Organoclays prepared from montmorillonites with different cation exchange capacity and surfactant configuration

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ABSTRACT

Organically modified montmorillonites ('organo-montmorillonites') have attracted a great deal of interest because of their wide applications in industry and environmental protection. We have synthesized organo-montmorillonites using montmorillonites with different cation exchange capacities (CEC) and surfactants with different alkyl chain number and chain length. The organo-montmorillonites were characterized by X-ray diffraction (XRD) and differential thermogravimetry (DTG). The basal spacing of the organo-montmorillonites increased with surfactant loading, while the maximum basal spacing increased as the alkyl chain length of the surfactant increased. For the same surfactant, the maximum basal spacing of the organo-montmorillonites was little influenced by the CEC of the montmorillonite component. The level of surfactant loading required to reach the maximum basal spacing, however, strongly depended on the CEC. For a given alkyl chain length, the maximum basal spacing increased when the chain number increased from one to two. These findings are important to the preparation of low-cost organoclays for industrial applications.

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1. Introduction

'Organo-montmorillonites' are montmorillonites that have been modified with organic surfactants. These hydrophobic materials have attracted much interest because they have found wide applications as adsorbents of organic pollutants (Stackmeyer, 1991; Zhu and Chen, 2000; Zhu et al., 2000; Theng et al., 2008), as components in the synthesis of clay-based polymer nanocomposites (Ray and Okamoto, 2003), and as precursors in the preparation of mesoporous materials (Ishii et al., 2005).

Different surfactants have been used to prepare organoclays. These include 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 nonionic surfactants (Shen, 2001). The organoclays formed, however, are structurally different even when the same surfactant was used under similar experimental conditions (Lagaly, 1981; Lee and Kim, 2002; Xi et al., 2005a; He et al., 2006a,b; Zidelkheir and Abdelgoad, 2008). This finding suggests that the structure and properties of the resultant organoclays are affected by both the type surfactant and clay mineral used. It is well known that the chemical composition of montmorillonites varies from one deposit to another. This variation is reflected by the magnitude of the cation exchange capacity (CEC), arising from isomorphous substitution (e.g., Mg^{2+} for Al^{3+} in the

octahedral sheet and/or Al^{3+} for Si^{4+} the tetrahedral sheet) in the montmorillonite layer. The resultant deficiency in positive layer charge is compensated by the adsorption of Na^+ or Ca^{2+} ions in the interlayer space. These inorganic cations can be exchanged with, or replaced by, other cations, including cationic surfactants. Little is known, however, about the relationship between layer charge (i.e., CEC) of montmorillonite and the properties of the resultant organoclays (maximum surfactant loadings and basal spacings). This information is important to the synthesis of clay–polymer nanocomposites as organoclays with the lowest cost and largest basal spacing would be favoured.

Here we report on the preparation of organo-montmorillonites using montmorillonites with different CEC and surfactants with different alkyl chain numbers and chain length. The structure of the resultant organo-montmorillonites was characterized in terms of surfactant loading and interlayer expansion (basal spacing).

