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Delamination of surfactant intercalated smectites in alcohols: Effect of chain length of the solvent

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Abstract

Cetyl trimethylammonium and stearyl trimethylammonium ion-intercalated montmorillonite delaminates in alcohols. While delamination is observed in all alcohols, the amount of delaminated particles and the stability of the resultant colloidal dispersion increases with the chain length of the alcohol. The organoclay could be easily reassembled from the colloidal dispersions either by evaporation or by the addition of a polar solvent.

Keywords: Smectites; Organoclays; Intercalation; Delamination

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1. Introduction

Polymer-clay nanocomposites consisting of different polymers have been intensively studied (Okamoto, 2004; Pinnavaia and Beall, 2000; Carrado, 2000). Nanocomposites of clays with other functional materials like clay-fullerenes (Mehrota et al., 1992), clay-carbon nanotubes (Gouruis et al., 2002) and clay-silica nanocomposites (Letaief and Ruiz-Hitzky, 2003) have been reported. In most of these nanocomposites the degree of dispersion of both clay mineral and guest species at nanoscale level determines the functionality of hybrid material. In general, interlayer space of the clay mineral is modified with large organic cations to make it organophilic and this hybrid is used for the preparation of the composites.

Three main approaches have been used in the preparation of clay-polymer composites: (i) melt blending, (ii) solution blending and (iii) in situ polymerization (Brown et al., 2000; Triantafillidis et al., 2002; Krishnamoorti et al., 1996). However, homogeneity at nanoscale level may not be fully achieved in these methods. One way of approaching this problem is completely delaminating the clay mineral particles to give colloidal dispersions of single layers in a suitable solvent and restacking the layers in presence of guest species. Delamination of clay minerals in aqueous medium is well known (Trifiro and Vaccari, 1996). To approach the method in a more general way and to account for variety of guest species and better flexibility, it is important to delaminate clays in organic solvents too.

Delamination of layered double hydroxides (LDHs) in organic media is known (Adachi-Pagano et al., 2000;

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Leroux et al., 2001; Hibino and Jones, 2001; O'Leary et al., 2002; Singh et al., 2004; Jobbagy and Regazzoni, 2004; Venugopal et al., 2006). In most of the reported studies, alcohols have been used as the solvent (Adachi-Pagano et al., 2000; Leroux et al., 2001; Singh et al., 2004; Venugopal et al., 2006). Possibly, alcohols with both non-polar and polar groups can interact with the interlayer alkyl chains and the hydroxyl groups of the metal hydroxide layer leading to good solvation of the layers. In the case of organoclays alcohols could also be the best solvents for achieving good delamination as the non-polar part is compatible with the alkyl groups of surfactant cations and the polar part can interact with hydroxyl groups at platelet edges through H-bonding (Jones, 1983).

There is a report by Jordan (1949) on the swelling behavior of organophilic bentonites in a binary mixture of toluene and alcohols. The swelling of organoclay compounds modified with a range of cationic surfactant in several organic solvents is reported by Williams-Daryn and Thomas (2002). The results suggest that the maximum expansion of the interlamellar space of organoclays in toluene is limited by the longest chain in the surfactant. Dekany et al. have reported the interactions of hydrophobic layer silicates with alcohol–benzene binary mixtures (Dekany et al., 1986a; Dekany et al., 1986b). They show that with increase in the alkyl chain length in the interlayer of montmorillonite the amount of benzene adsorbed increases, while that of methanol remains constant (Dekany et al., 1986a). The orientation of alkylammonium ions at the internal and external surfaces of the clay also affects the adsorption of the binary mixture (Dekany et al., 1986b). Their studies also point out the preference of methanol molecules to adsorb on the silicate surface not covered by alkyl chains while benzene molecules solvate the alkyl chains. Lagaly et al. have reported the partial delamination of organo-montmorillonites in various organic solvents (Lagaly and Malberg, 1990). To the best of our knowledge, until now there is no systematic study on factors influencing the delamination of organosmectites in various alcohols. In this study, we report the delamination of cetyl trimethylammonium (CTA^+) and stearyl trimethylammonium (STA^+) intercalated smectites in various alcohols.

2. Experimental

Bentonite was obtained from M/s Sigma Enterprises, Chennai, India and used without further purification. Montmorillonite was procured from Ashapur Chemicals, Gujarat, India. The magnetic impurities present in the montmorillonite sample were removed by repeatedly stirring the aqueous dispersion of the montmorillonite in a magnetic stirrer and removing the magnetic particles sticking to the pellet. To obtain surfactant intercalated montmorillonte, referred to as organoclays hereafter, 1 g of the montmorillonite was stirred with 60 ml aqueous solution containing 6 mmol (6 times excess the cation exchange capacity of the clay mineral) of the surfactant, cetyl trimethylammonium (CTA) bromide or stearyl trimethylammonium (STA) bromide for 8 days at room temperature. Resultant organoclays were washed repeatedly with distilled water followed by alcohol and dried in air at 65 °C to constant weight.

Delamination and colloidal dispersion of organoclays were carried out as follows. In separate experiments, pre-weighed batches of the samples were added to various solvents of known volume taken in a closed container and sonicated in a bath sonicator (35 kHz) at ~70 °C for 2 h. To ensure that the delamination is caused by the organophilic interlayer surfactant ions, Na-bentonite was also sonicated under the same conditions. In cases where colloidal dispersions were formed, the mixture was centrifuged at 2000 rpm to separate any undispersed solid. This undispersed solid was washed, dried and weighed to calculate the weight of solid dispersed to give the colloidal dispersion. The colloidal dispersion was then set aside and the amount of solid settled through spontaneous flocculation was monitored at regular intervals of time. When settling was observed, the colloidal dispersion was decanted and the settled particles were recovered by centrifugation, washing and drying. This process was continued till the total amount of the solid settled exceeded 50% of the amount of solid dispersed originally. The time needed for this process was taken as a measure of the stability of the colloidal dispersion.

The materials were characterized by powder X-ray diffraction (Siemens D5005, Bragg-Brentano θ–2θ geometry, CuK_α radiation, 4° 2θ per minute) and infrared spectroscopy (Nicolet Model Impact 400D FT-IR spectrometer, KBr pellets, 4 cm^{-1} resolution). For in situ XRD, the colloidal dispersions were taken in a glass holder of the same size as the sample holder of the diffractometer but with a deeper groove.

3. Results and discussion

The XRD patterns of bentonite and the surfactant-exchanged samples are shown in Fig. 1. While the basal spacing of the parent clay mineral is 1.48 nm, it increases to 2.12 nm and 4.11 nm, respectively, in the CTA^+ and STA^+ intercalated samples. The observed basal spacings suggest that the CTA^+ ions form a monolayer arrangement while STA^+ ions form a bilayer arrangement with partial interdigitation (~30%) if we assume that the alkyl chains are tilted at an angle of ~54° with respect to the platelets as it is the most favorable angle of tilt for all-trans *n*-alkyl chains (Johns and Sen Gupta, 1967; Williams-Daryn et al., 2002;