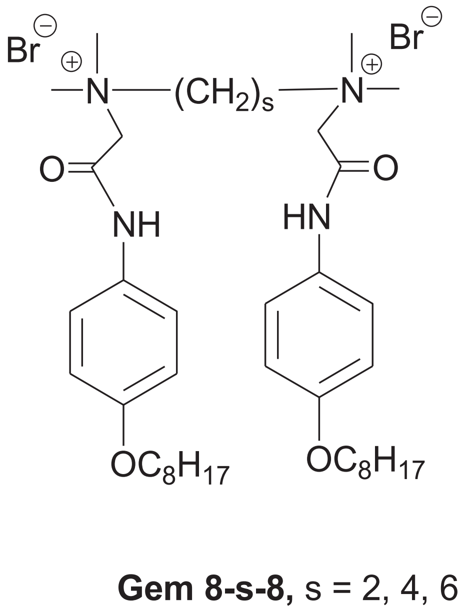

Fig. 1. Chemical structures of the studied gemini surfactants.

2.2. Preparation of organo-montmorillonites (OMt)

Series of OMt were prepared by ion exchange method according to the following procedure: 1 g of Mt was initially dispersed in 50 mL of deionized water at 60 °C for 24 h at stirring rate of 600 rpm. A solution of 0.2, 0.5, 1.0 or 1.5 equivalent of surfactant with regards to the cation exchange capacity (CEC) dissolved in 50 mL of water was slowly added under vigorous stirring. The mixture was stirred at 600 rpm for 5 h at 60 °C, then 12 h at room temperature. The resulting dispersion was filtered and washed several times with deionized water until no bromide ions were detected in the filtrate by $AgNO_3$ solution. The obtained products were dried in a vacuum oven at 70 °C for 12 h. The dried OMt were ground in an agate mortar and pulverized to pass through 50 μm sieve and, finally stored in a vacuum desiccator until use.

The obtained OMt were expressed as OMt(8-s-8)xCEC, where s is the carbon number of the spacer chain (s = 2, 4, 6) and x represented the equivalent number of gemini surfactant used in the modification with regards to the cation exchange capacity (CEC).

2.3. Characterizations

2.3.1. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra were obtained on BRUKER FTIR Vertex 70 v spectrophotometer using KBr pressed disk technique. 1 mg of clay mineral powder was mixed with 200 mg of KBr, a disk was obtained and used as specimen. The wavenumbers are measured from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.2. X-ray diffraction

The d-values of the clay and the OMt powders were measured by using X-ray diffractometer (XRD) MAR345. The XRD was operated at a working voltage and a current of 45 kV and 100 mA, respectively with Cu K_α radiation in a step scan mode. The angular range was scanned from 1.5 to 40° (2θ) at a step size of 0.02°/s. The d-value of the OMt were calculated according to Bragg's equation ($n\lambda = 2d_{001} \sin\theta$) where: n is an integer (n = 1), λ is the wavelength of incident wave (λ = 1.5418 Å), d_{001} is the basal spacing, θ is the angle between the incident ray and the scattering planes.

2.3.3. Thermal analysis

The adsorption amount of gemini surfactants on Mt and the thermal stability of corresponding OMt were studied by thermogravimetric analyses (TGA) using ATG/DSC1 METTLER TOLEDO instrument. The experiments were performed from 20 °C to 800 °C with a heating rate of 10 °C·min^{-1}, under high-purity nitrogen atmosphere with a gas flow rate of 80 mL·min^{-1}.

2.3.4. Elemental analysis

The N elemental microanalyses were performed on the CHNOS Elemental Analyzer of ISA-CNRS, Villeurbanne, France. The amount of loaded surfactant (X), expressed as mmol/g, was derived from the relationship $X = W_N/(M_N \times N)$, where W_N is the mass percentage of nitrogen obtained by CHN analysis, M_N is the molar mass of nitrogen (14.0 g/mol), and N is the number of nitrogen atoms in the surfactant molecule (N = 4). The absolute errors are 0.20%.

2.3.5. Morphological analysis

The morphology of the OMt was examined by scanning electron microscope JEOL JSM 6460-LV and transmission electron microscope MET Hitachi H9000-NAR at 300 kV (filament LaB6) with a resolution of 0.18 nm. The samples were dispersed in ethanol, then dropped on Cu 300 mesh grids and dried in an oven at 50 °C for 10 min.