2. Experimental

2.1. Materials

Ca-montmorillonites from Anji, Zhejiang province (AB-Ca), Nanghai, Guangdong province (HN-Ca), and Neimeng, Inner Mongolia (NM-Ca) were used. The purchased montmorillonite samples were dispersed in distilled water with pH ≈ 6–7 by vigorous stirring and the less than 2 μm particle size fractions were collected by sedimenting under gravity. Then the collected montmorillonite was dried at 105 °C, ground in an agate mortar and passed through a 200-mesh
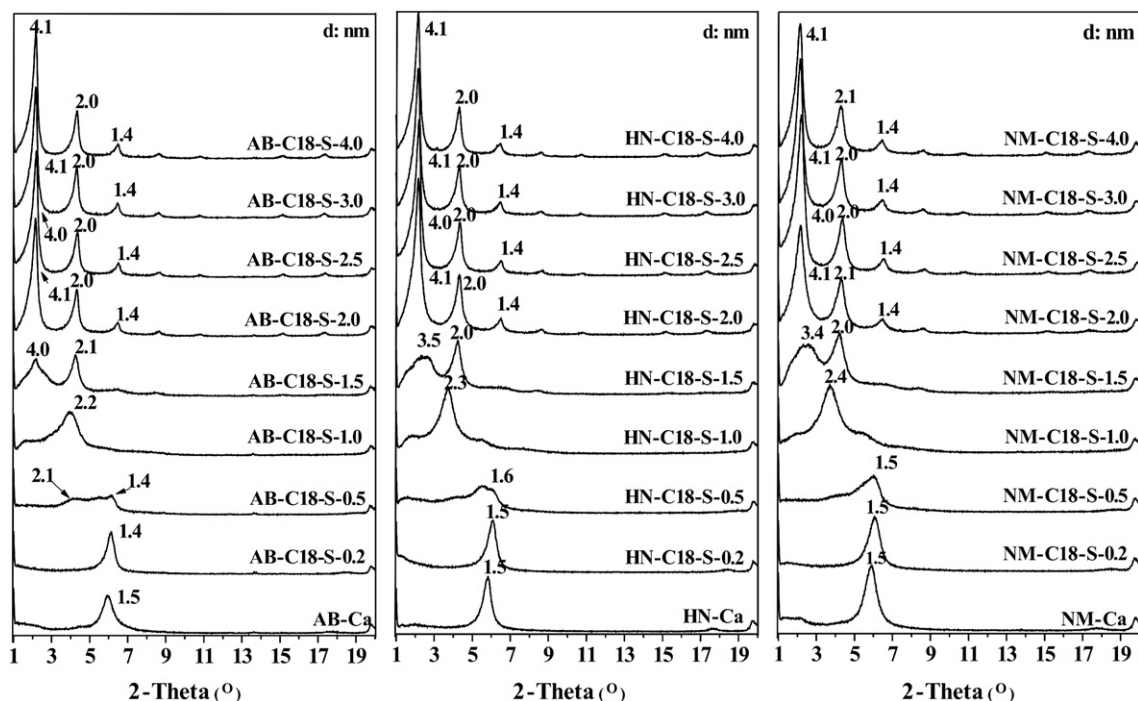
Fig. 1. XRD patterns of AB-Ca, HN-Ca and NM-Ca montmorillonites modified with C18-S surfactant.

sieve. The obtained samples were stored in a sealed bottle for further use. The cation exchange capacity (CEC), determined by adsorption of $[Co(NH3)6]^{3+}$ (Zhu et al., 2007) was 72.4 meq/100 g for AB-Ca, 88.8 meq/100 g for HN-Ca, and 106.5 meq/100 g for NM-Ca. The structural formulas for AB-Ca, HN-Ca and NM-Ca montmorillonites could be represented as $(Na_{0.02} K_{0.11} Ca_{0.17})[Al_{1.48} Fe_{0.10} Mg_{0.31}]Si_4 O_{10}$ $(OH)_2 \cdot nH_2O$, $(Na_{0.01} Ca_{0.19} Mg_{0.06})[Al_{1.44} Fe_{0.09} Mg_{0.47}][Si_{3.96} Al_{0.04}]O_{10}$ $(OH)_2 \cdot nH_2O$ and $(Na_{0.05} Ca_{0.18} Mg_{0.10})[Al_{1.58} Fe_{0.03} Mg_{0.39}][Si_{3.77} Al_{0.23}]O_{10}$ $(OH)_2 \cdot nH_2O$, respectively.

