

Interlayer Expansion of Organoclay by Cationic Surfactant

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ABSTRACT

Organoclay was prepared by Na-bentonite and followed by Hexadecyltrimethylammonium bromide (HDTMA) at levels equal to 1.0, 2.0 and 3.0 times of the cation exchange capacity (CEC). Na cations in the interlayer of Na-bentonite clay were exchanged with HDTMA ions, the changes in internal and external surface configuration were augmented by the intercalation of organic surfactants, showing a heterogeneous increase of interlayer spacings. The d-spacings of organoclay from X-ray diffraction patterns revealed that HDTMA loading increased from 1.0, 2.0 and 3.0 CEC, the d-spacings increased of 21.85, 35.85 and 36.46 Å, respectively. From TEM micrographs of the organoclay showed stacks of layers with an average basal spacing of ~21, ~34 and ~35 Å, which corresponding with results of XRD.

Key words: Organoclay, Expansion, Hexadecyltrimethylammonium bromide, TEM

INTRODUCTION

Organoclays form an important type of modified clay material. Their uses are many including some environmental applications. Organoclays are particularly useful in water purification e.g. by the removal of oil and toxic chemicals from water. Remediation of industrial waste waters is enabled through the use of organoclays. These types of materials are useful for the remediation of contaminated soils and they are also applied as clay liners in land fills. The development of some new nanocomposite materials is due to use of organoclays. Organoclays are synthesized by introducing cationic surfactants such as quaternary ammonium compounds into the interlayer space through ion exchange. Long-chain HDTMA cations can form a hydrophobic medium within the clay interlayer, and act in analogy to a bulk organic phase. The intergallery distance of d(001) plane of the clay which has not been organically modified, is relatively small, and the intergal-

lery environment is hydrophilic. Intercalation of an organic surfactant between the clay layers can not only change the surface properties from hydrophilic to hydrophobic, but also significantly increase the basal spacing of the layers (Yunfei et al., 2005). The objective of this work is to study the effect of HDTMA on interlayer expansion of organoclay.

MATERIALS AND METHODS

Materials

The clay used without further purification in this study is bentonite which is predominantly a montmorilloite clay, from Northern Chemicals and Glasswares Ltd. and the cation exchange capacity (CEC) is 71.5 meq/100g. The surfactant used in this study is Hexadecyltrimethylammonium bromide ($C_{19}H_{42}NBr$, FW: 364.45, 96% purity) was obtained from Fluka.

Preparation

The syntheses of surfactant clay hybrids were undertaken by the following procedure: 5 g of Na-bentonite was first dispersed in 500 ml of deionized water then under mechanical stirring for about 4 h. A predissolved stoichiometric amount of HDTMA solution was slowly added to the clay suspension at 70°C. Concentrations of HDTMA⁺ used are 1.0, 2.0 and 3.0 CEC of the bentonite, respectively. The reaction mixtures were stirred for 1 h at 70°C using mechanical stirring. All organoclay products were washed free of bromide anions, dried at 110°C, ground and sieved through 230 mesh, stored in a vacuum desiccator.

Characterization methods

X-ray diffraction

The bentonite and surfactant bentonite hybrids were pressed in glass slides sample holders. X-ray diffraction patterns were recorded using $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), The X-ray Diffraction is performed on powder samples using a Bruker D8Advance diffractometer equipped with a copper anode operating at 40 kV and 20 mA between 1 and 35° (2θ) at a step size of 0.02°.

Transmission Electron microscopy

Samples for TEM were prepared by small drops of dilute suspensions of 0.1 g of the clays dispersed in 5 cm³ acetone and then placed on Cu mesh grids which has been coated with a thin carbon film. The grids were air-dried then briefly placed in a 40°C oven to ensure complete drying prior to insertion into the instrument. The specimens were examined in a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

X-ray diffraction

From Figure 1, the Na-bentonite hydrated moderately under room temperature conditions showed a d-value of 12.06 Å, and as it was modified with the HDTMA loading of 1.0 time the CEC, the d-value of clay increased to 21.85 Å. It indicated that the structural configuration of alkyl chains in the interlamellar space was pseudotrimolecular layer (21.7 Å) (Seung Yeop Lee and Soo Jin Kim, 2002). The XRD patterns showed a low-angle reflection at 35.87 and 36.46 Å resulting from the expansion of interlayers due to the interpenetration of HDTMA ions into the layers with concentrations 2.0 and 3.0 times the CEC of bentonite. During the excess sorption of HDTMA (i.e.>1.0 CEC) into the silicate layers, there seems to occur the transition of alkyl chain configuration from the pseudotrimolecular layer (21.7 Å) to the paraffin complex (>22 Å) (Seung Yeop Lee and Soo Jin Kim, 2002). The previous study showed that the monolayer was formed at 13.7 Å, the bilayer at 17.7 Å, the pseudotrimolecular at 21.7 Å, and paraffin complex with basal spacings greater than 22.0 Å (Bonczek et al., 2002).

