

Infrared study of HDTMA⁺ intercalated montmorillonite

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Abstract

In this paper, FTIR spectroscopy using attenuated total reflection (ATR) and KBr pressed disk techniques has been used to characterize sorbed water and HDTMA⁺ in organo-clay. Sorbed water content decreases with the intercalation of HDTMA⁺. With the decrease of the sorbed water content, the position of the ν_2 mode shifts to higher frequency dramatically while the stretching vibration shifts to lower frequency slightly, indicating that H₂O is less strongly hydrogen bonded. This might be resulted from the polarization of H₂O molecules by the changeable cations and HDTMA⁺. FTIR spectra show that both antisymmetric and symmetric CH₂ stretching absorption bands shift to low frequencies with increase of amine concentration within the galleries of montmorillonite, elucidating the increase of ordered conformation. Furthermore, the present study demonstrates that the antisymmetric CH₂ stretching mode is more sensitive to the conformational ordering than the symmetric stretching mode. When KBr pressed disk technique used, two well resolved absorption bands at 730 and 720 cm⁻¹, and at 1473 and 1463 cm⁻¹, corresponding to the methylene scissoring and rocking modes, respectively, could be observed in FTIR spectra of organo-clays with relative higher concentration of surfactant. However, the FTIR spectra using ATR technique only display singlets and they are independent of amine concentration and chain conformation. Our present study demonstrates that FTIR spectroscopy using KBr pressed disk technique is more suitable to probe the conformational ordering of surfactant in organo-clays than that using ATR technique does.

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1. Introduction

Montmorillonite is a kind of 2:1 type layered clay minerals and has been widely used in various branches of industry due to their high cation exchange capacity, swelling ability and high surface area. The hydrophilic surface of montmorillonite can be changed to hydrophobic by replacement of interlayer hydrated cations with various organocations. These modified minerals, organo-clays, represent a family of materials which have a lot of applications in a range of key areas, such as adsorbents for organic pollutants [1], rheological control agents [2], reinforcing fillers for plastics [3] and electric materials [4]. Various IR techniques have been used to study the interactions between clay minerals and organic molecules [5–7]. The best information on the molecular conformation was first obtained by Vaia

et al. [5] using FTIR and the main results are summarized as follows: (1) under most conditions, a disordered conformation (*gauche*) is more predominant than the ordered (*all-trans*) conformation. (2) Increasing the packing density, or the chain length, improves the ordering of the chains. (3) High temperature favors the disordered conformation. Furthermore, more recent studies [5,8] show that the conformational ordering strongly depends on amine concentration and orientation and the ordered (*all-trans*) conformation would be more predominant when amine chains radiate away from the layered materials surface in high amine concentration. In this case, two doublets at 1463–1473 cm⁻¹ and 720–730 cm⁻¹, corresponding to the methylene scissoring and rocking modes, respectively, should be observed. However, previous reports [5,8] only show singlets of the two vibration modes and they are independent of amine concentration, chain conformation and chain packing despite that the FTIR spectrum of the pure crystalline amine displays doublets. This experimental result seems to contradict with the conclusion that the confined amine chains

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adopt an essentially all-trans conformation in the relatively higher concentration range. Hence, to get more detailed information about the conformational ordering of confined amine chains, various FTIR techniques were used in the present study and two well resolved doublets corresponding to the scissoring and rocking modes were observed in the FTIR spectra when KBr pressed disk technique was used.

The influence of montmorillonite surfaces on the chemical and physical properties of adsorbed H₂O molecules has been the subject of a number of recent studies using structural, thermodynamic, spectroscopic and computational methods [9–13]. Generally, the position of the ν_2 mode of H₂O decreases and H₂O-stretching band shifts to higher wavenumber upon lowering the H₂O content in metal-exchanged montmorillonite. At the same time, the cation type is determinative for total water content retained in clay minerals [14]. However, to the best of our knowledge, there is no report about the sorbed H₂O molecules in organo-clays and it is very important for the application of organo-clays. Hence, the situation of the sorbed H₂O molecules in organo-clays at different amine concentration is discussed in this paper.

In this present study, both attenuated total reflection (ATR) and KBr pressed disk techniques have been used. ATR technique has been found to be useful to obtain information on the wet clay samples [14]. KBr pressed disk technique with the same amounts of organo-clays was also used to get the FTIR spectra and compare with those obtained by ATR technique in the ranges of 1463–1473 cm⁻¹ and 720–730 cm⁻¹, corresponding to the methylene scissoring and rocking modes, respectively.