The surfactants (99% purity) are octadecyl trimethylammonium bromide (C18-S), dioctadecyl dimethylammonium bromide (C18-D), hexadecyl trimethylammonium bromide (C16-S), dihexadecyl dimethylammonium bromide (C16-D), dodecyl trimethylammonium bromide (C12-S), didodecyl dimethylammonium bromide (C12-D), tridodecyl methylammonium bromide (C12-T), octyl trimethylammonium chloride (C8-S), and bisoctyl dimethylammonium bromide (C8-D). C16-S and C8-S were purchased from Nanjing Robiot Co., Ltd., China, while the other surfactants were provided by Xiamen Pioneer Technology Co., Ltd., China.
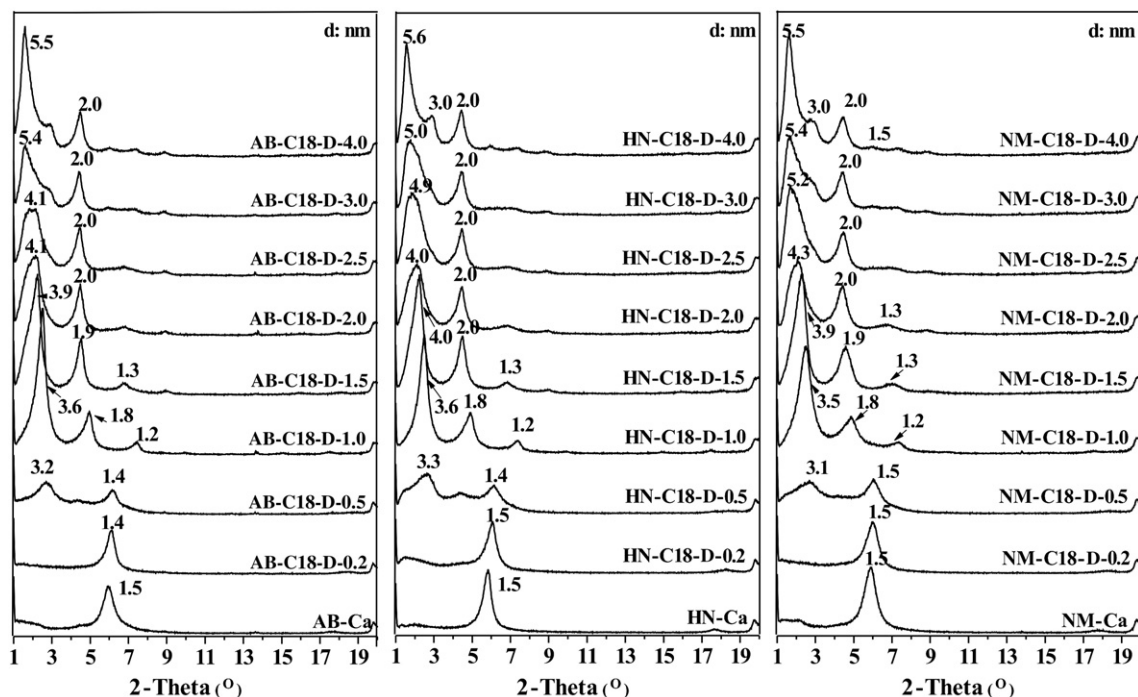

Fig. 2. XRD patterns of AB-Ca, HN-Ca and NM-Ca montmorillonites modified with C18-D surfactant.
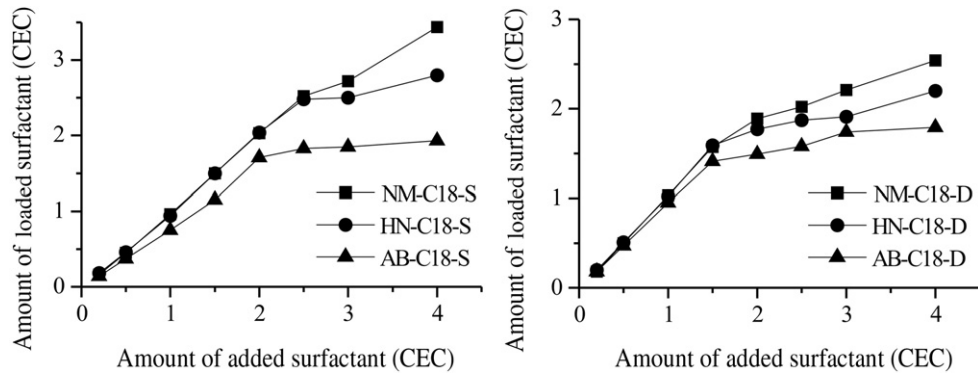
Fig. 3. Amount of loaded surfactant for AB-Ca, HN-Ca and NM-Ca montmorillonites modified with C18-S and C18-D surfactants.

