



## Infrared investigation of organo-montmorillonites prepared from different surfactants

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### ARTICLE INFO

#### Article history:

Received 26 October 2009

Received in revised form 24 February 2010

Accepted 26 February 2010

#### Keywords:

Organo-montmorillonite

Surfactant loading

FTIR

Conformation

### ABSTRACT

In this paper, a series of organoclays were prepared from montmorillonites with different CEC and surfactants with different alkyl chain numbers and chain length. Then, FTIR spectroscopy using ATR, DRIFT and KBr pressed disk techniques was used to characterize the local environments of surfactant and host clays in various surfactants modified montmorillonites under wet and dry states. The present study demonstrates that the alkyl chain length and chain number have significant influences on the local environment of the intercalated surfactants. Also, this study indicates that the surface property of the resulting organoclays is affected by the loading and configuration of the intercalated surfactants. In wet state, more gauche conformers are introduced into the alkyl chains in the organoclays with low surfactant loading, evidenced by the shift of CH<sub>2</sub> vibration to higher frequency. Meanwhile, in the case of the organo-montmorillonites with high surfactant loading, the interaction between the surfactant and silicate surface results in a re-arrangement of SiO<sub>4</sub> tetrahedral sheets and a splitting of Si–O stretching vibration. The KBr pressed disk technique is suitable to probe the conformational ordering of the confined amine chains and the reflectance spectroscopy with ATR and/or DRIFT technique is more suitable to probe the water in organoclays. These findings are of high importance to the preparation of organoclays with proper surfactants and investigation of the microstructure of the resulting organoclays using suitable techniques.

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### 1. Introduction

The special parallel structure of the silicate layers in clays provides an ideal model for fundamental understanding of molecules in one-dimensional confined space [1]. The clay layers are negatively charged, which are counterbalanced by the exchangeable cations (e.g. alkali-metal Na<sup>+</sup> and alkaline-earth-metal Ca<sup>2+</sup>) in the interlayer space. Organoclays may be synthesized by ion exchange of the mono- or divalent cation (e.g. Na<sup>+</sup>, Mg<sup>2+</sup> or Ca<sup>2+</sup>) with organic cations such as quaternary ammonium cationic surfactants [2]. The properties of these materials change from hydrophilic to hydrophobic/lipophilic [3,4]. These modified minerals, organoclays, represent a family of materials which have a lot of applications in a range of key areas, such as adsorbents for organic pollutants [5,6], rheological control agents [7], reinforcing fillers for plastics [8] and electric materials [9,10]. The most widely used technique for studying intercalated materials in the silicate galleries is X-ray diffraction (XRD), which provides information on the layered structure and the basal spacing. The orientation of the

intercalated alkyl chain was indirectly obtained on the basis of the basal spacing, with the assumption that all the molecules have all-trans conformation [1,11,12]. However, the characterization results from Fourier transform infrared spectrometry (FTIR) [6,13–15], Raman spectroscopic [16] and nuclear magnetic resonance (NMR) [11,17,18] indicated that the intercalated surfactant indeed adopt both ordered (*all-trans*) and disordered (*gauche*) conformations. Furthermore, most studies proposed that, the frequency of the –CH<sub>2</sub> stretching absorption bands of alkyl chains is extremely sensitive to the conformational changes of the chains which is strongly dependent on surfactant loading [1,19,20]. And –CH<sub>2</sub> scissoring and rocking modes are also diagnostic because their broad singlets relate to either a liquid-like molecular environment or disordered hexagonal subcell packing [14], whereas the doublet detection requires an all-trans conformation [21]. However, some contrary phenomena also have been observed from FTIR in previous reports [15,22]. He et al. [13] proposed that this might relate to the used FTIR techniques, for example, the KBr pressed disk technique is more suitable to probe the conformational ordering than other techniques. As described in the literature, FTIR spectroscopy using various techniques has been used to investigate the local environments of adsorbed water [23–25] and loaded surfactants in organoclays [3,13,26]. The choice of the characterization methods

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depends on many factors, including the physical form of the sample, the information to be obtained (bulk versus surface analysis) or the effort and time required for sample preparation [25]. Especially, almost all previous studies [26–29] were conducted on dried powder sample. However, in some applications, the organoclays are used in solutions rather than in dried powder. The insights obtained from the dried powder cannot explain the performance of organoclays happening in wet state.

Hence, in this study, organoclays in both dry and wet states were investigated using FTIR spectroscopy. Meanwhile, to get more detailed information about the organoclays, various FTIR techniques were carried out, including attenuated total reflection (ATR), KBr pressed disk technique and diffuse reflectance (DRIFT) technique. The traditional method of KBr pressed disk technique was found to be useful for examining the conformations of the intercalated surfactants. And attenuated total reflection technique (ATR) was successfully applied to obtain information on the wet clay samples. According to the results, we found that when the surfactants intercalated into montmorillonite, both changes of the host clays and guest surfactants can occur such as the adsorbed water content on montmorillonites, the Si–O stretching of SiO<sub>4</sub> tetrahedron and the conformational changes of the surfactants intercalated in the galleries. Moreover, the surfactant concentration, the configuration of surfactant (chain length and number), the state of samples and various FTIR techniques are important factors to affect these changes.

