

MICROSTRUCTURE OF HDTMA⁺-MODIFIED MONTMORILLONITE AND ITS INFLUENCE ON SORPTION CHARACTERISTICS

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Abstract—A series of organoclays with monolayers, bilayers, pseudotrilayers, paraffin monolayers and paraffin bilayers were prepared from montmorillonite by ion exchange with hexadecyltrimethylammonium bromide (HDTMAB). The HDTMAB concentrations used for preparing the organoclays were 0.5, 0.7, 1.0, 1.5, 2.0 and 2.5 times the montmorillonite cation exchange capacity (CEC). The microstructural parameters, including the BET-N₂ surface area, pore volume, pore size, and surfactant loading and distribution, were determined by X-ray diffraction, N₂ adsorption-desorption and high-resolution thermogravimetric analysis (HRTG). The BET-N₂ surface area decreased from 55 to 1 m²/g and the pore volume decreased from 0.11 to 0.01 cm³/g as surfactant loading was increased from Na-Mt to 2.5CEC-Mt. The average pore diameter increased from 6.8 to 16.3 nm as surfactant loading was increased. After modifying montmorillonite with HDTMAB, two basic organoclay models were proposed on the basis of HRTG results: (1) the surfactant mainly occupied the clay interlayer space (0.5CEC-Mt, 0.7CEC-Mt, 1.0CEC-Mt); and (2) both the clay interlayer space and external surface (1.5CEC-Mt, 2.0CEC-Mt, 2.5CEC-Mt) were modified by surfactant. In model 1, the sorption mechanism of p-nitrophenol to the organoclay at a relatively low concentration involved both surface adsorption and partitioning, whereas, in model 2 it mainly involved only partitioning. This study demonstrates that the distribution of adsorbed surfactant and the arrangement of adsorbed HDTMA⁺ within the clay interlayer space control the efficiency and mechanism of sorption by the organoclay rather than BET-N₂ surface area, pore volume, and pore diameter.

Key Words—BET-N₂ Surface Area, HDTMA⁺, Organoclay, Pore Size, Pore Volume, Sorption Efficiency, Surfactant Loading, Sorption Mechanism.

INTRODUCTION

Organoclays represent a family of materials with hydrophobic surfaces and are synthesized by modifying swelling clays with various surfactants. Over the last 50 years, organoclays have attracted great interest because of their potential use in a number of applications, such as sorbents for organic pollutants (Stackmeyer, 1991; Zhu and Chen, 2000; Zhu *et al.*, 2000), clay-based nanocomposites (Ray and Okamoto, 2003), and precursors for preparing mesoporous materials (Ishii *et al.*, 2005).

It is well known that montmorillonite is hydrophilic in nature due to the cations within its interlayer region, making natural clays ineffective sorbents for organic compounds. Modifying clay mineral surfaces with surfactants to convert the hydrophilic silicate surface to an organophilic surface is a strategic step in the preparation of clay-based sorbents for organic pollutants (Bergaya and Lagaly, 2001). Various organoclays have

been synthesized using different surfactants, including single and dual cationic surfactants (Smith and Galan, 1995; Zhu *et al.*, 1998; Wang *et al.*, 2004; Yilmaz and Yapar, 2004), anionic-cationic surfactants (Regev and Khan, 1996; Zhu and Chen, 2000) and non-ionic surfactants (Shen, 2001). The sorption capacity of organoclays increases with the surfactant loadings within the clay interlayer space (Wang *et al.*, 2004). Organoclays have been demonstrated to be effective as sorbents for organic pollutants in water (Smith and Galan, 1995; Zhu *et al.*, 1998; Shen, 2001; Wang *et al.*, 2004; Yilmaz and Yapar, 2004). Different sorption mechanisms are involved, depending strongly on the characteristics of the surfactants and organic pollutants used. For example, Boyd *et al.* (1988a) and Jaynes and Boyd (1991) showed that sorption of non-ionic organic compounds (NOCs) by large-alkyl organobentonites was essentially due to linear solute partitioning into the microscopic organic phase formed by the large alkyl chains of quaternary ammonium cations. Non-linear isotherms indicative of adsorption or co-sorption were observed when small-alkyl organobentonites were used as sorbents (Lee *et al.*, 1990). Smith and Galan (1995) examined the properties of hybrid organobentonites

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(dual-cation organobentonites) and their ability to sorb non-ionic organic contaminants from water and concluded that the sorption of organobentonites occurred by both adsorption and partition. Zhu and Chen (2000) demonstrated that the removal rate of p-nitrophenol from water was improved by synergistic solubilization in both anionic and cationic surfactant moieties of organobentonites. As indicated by previous studies (Boyd *et al.*, 1988a, 1988b; Lee *et al.*, 1990; Jaynes and Boyd, 1991; Smith and Galan, 1995; Zhu *et al.*, 1998; Shen, 2001; Wang *et al.*, 2004; Yilmaz and Yapar, 2004), characteristics of the surfactants and the organic pollutants significantly affect sorption mechanism and capacity.