2.2. Organo-montmorillonite synthesis and characterization

The different organo-montmorillonites were obtained by dispersing a calculated amount of surfactant in distilled water, stirring at 80 °C for 0.5 h, and slowly adding 20 g of montmorillonite. The amounts of surfactants were equivalent to 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 times the CEC of montmorillonite. The mass ratio of water/montmorillonite is 20:1. The reaction mixtures were stirred for 3 h at 80 °C. All products were washed 8 times with distilled water, dried at 60 °C, ground in an agate mortar and passed through a 200-mesh sieve. The organo-montmorillonite prepared by using NM-Ca montmorillonite and C18-S at a surfactant concentration of $0.5 \times$ CEC is marked as NM-C18-S-0.5 and the others are marked in a similar way.

Powder X-ray diffraction patterns (XRD) were recorded between 1° and 20° (2θ) at a step size of 0.0167° using a Bruker D8 Advance diffractometer with CuKα radiation (40 kV and 40 mA).

Thermogravimetric analysis (TG) was performed on a Netzsch STA 409PC instrument. About 20 mg of finely ground sample was heated in a corundum crucible from 30 to 1000 °C at a heating rate of 10 °C/min under a pure N_2 atmosphere (60 cm^3/min). The differential thermogravimetric curve was derived from the TG curve automatically. The surfactant loadings in the resultant organo-montmorillonites were determined by using TG curves in the temperature range of 200–500 °C.

3. Results and discussion

3.1. CEC and maximum basal spacing

Figs. 1 and 2 showed the XRD patterns of the organo-montmorillonites prepared from the three montmorillonites (AB-Ca, HN-Ca and NM-Ca) using the surfactants C18-S (single alkyl chain) and C18-D (double alkyl chains), respectively. The surfactant loadings of the resultant organo-montmorillonites were determined using the TG curves and shown in Fig. 3.

Table 1
Maximum basal spacings of the organo-montmorillonites when the added surfactants are 4.0 times CEC.

Montmorillonite		AB-Ca	HN-Ca	NM-Ca
CEC (meq/100 g)		72.4	88.8	106.5
d_{001} (nm)	C18-S	4.1	4.1	4.1
	C18-D	5.5	5.6	5.5
	C16-S	3.9	3.7	3.9
	C16-D	5.2	5.3	5.2
	C12-S	1.8	1.9	2.0
	C12-D	4.7	4.4	4.8
	C12-T	4.0	3.9	3.9
	C8-S	1.4	1.5	1.5
	C8-D	4.0	3.9	3.9

In accord with previous studies (Li and Ishida, 2003; Zhu et al., 2003), the basal spacing of the organo-montmorillonites increased with surfactant loading. When the amount of C18-S surfactant added was twice the CEC, the basal spacing reached a maximum of 4.1 nm
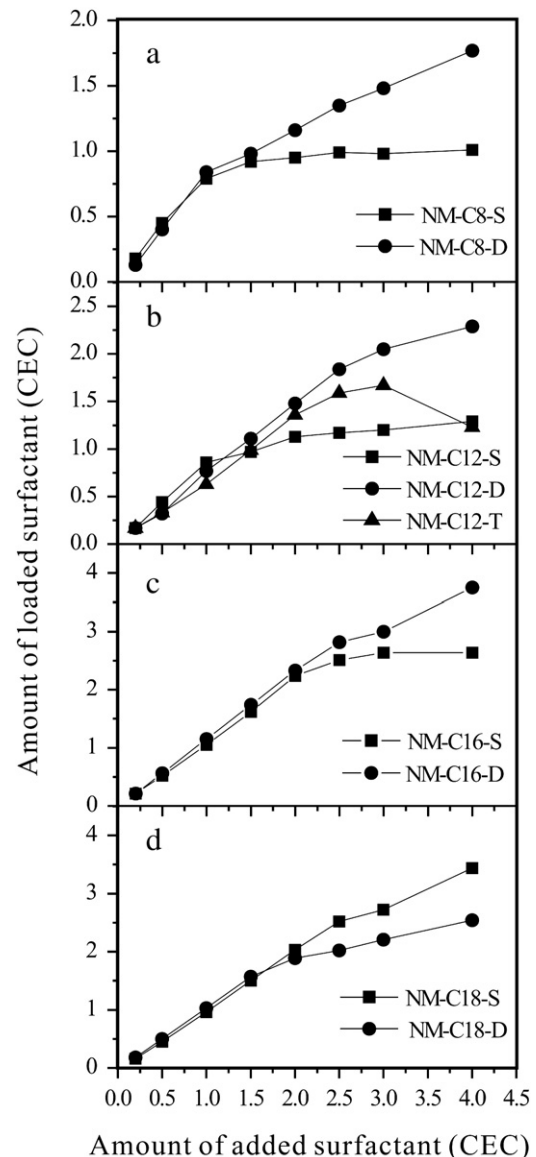