## 2. Experimental

### 2.1. Materials

Ca-montmorillonites, obtained from Neimeng (Inner Mongolia), were denoted as NM-Ca. The cation exchange capacity (CEC) is 106.5 meq/100 g, determined by [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> method as described in the literature [19]. The surfactants used in this study are octadecyl trimethyl ammonium bromide (C18-S), dioctadecyl dimethyl ammonium bromide (C18-D), hexadecyl trimethyl ammonium bromide (C16-S), dihexadecyl dimethyl ammonium bromide (C16-D), dodecyl trimethyl ammonium bromide (C12-S), didodecyl dimethyl ammonium bromide (C12-D), octyl trimethyl ammonium chloride (C8-S), and bisoctyl dimethyl ammonium bromide (C8-D), with a purity of 99%. C16-S and C8-S were provided by Nanjing Robiot Co., Ltd., China, and the others were provided by Xiamen Pioneer Technology Co., Ltd., China.

### 2.2. Preparation of the organoclays

The syntheses of surfactant modified montmorillonites were performed as the following procedure: a desired amount of surfactant was first dispersed in distilled water and stirred at 80 °C for 0.5 h to form homogeneous liquor, into which then 20 g montmorillonite was slowly added. The concentrations of surfactants were 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 times CEC of montmorillonite, respectively. The mass ratio of water/clay is 20:1. The reaction mixtures were stirred for 3 h at 80 °C in a water bath. All products were washed for 8 times by distilled water, dried at 60 °C, and ground in an agate mortar. The organoclay prepared by using NM-Ca montmorillonite and C18-S at a concentration of 0.5 CEC was marked as NM-C18-S-0.5 and the others were marked in a similar way.

### 2.3. Infrared spectroscopy

The FTIR spectra were obtained on Bruker Vertex-70 Fourier transform infrared spectrometer. The KBr pressed disk technique was conducted to obtain transmission spectra. To get well-proportioned mixture, each sample was prepared with an

organoclay/KBr ratio of approximate 1:100, and ground in an agate mortar for 10 min. Then the mixture was heated under a lamp for 3 min to minimize the amount of the adsorbed water before making the disk. The spectra were collected over the range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

The reflectance spectra were recorded by using attenuated total reflection technique (ATR) technique and diffuse reflection technique (DRIFT). The powder or wet mash was placed on the diamond attenuated total reflectance smart accessory. The spectra were collected over the range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. And for DRIFT technique, MCT detector with the record range of 500–4000 cm<sup>-1</sup> was equipped.

## 3. Results and discussion

### 3.1. Investigation of alkyl quaternary ammonium in organoclays

Vibrational spectroscopy has been extensively used for probing the conformation in amine chain assemblies. Infrared spectroscopic studies have led to detailed correlation of the spectra with structural features such as chain conformation, chain packing, and even specific conformational sequences [15,29]. The position, line shape, and splitting of the methylene stretching and bending modes have been used to determine the conformation of methylene units in various phases of *n*-alkanes [13]. In this section, the correlation of –CH<sub>2</sub> vibrational spectra with surfactant loading, alkyl chain length, alkyl chain number and sample state would be discussed.

#### 3.1.1. CH<sub>2</sub> stretching vibrations

Figs. 1 and 2 show the –CH<sub>2</sub> vibrational spectra of the organo-montmorillonites modified by C16. The intense FTIR absorption bands at 2919 and 2851 cm<sup>-1</sup> are attributed to the antisymmetric ( $\nu_{as}(\text{CH}_2)$ ) and symmetric –CH<sub>2</sub> stretching ( $\nu_s(\text{CH}_2)$ ) modes. It is well established that the frequencies of the –CH<sub>2</sub> stretching bands of hydrocarbon chains are extremely sensitive to the conformational changes of the chains [1,30]. Only when the chains are highly ordered (all-trans conformation), the narrow absorption bands appear around 2918 ( $\nu_{as}(\text{CH}_2)$ ) and 2850 cm<sup>-1</sup> ( $\nu_s(\text{CH}_2)$ ) in the infrared spectrum. If conformational disorder is included in the chains, their frequencies shift upward, depending upon the average content of gauche conformers. As shown in Figs. 1 and 2, the position of these bands for NM-C16-S and NM-C16-D shifted to higher frequencies, indicating the introduction of gauche conformation in the alkyl chain. Conformational changes of the confined alkyl as a function of its concentration can be qualitatively monitored by the wavenumber shift [1,13,20,29,31]. With the increase of surfactant loading,  $\nu_{as}(\text{CH}_2)$  shifts from 2926 to 2919 cm<sup>-1</sup> and  $\nu_s(\text{CH}_2)$  shifts slightly from 2855 to 2851 cm<sup>-1</sup> for the specimens from NM-C16-S-0.2 to NM-C16-D-4.0. And for the organoclays prepared from C16-D, the shifts of antisymmetric and symmetric stretching modes are 4 cm<sup>-1</sup> (2923–2919 cm<sup>-1</sup>) and 1 cm<sup>-1</sup> (2852–2851 cm<sup>-1</sup>), respectively. In the high surfactant loading range, the frequency of both  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  for the confined alkyl chains keeps relatively constant. They are very close to the frequency of the pure surfactant. This suggests that, in this relatively high surfactant loading range, the confined surfactant chains adopt an essentially all-trans conformation. However, in the relatively low surfactant loading range, the frequency shifted significantly to high wavenumber, indicating that a large number of the gauche conformation is introduced into the alkyl chains. Meanwhile, both  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  for NM-C16-D with a slight shifts suggest that the double chain surfactant prefers to adopt highly ordered conformation when compared with single chain surfactant.