2. Experimental

The montmorillonite (HM) was obtained from Hebei, China. The sample was purified by sedimentation and the <2 μ m fraction was collected and dried at 90 °C. The sample was ground through 200 mesh and sealed in a glass tube for use. As shown by XRD (Fig. 1), the collected montmorillonite contains a little illite and kaolinite, as indicated by the lack of intensity on the reflections at 1.01 and 0.72 nm. The cation exchange capacity was 57.9 meq/100 g. Its structural formula is [Na_{0.05}Ca_{0.18}Mg_{0.10}][Al_{1.58}Fe_{0.03}Mg_{0.39}][Si_{3.77}Al_{0.23}]O₁₀(OH)₂·*n*H₂O. The surfactant used in this study is hexadecyltrimethylammonium bromide with a purity of 99%.

The preparation of Na-montmorillonite (Na-Mont) was carried out by the following procedure. Ten grams of the mixture of montmorillonite and Na₂CO₃ in the ratio of 94:6 was added into 100 ml of deionized water and stirred at 80 °C for 3 h. Na-Mont was collected by centrifugation and washed with deionized water until the pH of the solution of Na-Mont was 7. The Na-Mont was dried at 90 °C, ground through 200 meshes and kept in a sealed bottle.

The syntheses of surfactant-clay hybrids were performed out by the following procedure. 2.5 g of Na-montmorillonite

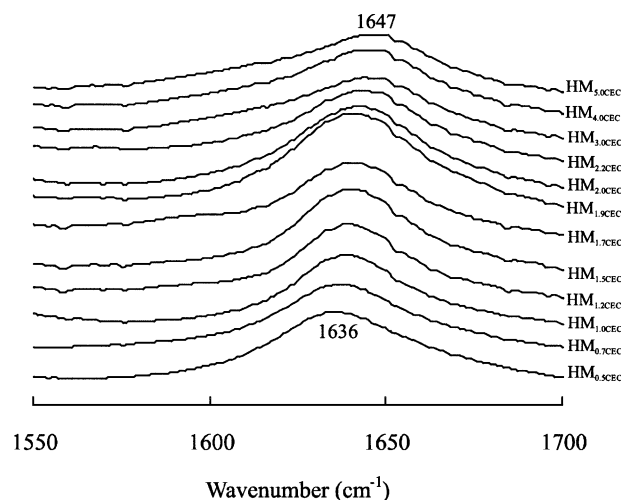


Fig. 1. FTIR spectra of the H–O–H bending region of H₂O (1600–1700 cm⁻¹).

was first dispersed in about 300 ml of deionized water and then a desired amount of hexadecyltrimethylammonium bromide was slowly added. The concentrations of HDTMA⁺ varied from 0.2 to 5.0 CEC of montmorillonite. The reaction mixtures were stirred for 10 h at 80 °C. All products were washed free of bromide anions, dried at 90 °C and ground in an agate mortar to pass through a 200 mesh sieve. The HDTMA⁺/montmorillonite hybrid prepared at the concentrations of 0.2 CEC was marked as HM_{0.2CEC} and the others were marked in the same way.

The FTIR spectra using ATR technique were recorded on Nicolet Nexus 870 Fourier transform infrared spectrometer with a diamond attenuated total reflectance (ATR) smart accessory. One hundred twenty-eight scans were collected for each measurement over the spectral range of 525–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

FTIR spectra using KBr pressed disk technique were conducted on Perkin–Elmer 1725X Fourier transform infrared spectrometer. For each sample, 0.9 mg organo-clay and 63 mg KBr were weighted and then were ground in an agate mortar for 10 min before making the pellets. The spectra were collected for each measurement over the spectral range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

3. Results and discussion

Our previous study [15] has shown that, with the increase of the concentration of surfactant, the arrangement of surfactant in the clay interlayer will vary from lateral-monolayer (0.5 CEC), to lateral-bilayer (0.7 CEC), then to paraffin-type monolayer (1.0–1.9 CEC) and last to paraffin-type bilayer (2.2–5.0 CEC). Accordingly, the packing density of surfactants within the montmorillonite galleries increases gradually and reaches a maximum in HM_{5.0CEC} as shown by TG analysis.