Fig. 4. Amount of loaded surfactant for NM-Ca montmorillonite modified with different surfactants.

(shown in Fig. 1). This value remained constant when the amount of surfactant added exceeded 2.0×CEC although the loading (amount of surfactant in the washed organo-montmorillonite) increased (Fig. 3). This observation indicates that the CEC of montmorillonite has little influence on the maximum basal spacing. We suggest that the amount of C18-S surfactant taken up beyond the added level of 2.0×CEC is largely contained in pores within the 'house-of-cards' structure (Lagaly and Ziesmer, 2003; He et al., 2006a) although some surfactants may be associated with the edge surface of montmorillonite particles (Lagaly, 2006).

Organo-montmorillonites prepared using surfactants with different alkyl chain numbers and chain length showed similar characteristics. Fig. 2 gave the XRD patterns of the organo-montmorillonites prepared from reacting AB-Ca, HN-Ca and NM-Ca montmorillonites with C18-D. The three series of organo-montmorillonites showed a maximum basal spacing at about 5.5 nm but the (00l) reflections were less well resolved than those of the corresponding C18-S organo-montmorillonites (Fig. 1). This might be because the interlayer stacking of the C18-D surfactant chains is less well ordered than that of C18-S.

Fig. 3 showed that organo-montmorillonites with a similar maximum basal spacing could have different amounts of loaded surfactant. Montmorillonite with a small CEC (AB-Ca) requires relatively less surfactant to reach its maximum basal spacing. That is to say, when the same surfactant is used, the CEC of montmorillonite has little influence on the maximum basal spacing. On the other hand, the amount of the loaded surfactant strongly depends on the CEC to reach the maximum basal spacing. This is very important to preparing low-cost organo-montmorillonites for industrial applications.

3.2. Alkyl chain number

Table 1 showed that the maximum basal spacings of montmorillonite modified with single alkyl chain surfactants were markedly lower than those of organo-montmorillonites with double alkyl chains. For example, the maximum basal spacing of organo-montmorillonites with C18-S (single alkyl chain) was 4.1 nm, while that of organo-montmorillonites with C18-D (double alkyl chains) was about 5.5 nm. In the case of C16 surfactant, increasing the alkyl chain number from single to double

caused the maximum basal spacing to increase from 3.9 to 5.2 nm. The corresponding values for C12 were from 2.0 to 4.8 nm, while those for C8 were from 1.5 to 3.9 nm.

Fig. 4 showed the amount of the loaded surfactants (loading levels) as a function of added surfactants for NM-Ca montmorillonite. When the maximum basal spacing was obtained (Figs. 1 and 2), there was an increase in surfactant loading as chain number increased from single to double in the case of C8, C12, and C16, but loading decreased in the case of C18 (Fig. 4). This suggests that surfactant configuration has a greater influence on basal spacing than surfactant loading. When a surfactant with three alkyl chains was used, the change in maximum basal spacing was very complex. For example, the basal spacing of NM-C12-T-4.0 was 3.9 nm while that of NM-C12-D-4.0 was 4.8 nm (Table 1 and Fig. 5), i.e., the organo-montmorillonite with a triple alkyl chain was less expanded than its double-chain counterpart. On the other hand, organo-montmorillonites prepared from C18-T had a larger basal spacing than those intercalated with C18-D (Zhou et al., 2007).