Various techniques have been used in the study of organoclays, including X-ray diffraction (XRD) (Lagaly, 1981; Zhu *et al.*, 2003), Fourier transform infrared spectroscopy (FTIR) (Vaia *et al.*, 1994; He *et al.*, 2004a), Raman spectroscopy (He *et al.*, 2004b), thermogravimetric measurement (TG) (Xie *et al.*, 2002; Yariv, 2004; He *et al.*, 2005), nuclear magnetic resonance (NMR) (He *et al.*, 2004c) and transmission electron microscopy (TEM) (Lee and Kim, 2002; Yaron-Marcovich *et al.*, 2005; He *et al.*, 2006). It has been demonstrated that the arrangement of surfactant in the clay interlayer space will vary from monolayer, to bilayer, then to paraffin-type monolayer and finally to paraffin-type bilayer with increase in the surfactant loading. In the case of paraffin type, the ammonium groups remain attached to the silicate layer and the alkyl chains point away from the clay surface. Wang *et al.* (2004) reported that the pore structure and surface characteristics of organoclays were closely related to the arrangement of the surfactant in the interlayer space. This implies that the microstructure of organoclay might have a prominent effect on their sorption capacity and mechanism.

To the best of our knowledge, only a few studies have attempted to correlate the microstructure and sorption characteristics of organoclays (Mandalia and Bergaya, 2006). Correlating these properties is a very important aspect of our understanding of sorption mechanism and for the selection of organoclays for wastewater treatment and contaminated-soil and groundwater remediation. Hence, the main aim of this study is to identify the relationship between organoclay microstructure and sorption mechanism. The compound p-nitrophenol was chosen as a model pollutant. This study might provide new insights into the effects of organoclay microstructure on sorption mechanism.

MATERIALS AND METHODS

Ca-montmorillonite (Ca-Mt) was obtained from Hebei, China. The sample was purified by sedimentation and the montmorillonite with a particle size of <2 μm was collected for use. Its CEC is 90.8 meq/100 g, determined by the NH_4^+ method as described in the

literature (He *et al.*, 2001). The surfactant used in this study is hexadecyltrimethylammonium bromide (HDTMAB) with a purity of 99%, provided by YuanJu Chem. Co. Ltd., China. Analytical grade p-nitrophenol with a water solubility of 1.6×10^4 mg/L was used.

Synthesis and characterization of the organoclay

The Na-montmorillonite (Na-Mt) and surfactant-modified montmorillonites were prepared as described by He *et al.* (2004c). In the preparation of Na-Mt, 10 g of the mixture of Ca-Mt (9.4 g) and Na_2CO_3 (0.6 g) were added to 100 mL of deionized water and stirred at 80°C for 3 h. Na-Mt was collected by centrifugation and washed with deionized water. The Na-Mt was dried at 105°C, ground and sieved through a 200 mesh and then placed in a bottle and sealed.

The syntheses of surfactant-modified montmorillonites were performed by the following procedure: 2 g of Na-Mt were first dispersed in ~300 mL of deionized water and then the desired amount of HDTMAB was added slowly. The reaction mixtures were stirred for 10 h at 60°C. All products were washed free of bromide anions (tested by AgNO_3), dried at 80°C, ground in an agate mortar and passed through a 200 mesh sieve. The organoclay prepared at a surfactant concentration of 0.5 CEC was marked as 0.5CEC-Mt and the others were marked in a similar fashion.

The XRD patterns of the samples were recorded between 1.5 and 20°2 θ at a scanning speed of 2°/min, using Rigaku D/max-1200 diffractometer (Rigaku Denki, Japan) using $\text{CuK}\alpha$ radiation (30 mA and 40 kV).

High-resolution thermogravimetric (HRTG) analysis was performed using a Q500 thermobalance (TA Instruments Inc., USA). Samples (30 mg) were heated from room temperature to 1000°C at a heating rate of 10°C/min with a resolution of 6°C under N_2 atmosphere (80 cm^3/min).

N_2 adsorption-desorption isotherms were measured at liquid nitrogen temperature using a Micromeritics ASAP 2010 gas sorption analyzer (Micromeritics, Norcross, GA, USA). Before measurement, the samples were preheated at 80°C under N_2 for ~24 h. The specific surface area was calculated by using the BET equation and the total pore volumes were evaluated from nitrogen uptake at relative pressure of ~0.99. The Barrett-Joyner-Halenda (BJH) method was used to evaluate the average pore diameter (APD) (Barrett *et al.*, 1951).

p-nitrophenol sorption

The Na-Mt or organoclay samples (0.1 g) were combined with 15 mL of p-nitrophenol solution (5–60 mg/L) in 50 mL Erlenmeyer flasks with glass caps. The flasks were shaken for 1 h at 25°C on a shaker at 200 rpm. The solution pH value was 8.0. After centrifugation, the p-nitrophenol concentration in the aqueous phase was determined by a UV-260 spectrophotometer (Shimadzu Co., Kyoto, Japan) at 317 nm

Table 1. Structural parameters and surfactant loadings of Na-Mt and the HDTMA organoclays.