At the same time, it can be seen that the frequencies of both  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  increase with the decrease of alkyl chain

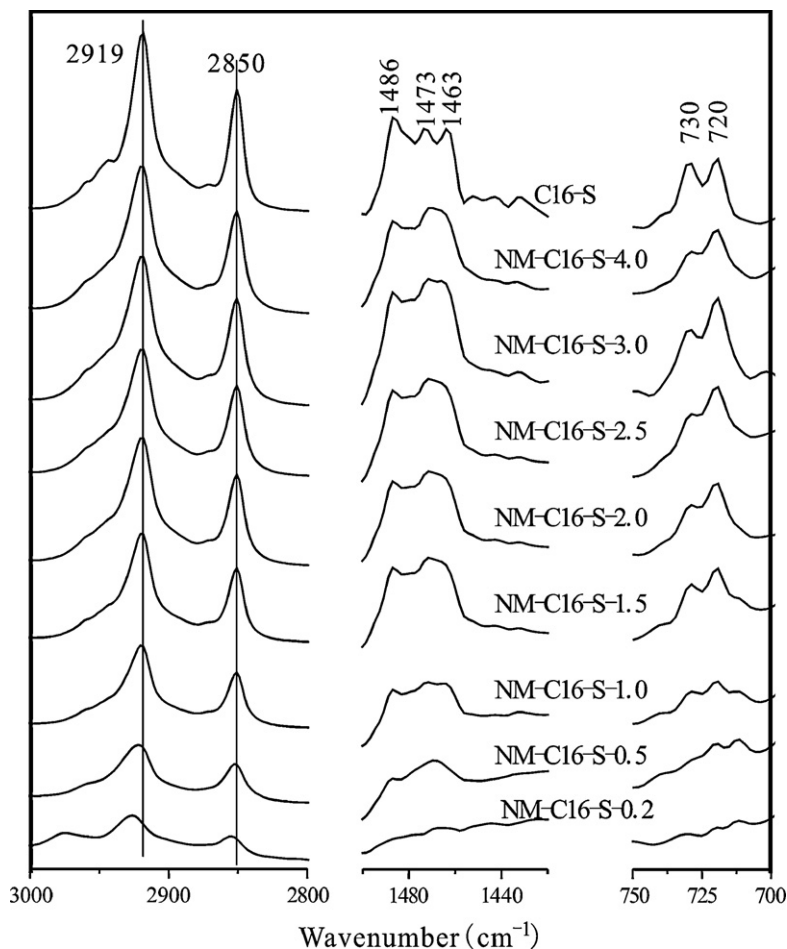


Fig. 1. The vibration spectra of  $\text{CH}_2$  in organo-montmorillonites prepared from C16-S (KBr pressed disk technique).

length as shown in Fig. 3. The  $\nu_{\text{as}}(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2)$  of the used pure surfactant (C8-S, C12-S, and C16-S) locate at ca. 2919 and 2850  $\text{cm}^{-1}$ . For the three series of organoclays (NM-C8-S, NM-C12-S and NM-C16-S), with the increase of surfactant loading, the maximum shifts of  $\nu_{\text{as}}(\text{CH}_2)$  are 2  $\text{cm}^{-1}$  (2930  $\rightarrow$  2928  $\text{cm}^{-1}$ ), 7  $\text{cm}^{-1}$  (2929  $\rightarrow$  2922  $\text{cm}^{-1}$ ) and 7  $\text{cm}^{-1}$  (2926  $\rightarrow$  2919  $\text{cm}^{-1}$ ), and those of  $\nu_{\text{s}}(\text{CH}_2)$  are 2  $\text{cm}^{-1}$  (2859  $\rightarrow$  2857  $\text{cm}^{-1}$ ), 3  $\text{cm}^{-1}$  (2856  $\rightarrow$  2853  $\text{cm}^{-1}$ ) and 4  $\text{cm}^{-1}$  (2855  $\rightarrow$  2851  $\text{cm}^{-1}$ ), respectively. When they were intercalated into montmorillonite, a significant frequency shift was observed, indicating more gauche conformational molecules introduced into alkyl chain with the decrease of alkyl chain length. The long alkyl chain within the gallery prefers to form a solid-like molecular environment, whereas the short alkyl chain to form liquid-like molecular environment.

Kung and Hayes [32] figured out the relative shifts of  $-\text{CH}_2$  vibrational energies can be used to assess the relative hydrophobic properties of the loaded surfactant, with lower energies reflecting a more structured and hydrophobic environment. The results mentioned above reflect that, the degree of the hydrophobic properties may be increased with the increment of surfactant loading, chain length and chain number. This deduction can be confirmed by the difference of  $-\text{CH}_2$  stretching vibration between dry and wet samples. Similar to the dry samples, when the amount of added surfactant increased, the alkyl intercalated into the silicate galleries via the change of liquid-like to solid-like in wet samples. Compared with the different surfactants, when the chain length is relatively short (e.g. C8 and C12), the frequency of the antisymmetric stretching mode of wet samples is higher than the dry ones. However, when the chain length reaches C16, the frequency of wet

