



Research paper

Intercalation of vermiculite in presence of surfactants

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ABSTRACT

Vermiculite was modified with surfactants in order to enable intercalation of vermiculite layers. Since vermiculite has negative charges on its surfaces, it was expected that cationic surfactant would expand the clay mineral layers more than an anionic surfactant. Nevertheless, negative parts of the anionic surfactants interacted with the positively charged edges of vermiculite and caused to super lattice structure so, unexpectedly the expansion of the layers was determined to be fully collapsed phase of vermiculite. Colloidal and structural properties of vermiculite dispersions were examined in presence of anionic, cationic and nonionic surfactants. The results showed that cationic surfactant covered the surface of the vermiculite with a second layer but the expansion of the clay mineral layer was limited compared to the anionic surfactant. The anionic surfactant produced electrostatic interaction with the positively charged edges of vermiculite and fully expanded the layer structure of the vermiculite.

1. Introduction

Layered structure clay minerals have been extensively used as naturally nano-sized particles, low-cost filler to enhance the mechanical and physical properties of polymer composites (Pinnavaia & Beall, 2000; Ray and Okamoto, 2003; Utracki, 2004; Bergaya et al., 2006; Liu et al., 2006; Gul et al., 2016).

Montmorillonite is mostly used as layered clay in many articles, and also in industrial uses. However, compared with montmorillonite, the clay mineral layers in vermiculite have a higher charge density, a key parameter facilitating the incorporation of organic modifiers to generate larger interlayer spacing (Slade and Gates, 2004; Bergaya et al., 2006). Vermiculite forms macroscopic crystals, that are potentially suitable for producing high aspect ratio nanofillers, and its natural abundance makes it economically attractive for industrial applications (Qian et al., 2011).

Vermiculites, 2:1 phyllosilicates, are generally composed of macroscopic particles, similar in appearance to micas. (Meisinger, 1985; Suquet, 1988; Suquet et al., 1991; Martins and Fernandes, 1992; Lv et al., 2017). The clay mineral surfaces have negative charges due to the isomorphic substitutions which create a deficit of positive charge, compensated by interlayer cations that can be easily exchanged and solvated by positively charged particles. Additionally, clay minerals are hydrophilic but the clay minerals are modified by alkylammonium ions to change the surfaces as hydrophobic surfaces so, the adsorption of polymer molecules is enhanced by the clay minerals. Composites (LeBaron et al., 1999; Pinnavaia and Beall, 2000; Ray and Okamoto,

2003; Utracki, 2004; Bergaya et al., 2006; Liu et al., 2006; Gul et al., 2016). Hence, with the purpose of increase the interaction of clay and polymer, clay particles are mostly modified with cationic surfactants to change the hydrophilic surface to the hydrophobic ones, also to expand the clay mineral interlayers. The expansion of the interlayer of vermiculite particles was studied detail in various articles with partially collapsed structure and fully collapsed phase of vermiculite alkyl ammonium complexes by Johns et al. Johns and A. S. G. P. K (1967); Serratos et al., 1970; Lee and Solin, 1991; Williams et al., 1996; Syrmanova et al., 2017).

The effects of the anionic surfactants on the properties of montmorillonite have been extensively studied in literature but not in particular for vermiculite (Lagaly et al., 1984; Kopka et al., 1988; Lagaly and F., 2001; Penner and Lagaly, 2001; Yalcin et al., 2002a,b; Yalcin et al., 2002a,b; Lagaly and Ziesmer, 2003; Gunister et al., 2004). There are three types of possible of interactions between negative charge-carrying clay particles and anionic surfactant. First, it is possible that ion exchange can take place between OH^- ions on clay mineral surfaces and the anionic part of surfactants. Second, H-bonds can form between clay particles and surfactant molecules. Third, it is possible that Ca^{2+} cation can establish electrostatic bridges between the anionic part of surfactants and the surface of clay particles (Parfitt and D.J., 1970; Parfitt, 1978; Lagaly, 1986, 1989; Kopka et al., 1988; Lagaly and F., 2001; Penner and Lagaly, 2001; Yalcin et al., 2002a, b).