Sample	d_{001} (nm)	S_{BET} (m^2/g)	V_{p} (cm^3/g)	APD_{HC} (nm)	APD	SL (%)	SL (vs. CEC)
Na-Mt	1.24	55	0.11	4.0	6.8	–	–
0.5CEC-Mt	1.48	12	0.06	3.3	7.5	9.73	0.33
0.7CEC-Mt	1.78	10	0.06	3.3	8.7	16.73	0.61
1.0CEC-Mt	1.95	9	0.06	3.3	9.1	22.13	0.86
1.5CEC-Mt	2.23	4	0.04	3.3	12.7	28.19	1.19
2.0CEC-Mt	3.61	1	0.01	3.3	14.1	38.73	1.9
2.5CEC-Mt	3.84	1	0.01	3.3	16.3	44.17	2.4

S_{BET} : specific surface area.

V_{p} : pore volume determined by BJH method from N_2 desorption isotherm.

APD_{HC} : pore diameter with the highest concentration, determined by the curve of BJH desorption dV/dD pore volume.

APD: average pore diameter determined by the curve of BJH desorption dV/dD pore volume.

SL: surfactant loading within the corresponding organoclay, evaluated from high-resolution thermogravimetric analysis.

SL(vs. CEC): surfactant loading expressed in CEC of montmorillonite (100 g).

with a detection limit of 0.05 mg/L. The p-nitrophenol uptake on Na-Mt or organoclays was calculated by the following equation:

$$Q = (C_0 - C_e)V/m$$

where Q is the p-nitrophenol uptake, C_0 is the initial concentration, C_e is the equilibrium concentration, V is the volume of p-nitrophenol solution and m is the quantity of the sorbent. The loss of p-nitrophenol by photochemical decomposition, sorption to Erlenmeyer flask and volatilization were found to be negligible (Zhu *et al.*, 2000).

RESULTS AND DISCUSSION

X-ray diffraction

The basal spacings of Na-Mt and the organoclays are shown in Table 1. The basal spacing of Na-Mt is 1.24 nm, which is characteristic of Na-montmorillonite. However, after modification with surfactant, the interlayer spacing of montmorillonite was obviously increased with an increase in surfactant concentration in the preparation solution (Table 1). On the basis of the configuration of HDTMA^+ and the interlayer spacings of montmorillonite and the organoclays, different HDTMA^+ arrangement models within the montmorillonite interlayer space are proposed, *i.e.* monolayer in 0.5CEC-Mt, bilayer in 0.7CEC-Mt, pseudotrilayer in 1.0CEC-Mt, paraffin monolayer in 1.5CEC-Mt and paraffin bilayer in 2.0CEC-Mt and 2.5CEC-Mt, respectively, in agreement with previous experimental and molecular modeling reports (Lagaly, 1981; Yui *et al.*, 2002; Zhu *et al.*, 2003; Zeng *et al.*, 2004; He *et al.*, 2006).

Microstructure of the organoclays

The structure parameters of Na-Mt and the organoclays, including specific surface area (S_{BET}), total pore volume (V_{p}), average pore diameter (APD), pore

diameter with highest concentration (APD_{HC}) and surfactant loading (SL), are summarized in Table 1.

From Figure 1, a dramatic decrease of the BET- N_2 surface area was observed from Na-Mt to 0.5CEC-Mt, followed by a smooth decrease until 1.0CEC-Mt, then a more pronounced decrease until 2.0CEC-Mt. A similar trend with a smoother decrease was also found for the pore volumes of Na-Mt and the organoclays.

Figure 2 shows the nitrogen adsorption-desorption isotherms of the starting montmorillonite (Na-Mt) and the organoclays. The adsorption isotherms are of Type II in the Brunauer, Demming, Demming and Teller (BDDT) classification (Brunauer *et al.*, 1940). A large uptake of nitrogen was observed close to saturation pressure, exhibiting multilayer adsorption and implying the presence of mesopores (Wang *et al.*, 2004). This is in agreement with the pore diameter calculated from the Barrett-Joyner-Halenda (BJH) desorption isotherm as shown in Table 1. The hysteresis loops of the isotherms of Na-Mt and the organoclays resemble H5 in the IUPAC classification (Gregg and Sing, 1982), indicating 'ink-bottle' like pores in the related clays. These pores

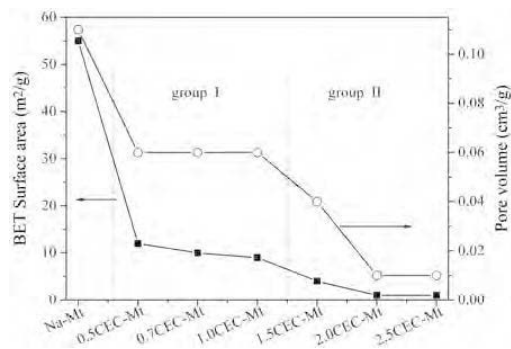


Figure 1. BET- N_2 surface area and pore volume of Na-Mt and organoclays. (■: BET surface area, ○: pore volume).

