The Effect of Surfactant Concentration on the Interlayer Structure of Organoclay

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ABSTRACT

An understanding of the interlayer structure of organoclays is of importance in the design of organoclay-based materials and their industrial applications. In this study, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM) were used to provide new insights into the interlayer structure of organoclays. XRD patterns showed the changes in the d(001) spacings, which gave details of the arrangement of surfactant in the organoclays. The d(001) values of 1.0, 2.0 and 3.0 CEC were 21.85, 35.85 and 36.46 Å. Thermal decomposition of organoclays was characterized by TGA. The concentration of 1.0, 2.0 and 3.0 CEC were given weight loss of 20.89, 32.69 and 37.62%, respectively. TEM micrographs showed the interlayer expansion of organoclays which corresponding to the results of XRD. The organoclay which intercalated with HDTMA equivalent to 1.0, 2.0 and 3.0 times of CEC showed interplanar spacings of ~21, ~34 and ~35 Å, respectively. Variation in the d-spacing, thermal decomposition and expanded layers of organoclay was found to be a step function of the surfactant concentration.

Keywords: Interlayer, Organoclay, X-ray diffraction, Transmission electron micros copy, Thermogravimetric analysis.

INTRODUCTION

The study of organoclays is a vital subject in current research since various organoclays are widely used as nanocomposite precursors [1-2], adsorbents for organic pollutants [3], rheological control agents [4] and electric materials [5]. The combination of the hydrophobic nature of the surfactant and the layered structure of the silicate layers leads to unique physicochemical properties. In these applications, the behavior and properties of the organoclays strongly depend on the structure and the molecular environment of the organic molecules within the galleries [6].

Organoclays are synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer

space. When long chain alkyl ammonium cations are used, a hydrophobic partition medium can form within the clay interlayer and function analogously to a bulk organic phase. The interlayer distance of the d(001) plane of the clay, which has not been organically modified, is relatively small, and the interlayer environment is hydrophilic. Intercalation of organic surfactant between layers of clays not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers [7].

The objective of this study is to study of interlayer expansion characteristics of organoclays which synthesized by cationic surfactant in different levels.

2. MATERIALS AND METHODS
Materials

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

Preparation

The preparation of Na-bentonite, the clay is saturated with Na cations by washing the clay repeatedly with a sodium chloride solution; this step is performed by 4 g of clay with 100 ml of 1.0 M NaCl solution and stirred at room temperature for 1 h, centrifuging the suspensions and decanting the supernatant solutions. This process is repeated three times. The Na-saturated bentonite is then washed three to four times with distilled water by centrifuging until the $AgNO_3$ test for chloride shows negative, in order to remove

the salts produced during the clay saturation with Na. The Na-bentonite was dried at 105 °C, ground and sieved through 230 mesh and kept in a sealed bottle.

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 hexadecyltrimethylammoniumbromide 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_α radiation (λ = 1.5418 Å). 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°.

Thermogravimetric analysis

Thermogravimetric analyses of the surfactant bentonite hybrids were obtained using Metler Toledo, TGA/SDTA STAR 851^e. TGA was operated at ramp 20 °C/min from room temperature to 1,000 °C in a high-purity flowing nitrogen atmosphere.

Transmission Electron microscopy

TEM samples were prepared by small drops of dilute suspensions of 0.1 g of the

clays dispersed in 5 cm^3 acetone and then were 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 ºC oven to ensure complete drying prior to insertion into the instrument. The specimens were examined in a JEOL JSM-2010 transmission electron microscope operated at an accelerating voltage of 200 kV.

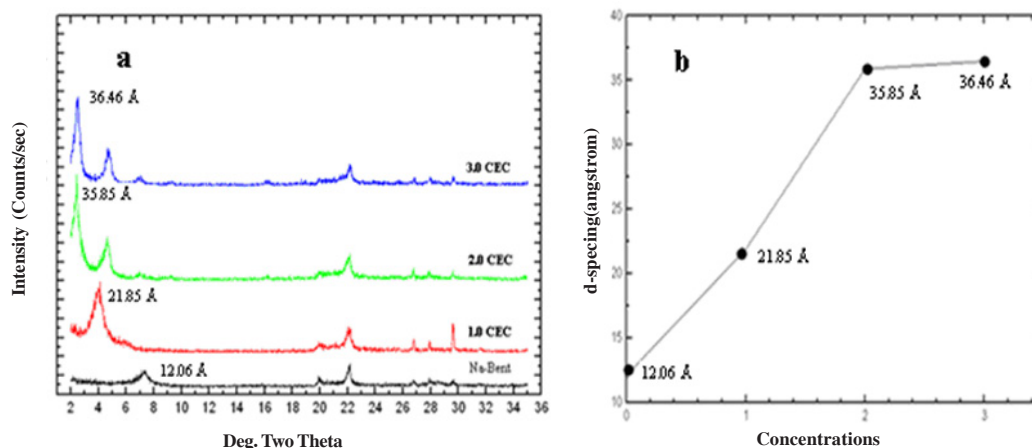## 3. RESULTS AND DISCUSSION
X-ray diffraction