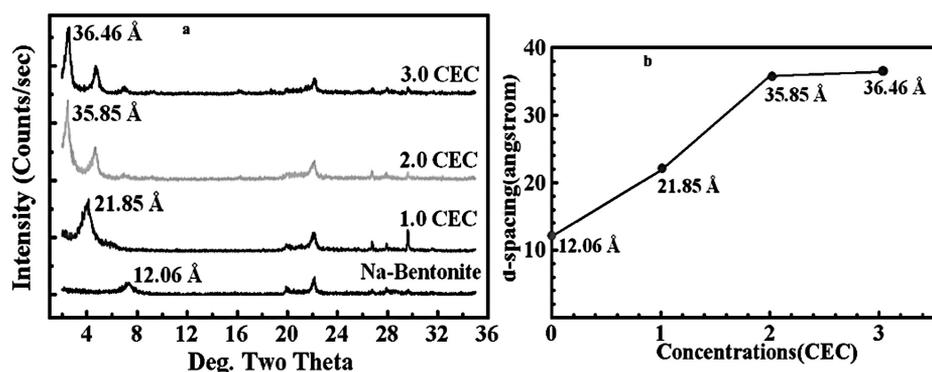


Figure 1. X-ray diffractogram of Na-bentonite and HDTMA-bentonite hybrids.

Transmission Electron microscopy

The organoclay intercalated with HDTMA equivalent to 1.0 time of the CEC showed interplanar spacings of ~21 Å (Figure 2a) which corresponding with results of XRD. This indicated that the alkyl chains are mostly incorporated as pseudotrimolecular layer. Equidistance spacing in the individual layers is generally prevalent, but several layers are deformed (Seung Yeop Lee and Soo Jin Kim, 2002). The organoclay which intercalated with HDTMA equivalent to 2.0 and 3.0 times of CEC showed interplanar spacings of ~34 and ~35 Å, respectively (Figure 2b and 2c). This indicated that the alkyl chains are mostly incorporated as paraffin complex (Seung Yeop Lee and Soo Jin Kim, 2002).

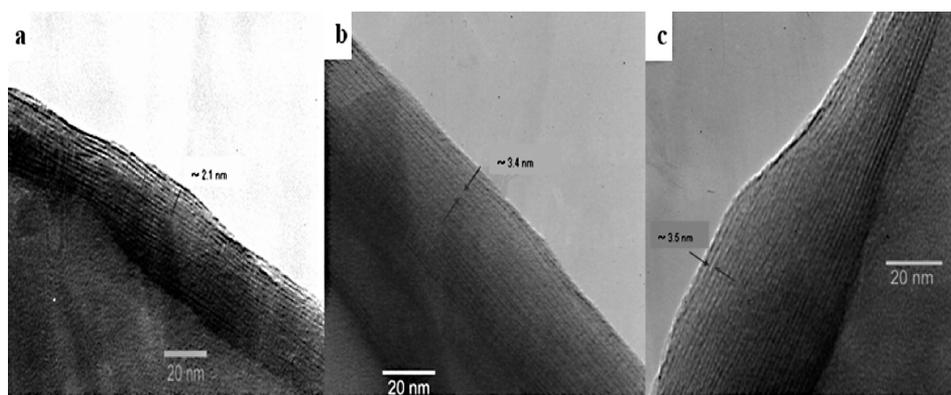


Figure 2. Lattice fringe image of smectite treated with HDTMA corresponding to 1.0 time of the CEC (a) 2.0 time of the CEC (b) and 3.0 time of the CEC (c).

After HDTMA cations enter into the silicate interlayers, they experience the interactions between the head group of HDTMA cation and silicate surface, the hydrocarbon chain of HDTMA cation and silicate surface and the hydrocarbon chain and hydrocarbon chain of HDTMA cations. The latter comprises the non-bonded van der Waals interactions, which are functions of HDTMA concentration. The strong electrostatic interaction between negative charged clay surface and the positively charged head group of HDTMA cation will hold the head group of HDTMA cation close to the clay surface as indicated by molecular simulation (Zeng et al., 2003). On the other hand, since the silicate surface of clay is hydrophilic whereas the hydrocarbon chains of HDTMA cation are hydrophobic, the silicate surface and hydrocarbon chain interaction is of a repulsive nature. The transformation of the curved plates to flat ones might be mainly controlled by the interactions between the hydrocarbon chain and silicate surface and the hydrocarbon chain and hydrocarbon chain of HDTMA cations (Hongping He et al., 2006). Previous reports (Klapyta et al., 2001; Lagaly, 1982) demonstrated that, in the organoclays with lower surfactant packing density (1.0 CEC), the alkyl chains within the interlayer space are parallel within the interlayer space and are individually separated. In this case, the repulsive interaction between the hydrocarbon chain and silicate surface is dominant whereas the interaction among the hydrocarbon chains is very weak. This repulsive interaction is an important factor to result in the transformation from the curved plates to flat ones (Hongping et al., 2006). The detailed mechanism of excessive non-electrostatic adsorption of ionic surfactants beyond the CEC (2.0 and 3.0 CEC) is not fully revealed (Bohmer and Koopal, 1992), it is generally accepted that this process is driven by the attraction of the hydrophobic alkyl chains. As the HDTMA is loaded beyond 1.0 CEC of the clay, extensive HDTMA adsorption via hydrophobic bonding can occur between layers. The expansion of silicate layers is associated with a magnitude or distribution of layer charge on surfaces (Seung Yeop Lee, and Soo Jin Kim, 2002).

CONCLUSION

The concentration of HDTMA had strongly effected on interlayer expansion of organoclay. The d-spacings of organoclay, which loading of HDTMA from 1.0, 2.0 and 3.0 CEC, were 21.85, 35.87 and 36.46 Å, respectively. From TEM micrographs of the organoclay revealed stacks of layers with an average basal spacing of ~21, ~34 and ~35 Å at concentration of surfactant used are 1.0, 2.0 and 3.0 CEC respectively.

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