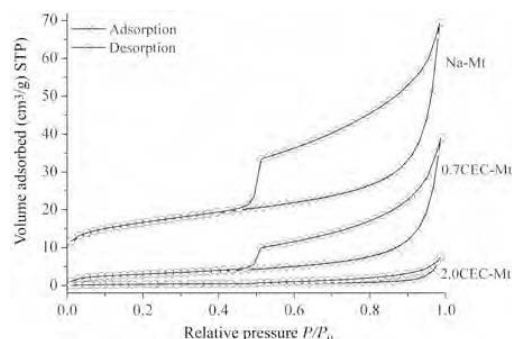


Figure 2. Nitrogen adsorption-desorption isotherms of Na-Mt and two representative organoclays (0.7CEC-Mt and 2.0CEC-Mt).

could be described as a ‘house of cards’ structure (Lagaly and Ziesmer, 2003).

The pore-size distribution calculated from the BJH desorption isotherm is shown in Figure 3. The pore-size distribution centers around 4.0 nm for Na-Mt and 3.3 nm for the organoclays. For Na-Mt and the organoclays prepared at low surfactant concentration, the pore-size distribution has only a small range between 3 and 20 nm.

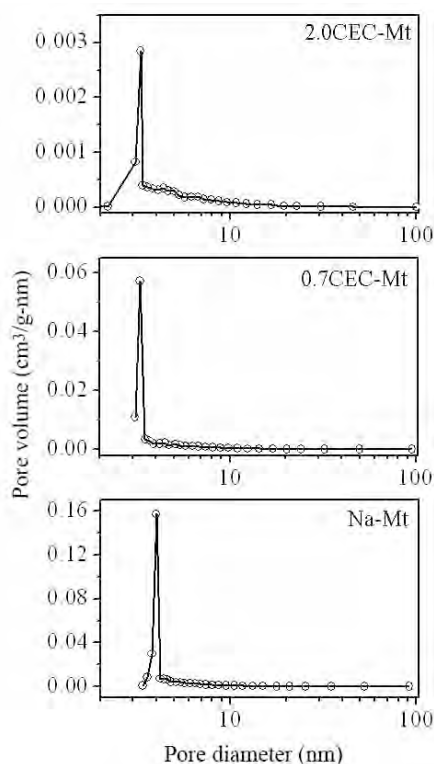


Figure 3. The pore-size distribution curves of Na-Mt and two representative organoclays (0.7CEC-Mt and 2.0CEC-Mt).

However, for 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt, there is a prominent distribution of pore sizes in the range from 4 to 100 nm. This is in agreement with the increase of APD from Na-Mt to organoclays with low surfactant loadings, and then to organoclays with high surfactant loadings.

Here, one very interesting question arises: why do both the BET-N₂ surface area and the pore volume decrease dramatically with loading of surfactant while the APDs increase? For example, the BET-N₂ surface area and the pore volume for 2.5CEC-Mt are only ~1.8% and 9%, respectively, of equivalent values for Na-Mt, whereas the APD of 2.5CEC-Mt is more than twice that of Na-Mt. This is attributed to the microstructure of the organoclays.

As is well known, montmorillonite is capable of interlamellar expansion with the intercalation of surfactants (Wang *et al.*, 2004). The large intercalated HDTMA⁺ cations may result in blocking of the interlamellar space that inhibits the passage of nitrogen molecules. Both molecular modeling and experiments (Zhu *et al.*, 2003; Zeng *et al.*, 2004) have demonstrated that the packing density of the surfactant within the clay interlayer space increases with increase of the intercalated surfactant, and the orientation of the hydrocarbon tail changes from parallel to the silicate surface within the interlayer space to being parallel to the surfactant chains at an angle to the silicate surface. This means that more sorption sites are accessible to the intercalated surfactant in the interlayer space. Accordingly, both cases will lead to a decrease in the BET-N₂ surface area and pore volume of the organoclays. As shown in Figure 1, the organoclays can be divided into two groups on the basis of their BET-N₂ surface area and pore volume. Group I includes 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt, with similar BET-N₂ surface areas of 9–12 m²/g and pore volumes of 0.06 cm³/g. Group II is 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt, with similar BET-N₂ surface areas of 1–4 m²/g and pore volumes of 0.01–0.04 cm³/g. As indicated by the XRD patterns, the intercalated HDTMA⁺ cations in 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt lie flat on the clay surface with a paraffin arrangement in 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt. It can be seen that the BET-N₂ surface area and pore volume of the organoclays depend strongly on the arrangement of the intercalated surfactants within the clay interlayer space.