samples is the same as dry ones at high surfactant loading, as shown in Fig. 4. Lagaly and Dekany [33] proposed that besides the liquid molecules that are strongly organized around the alkyl chains and on the bar silicate surface (composing the adsorption phase), an additional amount of liquid is taken up. These liquid molecules do not belong to the adsorption phase (i.e. they have bulk-like properties) and diminish the entropy loss of the system because they increase the conformational freedom of the alkyl chains (which are probably not in the all-trans conformation) and also the mobility of the liquid molecules [33]. At relatively high surfactant loading, most hydration cations were exchanged by surfactant cations, resulting in a decrease of the hydration water content and a surface property change from hydrophilic to hydrophobic. In this case, water molecules are difficult to be introduced into clay interlayer space and the gallery height is impossible to be expanded even if the montmorillonite particle was surrounded by abundance of water at the wet condition. This is strongly evidenced by the similar basal spacings of NM-C16-S series with high surfactant loading in wet and dry states (not shown).

### 3.1.2. $\text{CH}_2$ rocking and scissoring vibrations

The infrared absorption bands between 1480 and 1440  $\text{cm}^{-1}$ , due to the methylene scissoring modes, are quite similar to the methylene rocking modes at 750–700  $\text{cm}^{-1}$  in the position and shape of the bands (shown in Figs. 1 and 2). In the spectra of pure C16-S, doublets at 1473 and 1463  $\text{cm}^{-1}$  corresponds to the scissoring modes and those at 730 and 720  $\text{cm}^{-1}$  to the rocking modes, respectively. The splitting with 10  $\text{cm}^{-1}$  of the  $-\text{CH}_2$  scissoring and rocking bands is due to the intermolecular interaction

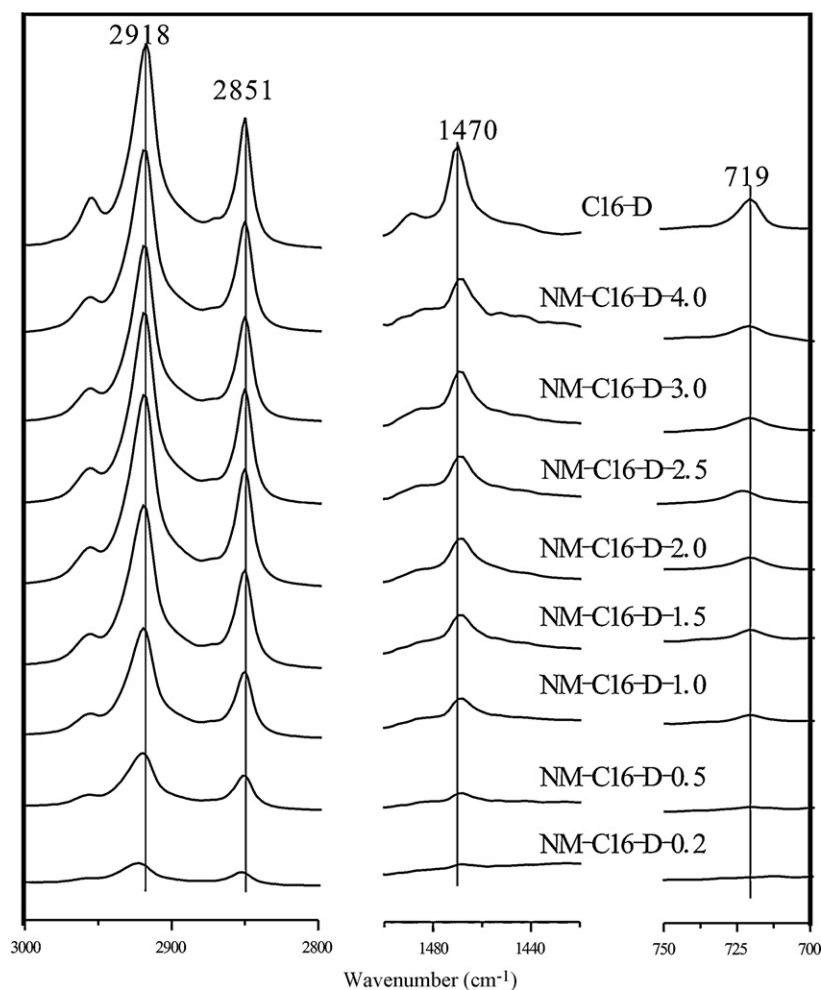


Fig. 2. The vibration spectra of  $\text{CH}_2$  in organo-montmorillonites prepared from C16-D (KBr pressed disk technique).

between the two adjacent hydrocarbon chains in a perpendicular orthorhombic subcell [34,35], and further requires an all-trans conformation for its detection [21]. When the alkyl intercalated into montmorillonite, doublets at  $1473$  and  $1463\text{ cm}^{-1}$  disappeared, which were substituted by a broad single band at  $1468\text{ cm}^{-1}$  for NM-C16-S-0.2 and NM-C16-S-0.5. With the increase of surfactant loading, the band splits again as described in the literature [14], but the intensity is weak. For the  $-\text{CH}_2$  rocking modes, when the loading is lower than 1 CEC, the FTIR spectra only display broad singlets at  $723\text{ cm}^{-1}$ , similar to  $-\text{CH}_2$  scissoring modes. However, with the further increase of surfactant loading, two well resolved

vibration bands at  $730$  and  $720\text{ cm}^{-1}$  were observed. This phenomenon is similar to those descriptions in previous researches [1]. Whether the doublets could be detected might be responsible to the used techniques. He et al. [13] pointed out that two well resolved absorption bands at  $730$  and  $720$ , and  $1473$  and  $1463\text{ cm}^{-1}$  were observed in FTIR spectra with KBr pressed disk technique while FTIR spectra obtained by ATR technique only display singlets at  $1468$  and  $720\text{ cm}^{-1}$ . This suggests that the KBr pressed disk technique is suitable to probe the conformational ordering of the confined amine chains within the clay galleries rather than ATR technique [13]. However, even if all the spectra shown in Figs. 1 and 2 were