In this study, the effects of the cationic surfactants hexadecyltrimethylammonium bromide (HDTABr), and octadecyltrimethylammonium bromide (ODTABr), the anionic surfactants sodium dodecyl

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sulfate (SDS), and ammonium lauryl sulfate (ALS), and the nonionic surfactant *N,N*-Dimethyldodecylamine N-oxide (DDAO) were investigated on the colloidal and structural properties of vermiculite. The results unexpectedly showed that anionic surfactant is much more suitable to expand the interlayer of vermiculite than cationic or nonionic surfactants. Anionic or cationic also the nonionic surfactants caused to super lattice structure by entering the interlayer of vermiculite with ion exchange and expanded the interlayer. Rheological measurements were used to examine particle–particle interactions, electrokinetical measurements were used to determine the effects of the surfactants on the surface properties of vermiculite particles. XRD, SEM results showed that the intercalation of vermiculite layers in presence of surfactants, and finally FTIR results showed the ion exchange between vermiculite and the surfactants.

2. Experimental study

2.1. Materials

Vermiculite sample were obtained from Gold Butte District, Clark County, Nevada, USA. Ore samples were identified as vermiculite clay minerals using X-ray diffractometer (Bruker D8 Advance model X-ray diffractometer), indicating trioctahedral structure of vermiculite. The vermiculite was subjected to a heat treatment at temperatures over 700 °C the mineral expands, multiplying its volume between 15 and 20 times, and the expanded form of the vermiculite was used in this study.

Hexadecyltrimethylammonium bromide, HDTABr, ($C_{16}H_{33}N(CH_3)_3Br$, $M_w = 364.46$ g/mol from Fluka), and Octadecyltrimethylammonium bromide, ODTABr, ($C_{18}H_{35}N^+(CH_3)_3Br$, $M_w = 392.52$ g/mol from Fluka) were used as cationic surfactants. Sodium dodecyl sulfate, SDS, ($C_{12}H_{25}NaO_4S$, $M_w = 288.38$ g/mol from Aldrich Chemical Co) and Ammonium lauryl sulfate, ALS, ($CH_3(CH_2)_{11}OSO_3NH_4$, $M_w = 283.40$ g/mol from Fluka) were used as anionic surfactants. *N,N*-Dimethyldodecylamine N-oxide ($C_{14}H_{31}NO$, $M_w = 229.43$ g/mol from Sigma) was used as nonionic surfactant.

2.2. Preparation of clay - surfactant dispersions

Vermiculite was dispersed in distilled water in an ultrasonic bath and then shaken overnight. The vermiculite dispersions were mixed with 5.10^{-5} to 5.10^{-2} mol/L concentrations of each surfactant. Then, the dispersions were shaken for 24 h, and ultrasonicated for 5 min.

3. Methods

Rheological properties such as viscosity, shear rate ($\dot{\gamma}$), and shear stress (τ) of the dispersions were measured using a Brookfield DVIII + type low-shear viscometer. The flow behavior of the clay dispersions was obtained by shear rate measurements within $0-330$ s $^{-1}$ shear rates. Rheological measurements were carried out in duplicate.

The electrophoretic mobility measurements were carried out using a Zetasizer 2000, Malvern Instruments. The optic unit contains a 5 mW He–Ne (638 nm) laser. The dispersions were prepared as explained above. Before the measurements, all the dispersions were centrifuged at 4500 rpm for 30 min. Supernatants were then used for zeta potential measurements. To make an electrophoretic mobility measurement in this instrument, laser beams are crossed at a particular point in the cell. Particles in the cell were illuminated by these beams. Electrophoretic mobility was measured, injecting a small portion of the dispersion into the cell of the Zetasizer 2000 instrument at 25 °C temperature. The electrophoretic mobility was then converted to zeta potential using Henry eq.