Previous studies (Juang *et al.*, 2002; He *et al.*, 2005) have demonstrated that the surfactant cations/molecules not only enter into the clay interlayer space but are also sorbed outside the clay interlayer. In this case, the loaded surfactant occupies the pores available between clay particles with a ‘house of cards’ structure. This will also result in a decrease in BET-N₂ surface area and pore volume, depending strongly on the surfactant loading. The surfactant loadings in the organoclays, evaluated

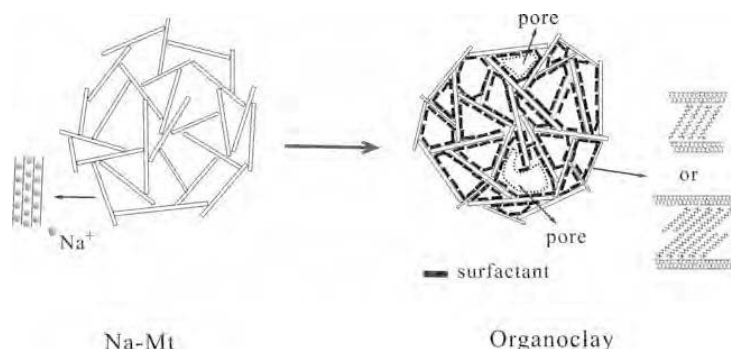


Figure 4. The schematics of Na-Mt and organoclays.

from high-resolution thermogravimetric (HRTG) analysis, are shown in Table 1. This evaluation clearly shows that more than 1 CEC of surfactant can be loaded in the organoclays (e.g. 1.5CEC-Mt, 2.0CEC-Mt, 2.5CEC-Mt). This excess of surfactant mainly occupies the interparticle pores, resulting in a dramatic decrease in pore volume and BET-N₂ surface area. The schematic structures of Na-Mt and the organoclays are shown in Figure 4. Obviously, two basic organoclay types are formed when modifying clay with surfactant on the basis of the distribution of surfactant: (1) the surfactant mainly occupies the clay interlayer space; and (2) both the clay interlayer space and external surface are modified by surfactant. This assumption is supported by the HRTG results (see below).

Figure 5 displays the HRTG and DTG curves of Na-Mt, neat HDTMAB and two representative organoclays

(0.7CEC-Mt and 2.0CEC-Mt). The DTG curve of Na-Mt is composed of three peaks around 34.4, 107.8 and 619.3°C, corresponding to surface adsorbed water, hydrated water of the interlayer cations and the structural water (bonded hydroxyl groups that undergo dehydroxylation), respectively (Xie *et al.*, 2002; Yariv, 2004; He *et al.*, 2005). For neat HDTMAB, only one peak at ~198.6°C was recorded in the DTG curve and should be attributed to its evaporation/decomposition when heated (Xi *et al.*, 2005).

As shown by the HRTG curve, montmorillonite is relatively stable in the temperature range 150–450°C, *i.e.* the weight loss of the organoclays in this temperature range should be attributed to the evaporation/decomposition of the loaded surfactant. Our previous study has demonstrated that there are 1–3 peaks (~210, 280 and 375°C, respectively) in the DTG curve of HDTMAB-

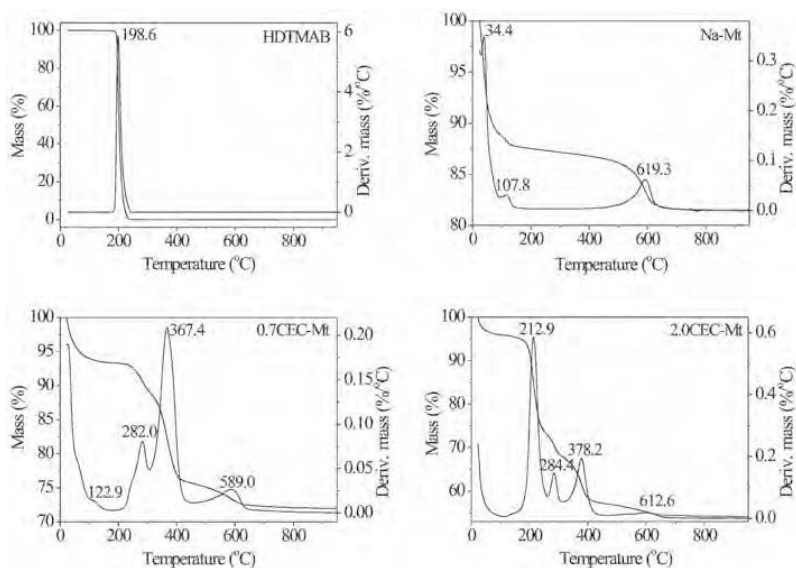


Figure 5. TG and DTG curves of Na-Mt, HDTMAB and two representative organoclays (0.7CEC-Mt and 2.0CEC-Mt).

modified montmorillonites at 150–450°C (He *et al.*, 2005). The peak at ~210°C corresponds to the evaporation of surface-adsorbed surfactant (outside clay interlayer) while the other two at 280 and 375°C correspond to the decomposition of the intercalated surfactants within the clay interlayer space (He *et al.*, 2005). In the DTG curves of 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt, the recorded peaks at 284 and 378°C and a lack of the peak at 210°C suggest that almost all loaded surfactant has entered into the clay interlayer space. On the contrary, besides the peaks at 282 and 367°C, a prominent peak at 210°C was recorded in the DTG curves of 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt. This is a reflection of the fact that the surfactant is located not only within the clay interlayer space but also outside the clay interlayer (*i.e.* the surfactant occupies the interparticle pores with a ‘house of cards’ structure).