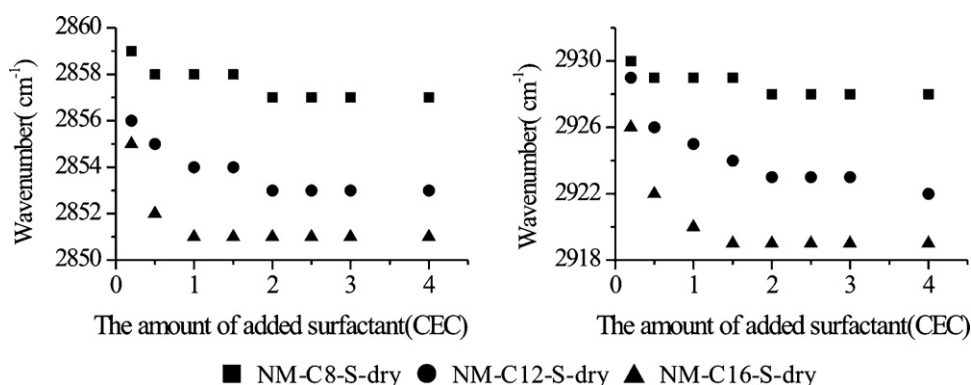
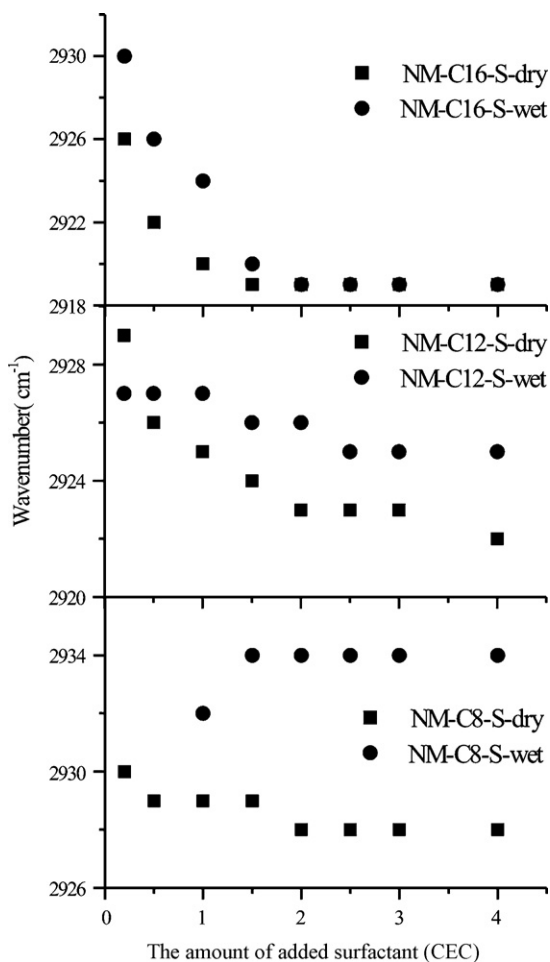


Fig. 3.  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  of organo-montmorillonites prepared from surfactants with different alkyl chain lengths (KBr pressed disk technique).

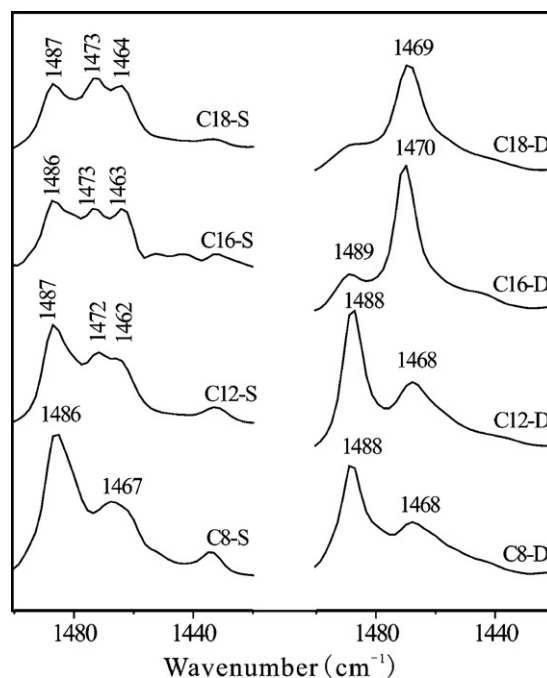


**Fig. 4.** Comparison of  $\nu_{as}(\text{CH}_2)$  in organo-montmorillonites prepared from surfactants with different alkyl chain lengths at dry and wet states (KBr pressed disk and ATR technique).

obtained using KBr pressed disk technique, for the organoclays modified by C16-D, there are no doublets observed for both  $-\text{CH}_2$  scissoring and rocking modes, instead of only single band occurring at 1469 and 721  $\text{cm}^{-1}$ . Especially, even for neat C16-D, only single bands at 1470 and 719  $\text{cm}^{-1}$  were recorded. To get more information, the FTIR spectra of the surfactants with different chain lengths and numbers were obtained using KBr pressed disk technique and displayed in Fig. 5. It is found that there are no doublets of  $-\text{CH}_2$  scissoring modes for the surfactants with double chain, as well as C8-S. The above results suggest that splitting of the methylene scissoring and rocking modes not only relates with the used investigation technique and surfactant loading, but also relates with the configuration of the used surfactants.