3.3. Alkyl chain length and surfactant loading

The effect of alkyl chain length and surfactant loading on the basal spacing of organoclays and arrangement of intercalated surfactants has been the subject of many investigations (Lagaly, 1981; Heinz et al., 2007; Zhu et al., 2007). In agreement with previous findings (Lagaly, 1981; Tamura and Nakazawa, 1996; Lagaly and Dekany, 2005), we observed that the basal spacing of the organo-montmorillonites generally increased with surfactant loading, while the maximum basal spacing increased as the alkyl chain length of the surfactant increased.

Organo-montmorillonites intercalated with single alkyl chain surfactants (CS-8, C12-S, C16-S and C18-S) showed broad to sharp basal reflections. The (maximum) basal spacings of organo-montmorillonites at 1.4–1.5 nm for C8-S (Fig. 6) and at 1.9–2.0 nm for C12-S (Fig. 5) were indicative of a lateral monolayer arrangement; that is, with the alkyl chain lying parallel to the montmorillonite layer (Lagaly, 1981; Zhu et al., 2003). For organo-montmorillonites intercalated with C16-S and C18-S, the basal spacings of 3.9 and 4.1 nm indicated a paraffin bilayer arrangement. Fig. 7 showed the variation in maximum basal spacings with amount of added surfactant for organo-montmorillonites prepared
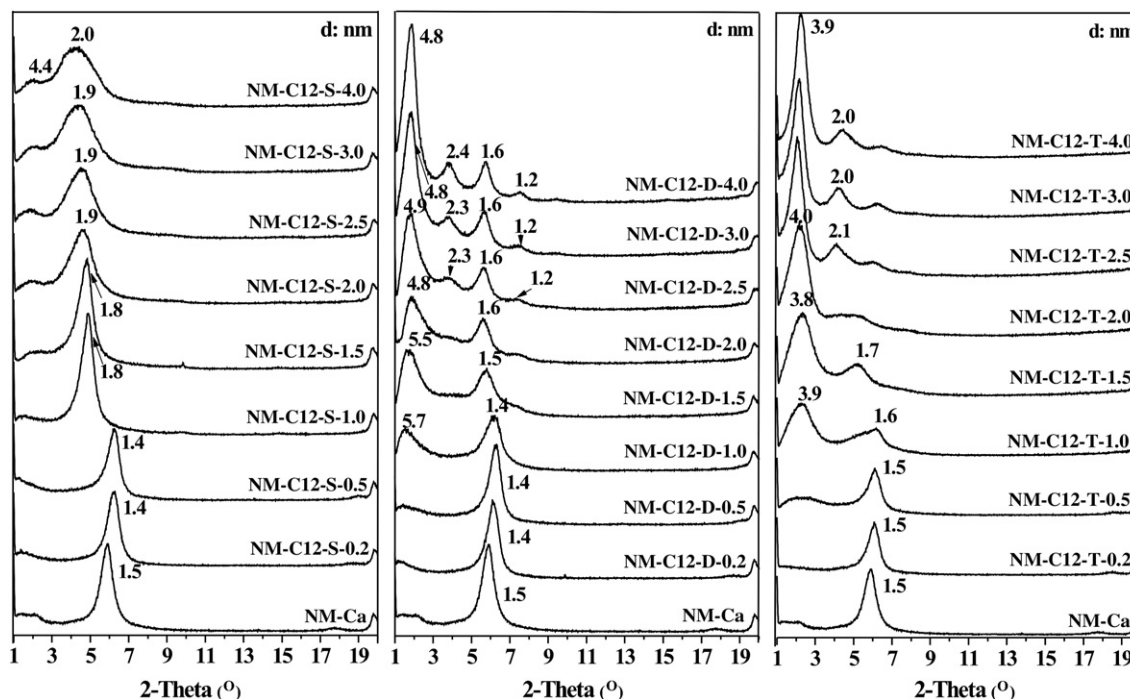