Sorption curves and mechanisms

Sorption curves for p-nitrophenol at pH = 8 and 25°C on Na-Mt and the organoclays are shown in Figure 6. These sorption curves of organoclays can be divided into two groups: (1) group I includes 0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt, in which the loaded surfactant adopts an arrangement parallel to the silicate surface and mainly occupies the clay interlayer space; and (2) group II includes 1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt, in which the loaded surfactant adopts a paraffin arrangement and occupies both the clay interlayer space and the pores.

For Na-Mt and organoclays in group I (0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt), the adsorption curves display S-type isotherms. The sorption curve of Na-Mt contains two regions. In the first region ($C_e = 0\text{--}15\text{ mg/L}$), there is a relatively small increase in the amount of sorbed p-nitrophenol, whereas a rapid increase occurs when $C_e > 15\text{ mg/L}$. This is similar to that reported by Yilmaz and Yapar (2004). The interaction between clay (without modification) and organic compounds has been demonstrated to be surface adsorption (Banat *et al.*, 2000; Al-Asheh *et al.*, 2003; Yilmaz and Yapar, 2004). As shown in Figure 6, the sorption curves for group I (0.5CEC-Mt, 0.7CEC-Mt and 1.0CEC-Mt) are very similar and show S-type isotherms. These sorption curves almost overlap each other (especially for 0.5CEC-Mt and 0.7CEC-Mt), reflecting a similar sorption mechanism involved. As indicated by a number of previous studies, the sorption mechanisms for montmorillonite modified by HDTMAB below 1.0 CEC concentration contains both adsorption and partition (Zhu *et al.*, 2000; Al-Asheh *et al.*, 2003; Cruz-Guzmán *et al.*, 2004). However, for group II (1.5CEC-Mt, 2.0CEC-Mt and 2.5CEC-Mt), the sorption curves are definitely linear, reflecting a partition process (Boyd *et al.*, 1988b; Chun *et al.*, 2003).

Organoclays in group II are the most efficient at sorbing p-nitrophenol and Na-Mt is the least efficient

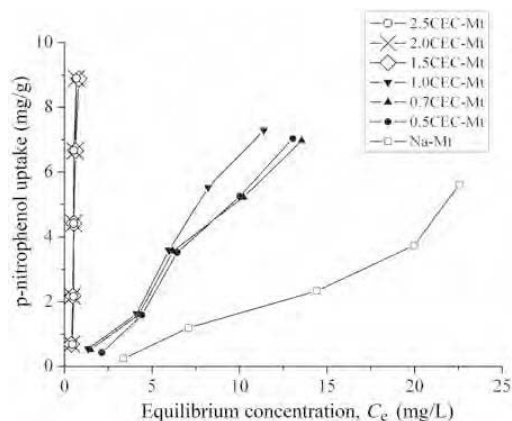


Figure 6. Sorption curves of p-nitrophenol in Na-Mt and organoclays (pH = 8.0, $T = 25^\circ\text{C}$).

(Figure 6). Our structural analysis demonstrates that Na-Mt has the largest BET- N_2 surface area and pore volume whereas organoclays in group II have the smallest BET- N_2 surface area and pore volume. This suggests that the BET- N_2 surface area and pore volume are not the key factors that control the affinity between clay/organoclay and organic pollutants.

As indicated by HRTG analysis, surfactant loading in the organoclays of group II exceeds the CEC and the excess surfactant probably occupies interparticle pores within the ‘house of cards’ structure. Meanwhile, the intercalated surfactant within the clay interlayer space adopts a paraffin arrangement. In this case, the clay layers are almost completely enclosed by surfactant and an organic medium can be visualized as formed within the clay layer space and in the interparticle pores. This organic medium is of importance for the excellent affinity between organoclay and organic pollutants, and is available as a partition medium for contaminant sorption (Boyd *et al.*, 1988b; Chun *et al.*, 2003).

For organoclays in group I, the surfactant mainly occupies the clay interlayer space rather than the interparticle pores, *i.e.* only a limited amount of organic medium is formed in the clay interlayer space. In this case, the clay interlayer surface is organophilic whereas the external clay surface (also for the pores) is mainly hydrophilic. The organophilic clay interlayer space is available as a partition medium for contaminant sorption, whereas the external clay surface is available for adsorption (Lee *et al.*, 1990; Jaynes and Boyd, 1991; Celis *et al.*, 2000; Cruz-Guzmán *et al.*, 2004). Accordingly, both adsorption and partition are involved in the sorption mechanism of the organoclays in group I.