### 3.2. Investigation of water in organoclays

Spectral hydration features in montmorillonite have been attributed to structural OH in the octahedral layer, water adsorbed on the clay external surfaces and water adsorbed in the interlayer regions. The character of these interlayer water molecules is greatly dependent on the moisture level and the interlayer cation [25,36,37]. In this study, the spectra with KBr pressed disk technique mainly show a relatively weak band at 1630  $\text{cm}^{-1}$  corresponding to H–O–H bending vibrations and a strong band at ca. 3430  $\text{cm}^{-1}$  ascribed to adsorbed water (shown in Fig. 6a). And the frequency of these bands fluctuates with the increase of the surfactant loading. Due to KBr matrix is hygroscopic, absorption



**Fig. 5.** The spectra of  $\text{CH}_2$  scissoring mode for different surfactants (KBr pressed disk technique).

bands of water molecules adsorbed on KBr and those present in the montmorillonites overlap. Therefore, it is not possible to distinguish individual water vibrations in unheated samples [25] and assess the water content in organoclays. Here, we found that the reflectance spectroscopy with ATR and/or DRIFT technique is more suitable to probe the water in organoclays than the FTIR spectroscopy with KBr pressed disk technique. The reflectance spectra using ATR and DRIFT technique are shown in Fig. 6b and c. The spectra display more obvious absorption band at 3620  $\text{cm}^{-1}$  due to the OH stretching vibrations of structural OH groups and the frequency is independent on the surfactant loading, which is consistent with the result reported in the literatures [13,38]. In the region of 3100–3500  $\text{cm}^{-1}$ , the spectra show a broad band around 3400  $\text{cm}^{-1}$  corresponding to the overlapping symmetric  $\nu_1$  (H–O–H) and asymmetric  $\nu_3$  (H–O–H) stretching vibrations [25], and a shoulder around 3250  $\text{cm}^{-1}$  due to an overtone ( $2\nu_2$ ) of the bending mode [23,36]. The frequency of the band around 3400  $\text{cm}^{-1}$  gradually shifts to the lower frequency with the increase of surfactant loading, whereas the H–O–H bending vibration shifts from 1634  $\text{cm}^{-1}$  (NM-C18-S-0.2) to high frequency of 1649  $\text{cm}^{-1}$  (NM-C18-S-4.0). When the surfactants intercalated into the gallery of montmorillonites, the water bound directly to the hydrated cations was removed with the replacement of the hydrated cations by surfactant cations. Therefore, the detected absorption bands are mainly attributed to adsorbed water molecules especially at high surfactant loading. Simultaneously, with the intercalation of surfactants, the surface property of montmorillonite is modified, i.e. the hydrophilic surface of montmorillonite has been changed to hydrophobic. Hence,  $\text{H}_2\text{O}$  is not easy to be adsorbed by organo-montmorillonite [13]. This has been reflected in the vibration frequency shifts observed in the reflectance spectra.

### 3.3. Si–O stretching vibrations

When the surfactant intercalated into interlayer space of montmorillonites, the frequency change of the Si–O stretching band in the tetrahedral network was investigated. As seen from Fig. 7a, for the NM-Ca montmorillonite, the band in the region

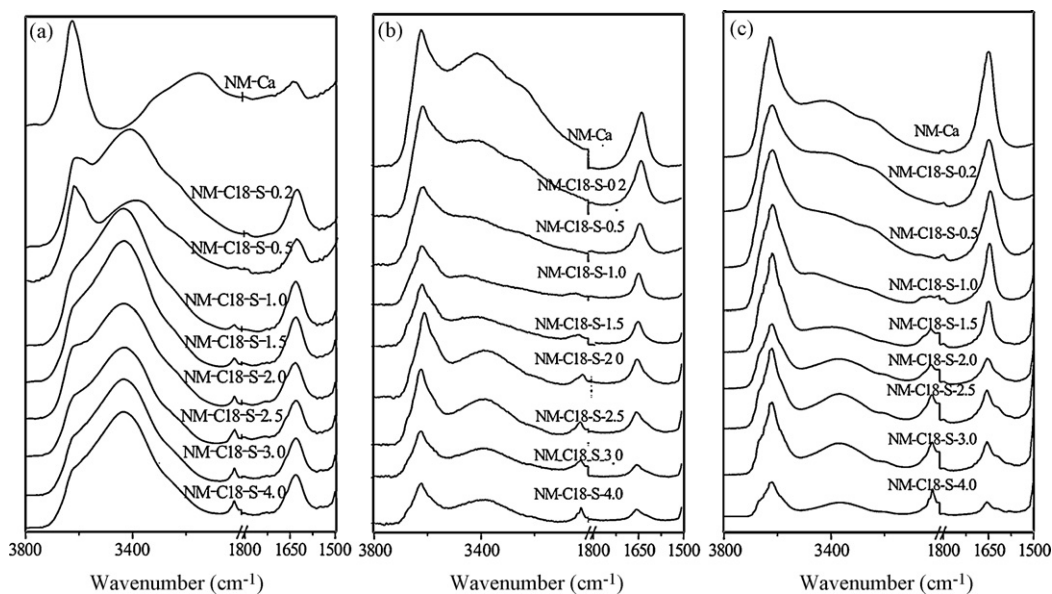


Fig. 6. The spectra of H–O–H stretching and bending vibrations (a: KBr pressed disk technique, b: ATR technique, and c: DRIFT technique).