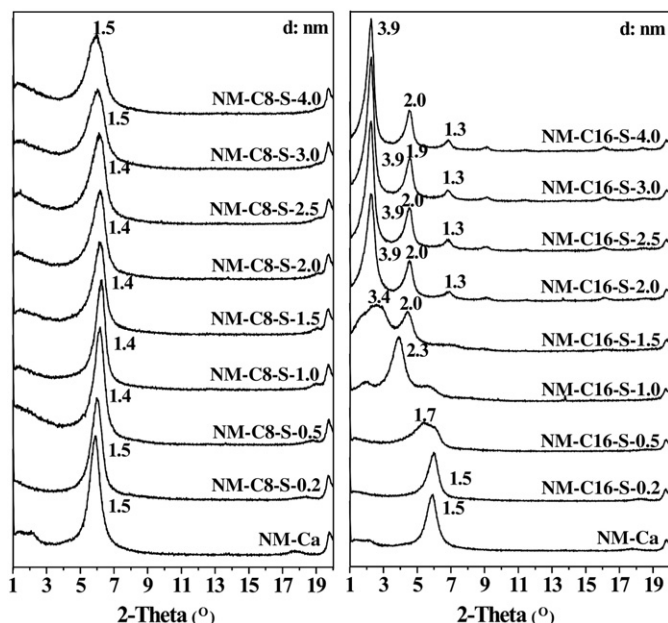Fig. 5. XRD patterns of NM-Ca montmorillonite modified with C12-S, C12-D and C12-T surfactants.

Fig. 6. XRD patterns of NM-Ca montmorillonite modified with C8-S and C16-S surfactants.

The DTG curve of NM-Ca was composed of two peaks at about 127 and 726 °C. The peak at 127 °C corresponded to surface-adsorbed water and water associated with the interlayer cations while that at 726 °C is due to structural water arising from dehydroxylation of the montmorillonite layers (Xie et al., 2002; Yariv, 2004; He et al., 2005; Hedley et al., 2007). For neat C18-S, the single peak at about 269 °C may be ascribed to its volatilization/decomposition (Xi et al., 2005a). Li and Jiang (2009) reported that the temperature at which intercalated surfactants decompose was higher than that of the corresponding bulk-state counterparts. Thus, the main peaks in the DTG curves of NM-C18-S-0.2 and NM-C18-S-0.5 at 413 and 419 °C, respectively, are presumably due to decomposition of the interlayer surfactants in accordance with the XRD results. At high surfactant loadings, another peak at 279–310 °C appeared in the DTG curves of organo-montmorillonites. This endotherm may be identified with surfactants located in the pores between-montmorillonite particles making up a 'house-of-cards' structure (He et al., 2006a). The thermal evolution of organo-montmorillonites prepared from C18-D was similar to that of their C18-S counterparts, and accorded with previous studies (He et al., 2005, 2006a). The ability of surfactants to enter interparticle pores of montmorillonite 'house-of-cards' aggregates is very important to using organo-montmorillonites as adsorbents of organic contaminants (He et al., 2006a).

from NM-Ca and single alkyl chain surfactants with different chain length. The basal spacings of organo-montmorillonites derived from surfactants with relatively short chain length (C8-S and C12-S) were markedly different from those of their counterparts with long chain length (C16-S and C18-S). Figs. 3 and 4 indicated that at low amounts of added surfactant (e.g., 0.2×CEC and 0.5×CEC), the alkyl chain of all four surfactants appeared to adopt a lateral-layer arrangement. At higher amounts of added surfactant, however, the alkyl chains of C16-S and C18-S might assume both a lateral- and paraffin-type layer structure (Vaia et al., 1994; Xi et al., 2005b). Thus, chain length has a significant effect on the basal spacing of the resultant organo-montmorillonites, and the interlayer arrangement of the surfactant.