X-ray diffraction (XRD) measurements were performed Bruker D8 Advance model X-ray diffractometer at room temperature using Ni-filtered and Cu tube. The diffractograms were scanned in 2θ ranges from 2 to 40° at a rate of 2°/min.

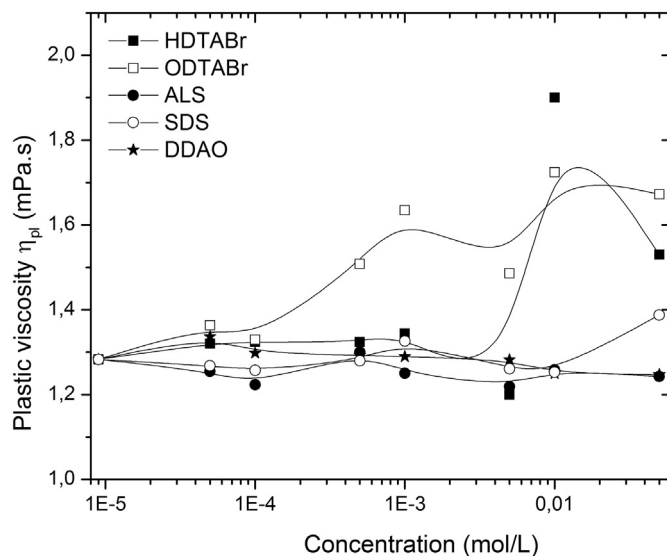


Fig. 1. The changes of the plastic viscosity of vermiculite-water systems in presence of surfactants.

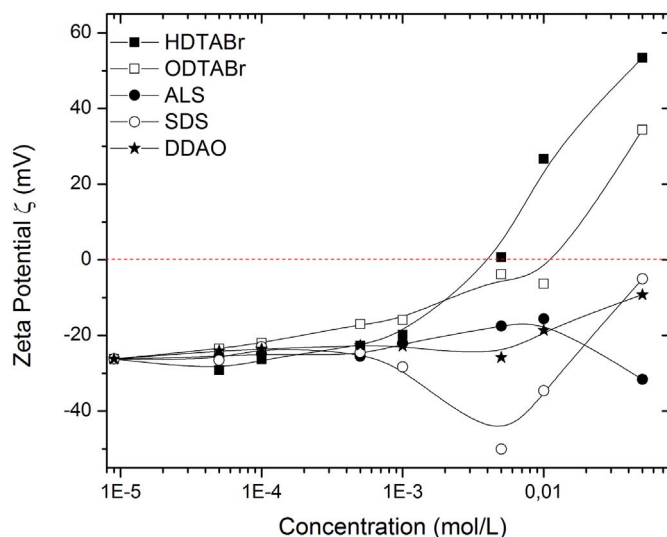


Fig. 2. The changes of the zeta potential values of vermiculite-water systems in presence of surfactants.

The morphology of the fractured surfaces of the clay films was investigated with a FEI Quanta Feg 250 scanning electron microscope. SEM measurements were operated at 15 kV. The specimens were frozen under liquid nitrogen, and then fractured, mounted, and coated with gold on Edwards S 150B sputter coater.

FTIR analyses ($400-4000$ cm $^{-1}$) were performed on Perkin Elmer Spectrum 100 FTIR spectrophotometer using KBr pellets with a concentration of 1% or film. Spectral outputs were recorded either in absorbance or transmittance mode as a function of wave number.

4. Results & discussion

4.1. The effect of the surfactants on the flow and the electrokinetical properties of vermiculite dispersions

Vermiculite dispersions in water showed Bingham plastic behavior according to their concertina-like swelling properties. At low shear rates, the system exhibits non-Newtonian flow, and after a certain value of the shear rate, the flow curve becomes linear. Vermiculite has a lower swelling potential than other swelling clay minerals and in some

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