of 950–1100  $\text{cm}^{-1}$  corresponding to stretching vibration of Si–O group splits into a sharp band at 1033  $\text{cm}^{-1}$  with a shoulder around 1088  $\text{cm}^{-1}$  attributed to perpendicular Si–O stretching [38]. However, for the organo-montmorillonites, the change of the band shape and its frequency strongly depend on the surfactant loading and alkyl chain length. For the organoclays prepared from C16-S with a low surfactant loading (e.g. 0.2 and 0.5 CEC), the shoulder at ca. 1088  $\text{cm}^{-1}$  is markedly reduced. With the increase of surfactant loading, the shoulder band was recorded again and shifted to

high frequency, from 1081  $\text{cm}^{-1}$  for NM-C16-S-1.5 to 1086  $\text{cm}^{-1}$  for NM-C16-S-2.0. When further increasing the surfactant loading, the frequency almost keeps unchanged. Fig. 8 shows that, when the length of surfactant was changed from C8 to C18, the band shifts to higher frequency and its intensity is increased. When the chain number increased from single to double, the band of perpendicular Si–O vibration was more prominent. The present study shows that the larger the interlayer space expanded, the more obvious the splitting of the Si–O vibration observed. This implies that the split-

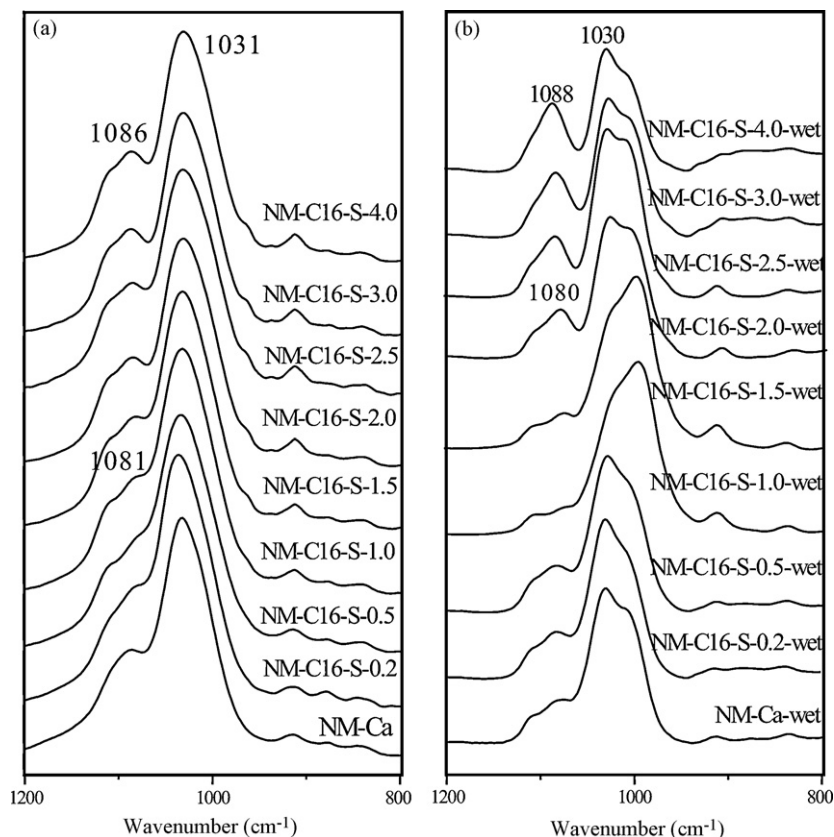


Fig. 7. The spectra of Si–O vibration in organo-montmorillonites prepared from C16-S (a: dry state and KBr pressed disk technique, b: wet state and ATR technique).

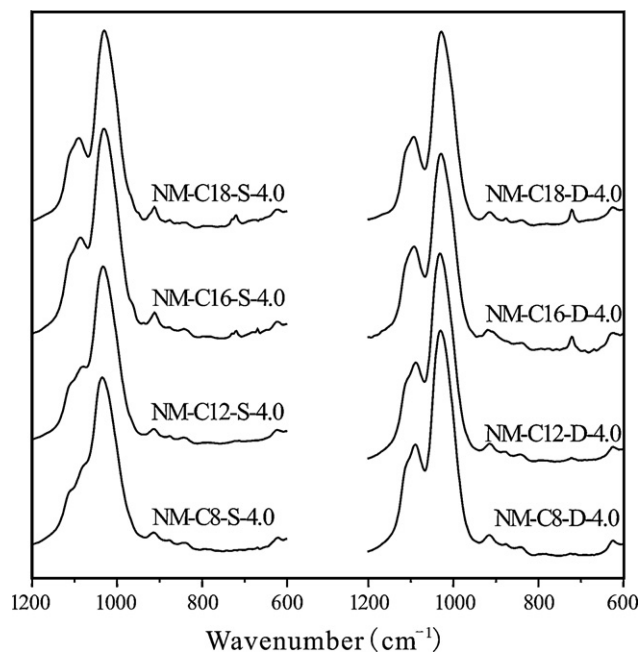


Fig. 8. The spectra of Si–O vibration in organo-montmorillonite prepared from different surfactants at 4.0 CEC (KBr pressed disk technique).