Figure 1. X-ray diffractogram (a) and d(001) basal spacings (b) of Na-bentonite and surfactant-bentonite hybrids

With the cation exchange of the sodium ion for the cationic surfactant, expansion of the bentonite clay layers occurs. This expansion is readily measure by X-ray diffraction. Figure 1a showed the XRD patterns of Na-bentonite and the three organoclays prepared at different surfactant concentrations. Upon intercalation, the basal spacings are expanded as expected depending on the surfactant concentrations. The d(001) values of 1.0, 2.0 and 3.0 CEC were 21.85, 35.87 and 36.46 Å, respectively. The basal spacings expansion due to the interpenetration of HDTMA ions into the layers of bentonite.

Figure 1b clearly showed the increase in the basal spacing from 21.85 to 36.46 Å, as concentration of the surfactant used is increased. The increasing of d-spacing values are 21.85, 35.85 and 36.46 Å due to increasing of HDTMA loading at concentration of 1.0, 2.0 and 3.0 CEC, respectively. For the Na-bentonite hydrated moderately under room temperature conditions showed a value of 12.06 Å, and as it is modified with the HDTMA loading of 1.0 CEC, the d-spacing value of clay increases to 21.85 Å. It indicated that the structural configuration of alkyl chains in the interlamellar space is pseudotrimolecular layer (21.7 Å). The pseudotrimolecular layer consists of three alkyl chains in which the nonpolar chain ends are shifted one above the other by the formation of kinks [8]. At concentration 2.0 CEC and 3.0 CEC of surfactant is used, the basal spacings increase from 21.85 to 35.85 and 36.46 Å, respectively. 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) [8]. The previous study showed that the monolayer is 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[7].

Thermogravimetric analysis

The thermogravimetric analysis showed that the thermal decomposition of organoclays which used the different of the concentration of the surfactant. It was found that percent weight loss showed the different values. The concentration 1.0, 2.0 and 3.0 CEC were given weight loss 20.89, 32.69 and 37.62%, respectively (Figure 2). The percent weight loss depended on amount of concentration of the surfactant. When increased loading of the concentration of surfactant making value of the percent weight loss increased due to molecules of surfactant desorbed from the silicate layer. It is noted that the utilization of thermogravimetric analysis allows distinguishing between different concentrations of surfactant modifying clay properties.
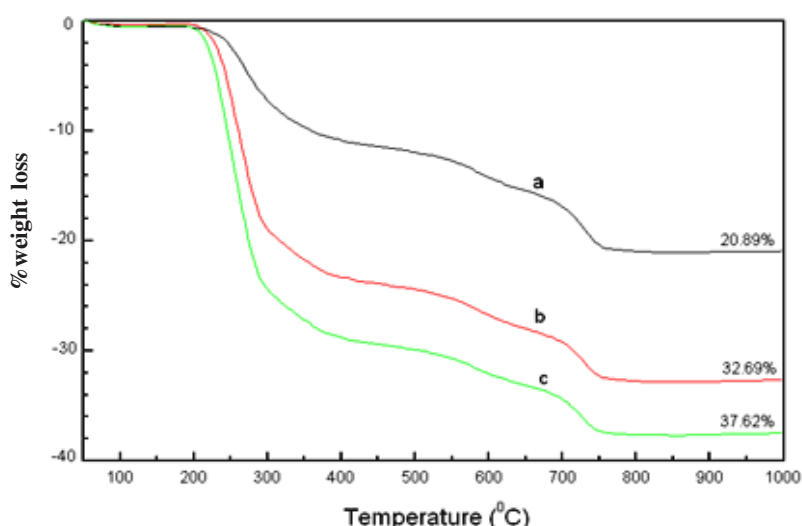

Figure 2. Percent weight loss of organoclays: (a) 1.0 CEC, (b) 2.0 CEC, (c) 3.0 CEC

TRANSMISSION ELECTRON MICROSCOPY

The organoclay intercalated with HDTMA equivalent to 1.0 times of the CEC showed interplanar spacings of ~21 Å (Figure 3a) which is similar to the analysis of XRD Figure1. 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 [8]. 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 3b and 3c). This indicated that the alkyl chains are mostly incorporated as paraffin complex [8].