CONCLUSIONS

Our study indicates that both the BET- N_2 surface area and pore volume of the organoclays decreased as the

surfactant loading increased from low to high. The average pore diameter increased depending on the organoclay interlayer arrangements and the amount of surfactant within the pores. Generally, the surfactant-modified montmorillonites can be divided into two basic types on the basis of the surfactant distribution: (1) the surfactant mainly occupies the clay interlayer space; and (2) both the clay interlayer space and external surface are modified by surfactant. The distribution and arrangement of surfactant in the organoclays control sorption efficiency and mechanism rather than BET- N_2 surface area, pore volume, or pore diameter. The sorption of p-nitrophenol to organoclays with surfactant loading up to the CEC involves both surface adsorption and partition, whereas p-nitrophenol sorption to organoclays with surfactant loadings greater than the CEC involves mainly partitioning.

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REFERENCES

- Al-Asheh, S., Banat, F. and Abu-Aitah, L. (2003) Adsorption of phenol using different types of activated bentonites. *Separation and Purification Technology*, **33**, 1–10.
- Banat, F.A., Al-Bashir, B., Al-Asheh, S. and Hayajneh, O. (2000) Adsorption of phenol by bentonite. *Environmental Pollution*, **107**, 391–398.
- Barrett, E.P., Joyner, L.G. and Halenda, P.P. (1951) The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical Society*, **73**, 373–380.
- Bergaya, F. and Lagaly, G. (2001) Surface modification of clay minerals. *Applied Clay Science*, **19**, 1–6.
- Boyd, S.A., Lee, J.F. and Mortland, M.M. (1988a) Attenuating organic contaminant mobility by soil modification. *Nature*, **333**, 345–349.
- Boyd, S.A., Mortland, M.M. and Chiou, C.T. (1988b) Sorption characteristics of organic compounds on hexadecyltrimethylammonium smectite. *Soil Science Society of America Journal*, **52**, 652–657.
- Brunauer, S., Demming, L.S., Demming, W.S. and Teller, E. (1940) On a theory of the van der Waals adsorption of gases. *Journal of the American Chemical Society*, **62**, 1723–1732.
- Celis, R., Hermosin, M.C. and Cornejo, J. (2000) Heavy metal adsorption by functionalized clays. *Environmental Science and Technology*, **34**, 4593–4599.
- Chun, Y., Sheng, G.Y. and Boyd, S.A. (2003) Sorptive characteristics of tetra-alkylammonium-exchanged smectite clays. *Clays and Clay Minerals*, **51**, 415–420.
- Cruz-Guzmán, M., Celis, R., Hermosin, M.C. and Cornejo, J. (2004) Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations. *Environmental Science and Technology*, **38**, 180–186.
- Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption, Surface Area and Porosity*, 2nd edition. Academic Press, New York, chapters 2 and 3.
- He, H.P., Guo, J.G., Xie, X.D. and Pen, J.L. (2001) Location and migration of cations in Cu^{2+} -adsorbed montmorillonite. *Environment International*, **26**, 347–352.
- He, H.P., Frost, R.L. and Zhu, J.X. (2004a) Infrared study of HDTMA⁺ intercalated montmorillonite. *Spectrochimica Acta Part A*, **60**, 2853–2859.
- He, H.P., Frost, R.L., Xi, Y.F. and Zhu, J.X. (2004b) Raman spectroscopic study of organo-montmorillonites. *Journal of Raman Spectroscopy*, **35**, 316–323.
- He, H.P., Frost, R.L., Deng, F., Zhu, J.X., Weng, X.Y. and Yuan, P. (2004c) Conformation of surfactant molecules in the interlayer of montmorillonite studied by ^{13}C MAS NMR. *Clays and Clay Minerals*, **52**, 350–356.
- He, H.P., Ding, Z., Zhu, J.X., Yuan, P., Xi, Y.F., Yang, D. and Frost, R.L. (2005) Thermal characterization of surfactant-modified montmorillonites. *Clays and Clay Minerals*, **53**, 286–292.
- He, H.P., Frost, R.L., Bostrom, T., Yuan, P., Duong, L., Yang, D., Xi, Y.F. and Klopogge, T.J. (2006) Changes in the morphology with HDTMA⁺ surfactant loading. *Applied Clay Science*, **31**, 262–271.
- Ishii, R., Nakatsuji, M. and Ooi, K. (2005) Preparation of highly porous silica nanocomposites from clay mineral: a new approach using pillaring method combined with selective. *Microporous and Mesoporous Materials*, **79**, 111–119.
- Jaynes, W.F. and Boyd, S.A. (1991) Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. *Soil Science Society of American Journal*, **55**, 43–48.
- Juang, R.S., Lin, S.H. and Tsao, K.H. (2002) Mechanism of sorption of phenols from aqueous solutions onto surfactant-modified montmorillonite. *Journal of Colloid and Interface Science*, **254**, 234–241.
- Lagaly, G. (1981) Characterization of clays by organic compounds. *Clay Minerals*, **16**, 1–21.
- Lagaly, G. and Ziesmer, S. (2003) Colloid chemistry of clay minerals: the coagulation of montmorillonite dispersions. *Advances in Colloid and Interface Science*, **100**, 105–128.
- Lee, J.F., Mortland, M.M., Chiou, C.T., Kile, D.E. and Boyd, S.A. (1990) Adsorption of benzene, toluene, and xylene by tetramethylammonium-smectites having different charge densities. *Clays and Clay Minerals*, **38**, 113–120.
- Lee, S.Y. and Kim, S.J. (2002) Expansion characteristics of organoclay as a precursor to nanocomposites. *Colloid Surface A*, **211**, 19–26.
- Mandalia, T. and Bergaya, F. (2006) Organo clay mineral-melted polyolefin nanocomposites effect of surfactant/CEC ratio. *Journal of Physics and Chemistry of Solids*, **67**, 836–845.
- Ray, S.S. and Okamoto, M. (2003) Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science*, **28**, 1539–1641.
- Regev, O. and Khan, A. (1996) Alkyl chain symmetry effects in mixed cationic-anionic surfactant systems. *Journal of Colloid and Interface Science*, **182**, 95–109.
- Shen, Y.-H. (2001) Preparations of organobentonite using non-ionic surfactants. *Chemosphere*, **44**, 989–995.
- Smith, J.A. and Galan, A. (1995) Sorption of nonionic organic contaminants to single and dual organic cation bentonites from water. *Environmental Science and Technology*, **29**, 685–692.
- Stackmeyer, M.R. (1991) Adsorption of organic compounds on organophilic bentonites. *Applied Clay Science*, **6**, 39–57.
- Vaia, R.A., Teukolsky, R.K. and Giannelis, E.P. (1994) Interlayer structure and molecular environment of alkylammonium layered silicates. *Chemistry of Materials*, **6**, 1017–1022.
- Wang, C.C., Juang, L.C., Lee, C.K., Hsu, T.C., Lee, J.F. and