The maximum basal spacings of the organo-montmorillonites were similar to those reported by He et al. (2006a). The level of loading can increase beyond the maximum basal spacing. Thus, the amount of surfactant taken up over and above the level required to give the maximum basal spacing, did not cause further layer expansion. Following Juang et al. (2002) and He et al. (2005, 2006a), we propose that at high loadings the surfactant cations/molecules not only enter into the montmorillonite interlayers but also occupy the interparticle pores within the 'house-of-cards' aggregate structure. This suggestion is further supported by the results of differential thermogravimetric (DTG) analysis of NM-Ca, neat C18-S and C18-D, and the resultant organo-montmorillonites (Fig. 8).
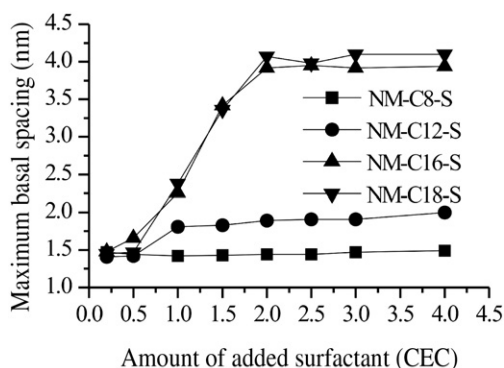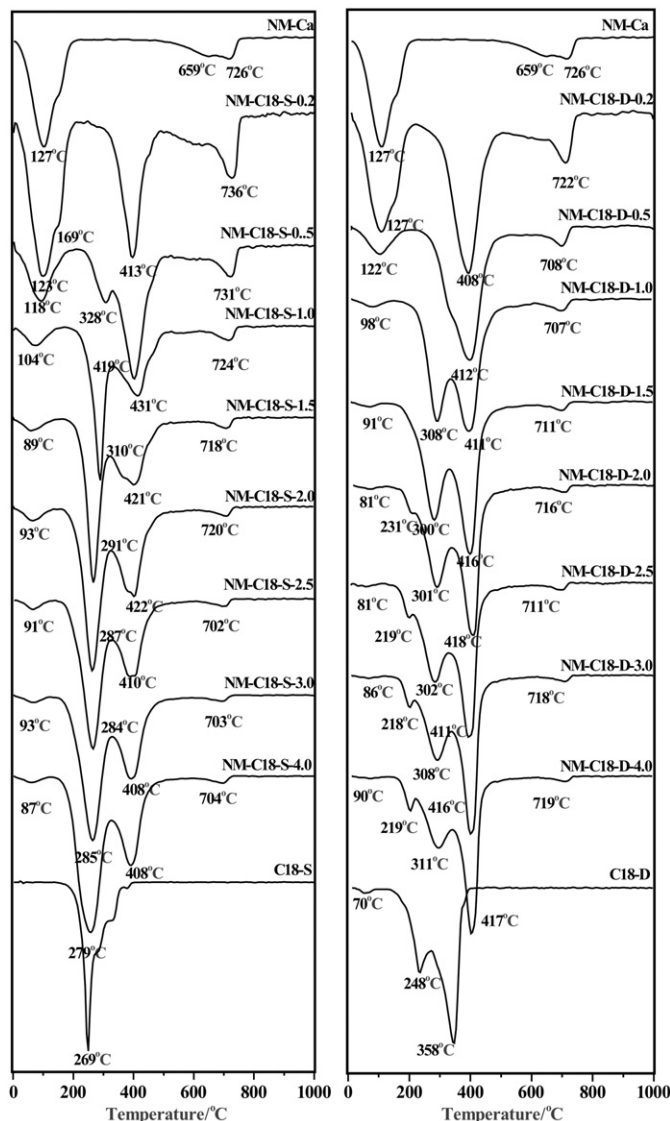

Fig. 7. Basal spacings of organoclays prepared from NM-Ca montmorillonite and different surfactants.

Fig. 8. DTG curves of NM-Ca montmorillonite modified with C18-S and C18-D surfactants.

4. Conclusions

We prepared organo-montmorillonites using montmorillonites with different cation exchange capacities (CEC) and surfactants with different alkyl chain numbers and chain length. The basal spacing increased with surfactant loading. The maximum basal spacing also increased with the alkyl chain length of the surfactant. For a given chain length, the maximum basal spacing increased as the chain number increased from one to two. The thermal analysis indicated that the surfactant is located in both the clay mineral interlayer spaces and the interparticle pores with a "house-of-cards" structure. For a given surfactant, the CEC of the montmorillonite component had little influence on the maximum basal spacing of the organo-montmorillonite when the same surfactant was used. The level of surfactant loading, however, strongly depended on the CEC. These findings are important and relevant to the preparation of low-cost organoclays for industrial applications.

Acknowledgement

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