ting of Si–O stretching vibration is a consequence of the increase of the basal spacing. As reported in the literature [38,39], the intercalation of octadecylamine (as cation, or a neutral molecule) into the interlayer space is accompanied by a marked interlayer swelling, during which a perpendicular sorbate orientation is reached. In this way, the interlayer distance is markedly increased (similarly as in montmorillonite slurried with water), the orientation of the SiO<sub>4</sub> tetrahedral is changed, most probably towards a better ordered arrangement and more marked manifestation of the perpendicular Si–O vibrations.

However, compared with dry samples, there are some new insights of the Si–O vibration for wet samples. Fig. 7b shows the FTIR spectra of Si–O vibration of the organoclays prepared from C16-S. A dramatic increase of the shoulder intensity at ca. 1088 cm<sup>-1</sup> was observed. In the case of the organo-montmorillonites with relatively high surfactant loading (e.g. NM-C16-S-2.0), the perpendicular Si–O vibration shifts to a higher frequency. When the added surfactant was more than twice the CEC, the basal spacing reaches a maximum of 3.9 nm and keeps constant in XRD patterns (not shown). Therefore, the basal spacing is not an exclusive factor to affect the Si–O vibration. Xi et al. [3] proposed that the significant changes in Si–O stretching band suggest that there is an interaction between the surfactant molecules and siloxane (Si–O) surface. Thus, the different changes of Si–O stretching band between dry and wet samples are proposed as an increase of the interaction between the surfactant and silicate surfaces when organo-montmorillonites are in solutions.

#### 4. Conclusions

We have prepared organoclays using montmorillonites and surfactants with different alkyl chain numbers and chain lengths. The FTIR investigation of the samples at dry and wet state provides fundamental information on the changes of alkyl chain conformation, water content and orientation of the SiO<sub>4</sub> tetrahedron in the resulting organoclays. –CH<sub>2</sub> stretching (3000–2800 cm<sup>-1</sup>), scissoring (1480–1450 cm<sup>-1</sup>), and rocking (740–710 cm<sup>-1</sup>) modes are diagnostic for the conformation of the intercalated surfactants within the clay galleries. Both  $\nu_{as}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  shift towards

the frequency of the pure surfactant with the increase of surfactant loading within the montmorillonite galleries, indicating more and more all-trans conformational molecules are introduced into the alkyl chains and the molecular environment gradually changes from liquid-like to solid-like. The maximum shifts of the antisymmetric stretching mode are 2 cm<sup>-1</sup> (NM-C8-S), 7 cm<sup>-1</sup> (NM-C12-S) and 7 cm<sup>-1</sup> (NM-C16-S), respectively and the frequencies of the organoclays prepared from the surfactants with short chain length are higher than those from the surfactants with long chain length. This demonstrates that the alkyl chain length has significant influences on the local environment of the intercalated surfactants, as well as the alkyl chain number. In the FTIR spectra of the two series samples (NM-C18-S and NM-C16-S) with relatively higher surfactant loadings, two well resolved vibrations at 1473 and 1463 cm<sup>-1</sup>, and at 730 and 720 cm<sup>-1</sup> was observed. However, this splitting is absent in the organo-montmorillonites prepared from the surfactants with short chain and/or double chains, instead of singlets at ca. 1468 and 720 cm<sup>-1</sup>, respectively. This implies that the configuration of the used surfactant cannot be neglected when assessing the surfactant conformation. With the increase of the surfactant loading, the frequency of the  $\nu_2$  (H–O–H) mode shifts to higher frequency dramatically whereas the stretching vibration shifts to lower frequency slightly, indicating adsorbed water content decreases due to the surface property changed from hydrophilic to hydrophobic. Meanwhile, the intercalation of surfactant into the clay interlayer spaces has a significant influence on the arrangement of SiO<sub>4</sub> tetrahedral layers evidenced by the splitting of Si–O stretching vibration. This is due to the interaction between the surfactant and silicate surfaces. This present study shows that the KBr pressed disk technique is suitable to probe the conformational ordering of the confined amine chains within the clay galleries rather than ATR technique, and the reflectance spectroscopy with ATR and/or DRIFT technique is more suitable to probe the water in organoclays than that with KBr pressed disk technique. These new insights are of high importance for preparation and application of organoclays in industry.

#### Acknowledgements

We gratefully acknowledge financial support from the Knowledge Innovation Program of the Chinese Academy of Sciences (Grant No. KZCX2-yw-112), the National Science Fund for Distinguished Young Scholars (Grant No. 40725006), the grant of the National Natural Science Foundation of China (Grant No. 40673077) and the National High Technology Research and Development Program of China (Grant No. 2008AA06Z328). This is contribution No. IS-1171 from GIGCAS.

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