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 nonbonded van der Waals interactions, which are functions of HDTMA
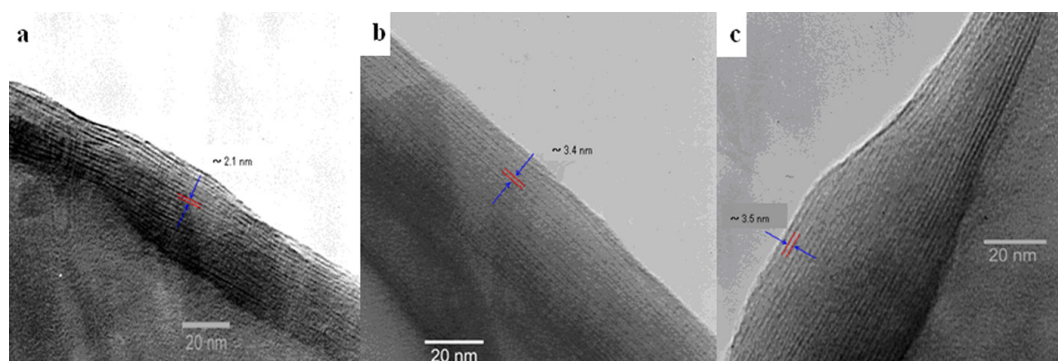
Figure 3. Lattice fringe image of smectite treated with HDTMA corresponding to 1.0 time of the CEC (a), 2.0 time of the CEC (b) and 3.0 time of the CEC (c)

concentration [6]. 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 [9]. 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 [6]. The transformation of the curved plates to flat ones might be mainly controlled by the interactions between the hydrocarbon chain
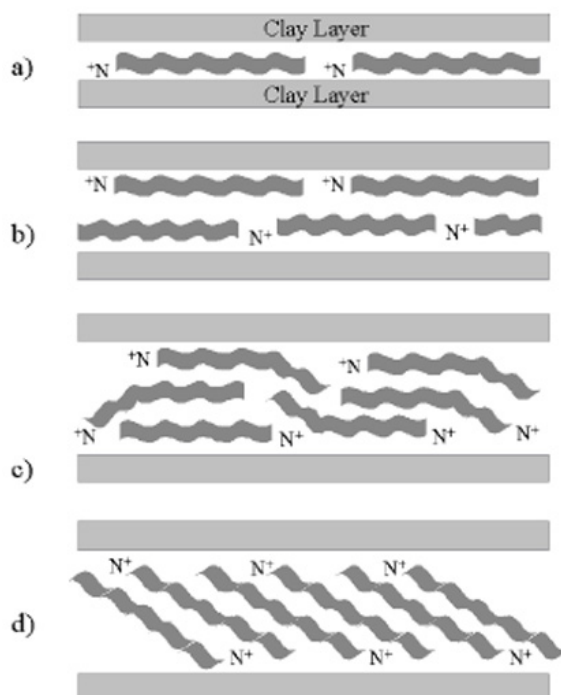

Figure 4. Potential configuration of interlayer cations [12]: (a) monolayer (13.7 Å), (b) bilayer (17.7 Å), (c) pseudotrimolecular layer (21.7 Å), (d) Paraffin complex (>22 Å)

and silicate surface and the hydrocarbon chain and hydrocarbon chain of HDTMA cations [6]. Previous reports [11-12] have 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 [6].

The detailed mechanism of excessive non-electrostatic adsorption of ionic surfactants beyond the CEC (2.0 and 3.0 CEC) is not fully revealed [13], 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 [8]. The expansion of silicate layers is associated with a magnitude or distribution of layer charge on surfaces.

A probable mechanism for HDTMA molecule adsorption in smectite is shown in Figure 4. The illustration demonstrated the relationship between HDTMA adsorption and the structure of the adsorption layer influenced by the charge distribution of the clay surface. Initially (<0.7 CEC), HDTMA adsorption nearly takes place by cation exchange (Figure 4a) [14]. As the HDTMA loading approaches the CEC (0.8-1.0 CEC) of smectite, the selective intercalation of HDTMA develops along the silicate layers (Figure 4b), causing the non-uniform interlayer swelling (Figure 3a). As HDTMA loading increases beyond the CEC (>1.0 CEC) of the smectite, HDTMA adsorption may predominantly occur via hydrophobic bonding, increasing interlayer spacings to ~40

Å (Figure 4c and 4d) [14].

4. CONCLUSION

The d(001) spacings changed as a function of surfactant concentration. The basal spacing obtained from X-ray diffraction gave details of arrangement of surfactant in the organoclays. For 1.0 CEC, there was a pseudotrimolecular layer arrangement of $HDTMA^+$ in the interlayer space of bentonite. For 2.0 CEC and 3.0 CEC, the d basal spacings reached >20 Å, which reflected a paraffin complex arrangement. The concentration 1.0, 2.0 and 3.0 CEC were given weight loss 20.89, 32.69 and 37.62%, respectively. The TEM image of the HDTMA treated smectite 1.0 CEC reveals stacks of slightly curved layers with an average basal spacing of ~21 Å. While images of the HDTMA treated smectite 2.0 and 3.0 CEC revealed stacks of regular layers with an average basal spacing of ~34 and ~35 Å, respectively.

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