- Chao, H.P. (2004) Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite. *Journal of Colloid and Interface Science*, **280**, 27–35.
- Xi, Y.F., Frost, R.L., He, H.P., Klopogge, J.T. and Bostrom, T. (2005) Modification of Wyoming montmorillonite surfaces using a cationic surfactant. *Langmuir*, **21**, 8675–8680.
- Xie, W., Xie, R.C., Pan, W.P., Hunter, D., Koene, B., Tan, L.S. and Vaia, R. (2002) Thermal stability of quaternary phosphonium modified montmorillonites. *Chemistry of Materials*, **14**, 4837–4845.
- Yariv, S. (2004) The role of charcoal on DTA curves of organo-clay complexes: an overview. *Applied Clay Science*, **24**, 225–236.
- Yaron-Marcovich, D., Chen, Y., Nir, S. and Prost, R. (2005) High resolution electron microscopy structural studies of organo-clay nanocomposites. *Environmental Science and Technology*, **29**, 1231–1238.
- Yilmaz, N. and Yapar, S. (2004) Adsorption properties of tetradecyl- and hexadecyltrimethylammonium bentonites. *Applied Clay Science*, **27**, 223–228.
- Yui, T., Yoshida, H., Tachibana, H., Tryk, D.A. and Inoue, H. (2002) Intercalation of polyfluorinated surfactants into clay minerals and the characterization of the hybrid compounds. *Langmuir*, **18**, 891–896.
- Zeng, Q.H., Yu, A.B., Lu, G.Q. and Standish, R.K. (2004) Molecular dynamics simulation of the structural and dynamic properties of dioctadecyldimethyl ammoniums in organoclays. *Journal of Physics and Chemistry B*, **108**, 10025–10033.
- Zhu, J.X., He, H.P., Guo, J.G., Yang, D. and Xie, X.D. (2003) Arrangement models of alkylammonium cations in the interlayer of HDTMA⁺ pillared montmorillonites. *Chinese Science Bulletin*, **48**, 368–372.
- Zhu, L.Z. and Chen, B.L. (2000) Sorption behavior of p-nitrophenol on the interface between anion-cation organobentonite and water. *Environmental Science and Technology*, **34**, 2997–3002.
- Zhu, L.Z., Ren, X.G. and Yu, S.B. (1998) Use of cetyltrimethylammonium bromide bentonite to remove organic contaminants of varying polar character from water. *Environmental Science and Technology*, **32**, 3374–3378.
- Zhu, L.Z., Chen, B.L. and Shen, X.Y. (2000) Sorption of phenol, p-nitrophenol and aniline to dual-cation organobentonites from water. *Environmental Science and Technology*, **34**, 468–475.

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