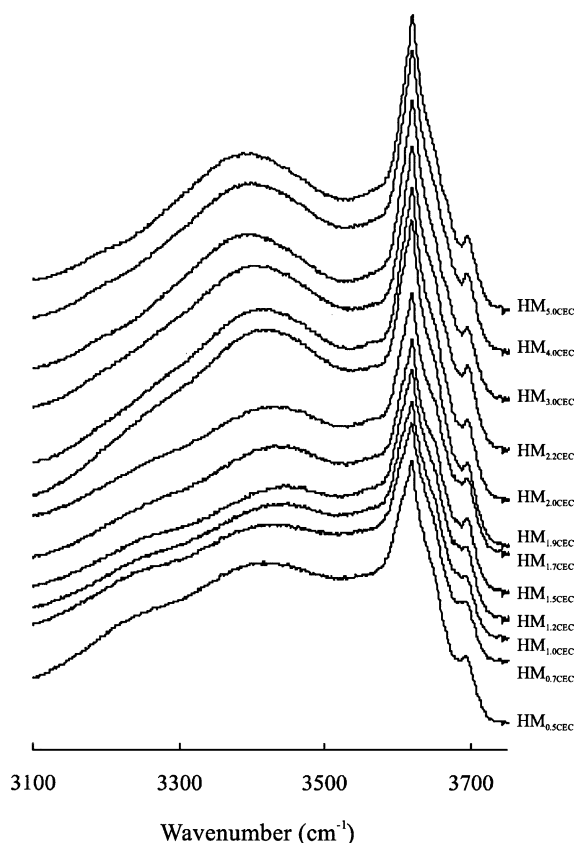


Fig. 2. FTIR spectra of the O–H stretching region of H₂O (3100–3700 cm⁻¹).

3.1. Sorbed water in organo-clays

The spectral regions of interest are the H–O–H bending region (Fig. 1) and OH-stretching region of H₂O (Fig. 2). Sorbed water contributes to the H–O–H bending region (1600–1700 cm⁻¹) and to the O–H stretching region (3100–3700 cm⁻¹). Fig. 1 shows the changes of the absorption band related to the ν_2 (H–O–H) bending vibrations of water molecules adsorbed on montmorillonite. The position of this band is gradually shifted from 1636 cm⁻¹ (for sample HM_{0.5}CEC) to 1647 cm⁻¹ (for sample HM_{5.0}CEC) with increase of surfactant concentration. Simultaneously, the intensity of this absorption decreases significantly. The decrease of the band intensity reflects that the amount of hydrogen bonded H₂O molecules present in the organo-clays with higher concentration of surfactant is less than those with lower concentration of surfactant. This could be explained by that the H₂O content is reduced with the replacement of the hydrated cations by HDTMA⁺ ions. 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, H₂O is not easy to be sorbed by montmorillonite except those coordinated H₂O molecules of cations in the interlayer. Those coordinated H₂O molecules are restricted in their ability to form hydrogen bonds with adjacent H₂O molecules [12].

Fig. 2 displays a sharp strong band at 3620 cm⁻¹ due to the OH stretching vibrations of the structural OH groups and a broad band at 3100–3550 cm⁻¹ due to sorbed water. The position of the sharp band corresponding to the OH stretching vibrations of the structural OH groups shows independent of the concentration of the surfactant whereas the broad band at 3100–3550 cm⁻¹ strongly depends on the concentration of the surfactant. At relatively low concentration of surfactant, the FTIR spectra of organo-clays display a broad absorption band near 3440 cm⁻¹ and a shoulder near 3250 cm⁻¹, corresponding to the overlapping antisymmetric ν_3 and symmetric ν_1 (H–O–H) stretching vibrations of H-bonded water [13] and an overtone ($2\nu_2$) of the bending mode of cation hydration water [16], respectively. At relatively high concentration of surfactant, the FTIR spectra only show one broad absorption band due to the stretching vibrations of H-bonded water and the band shifts to lower frequency.

With the decrease of H₂O content in montmorillonite, the frequency shift trends of the H–O–H bending and stretching vibrations of organo-clays in the present study are contrary to those of various metals exchanged montmorillonites in most literature [10,11,13,17], in which it was reported that the position of the ν_2 mode of H₂O decreases and H₂O-stretching band shifts to higher wavenumber upon lowering the H₂O content in metal-exchanged montmorillonite. Yan and et al. [10,11] interpreted the decrease in frequency of the ν_2 mode to a coupling between H₂O molecules and the Si–O stretching vibrations of the 2:1 layer through the formation of hydrogen bonds. The shift of the ν_2 mode to lower frequency, however, is not consistent with the observed frequency shift of the ν (OH) modes of sorbed H₂O reported here. Our results are similar to that reported by Xu et al. [12] and indicate that H₂O is less strongly hydrogen bonded at low-H₂O content. H₂O molecules clustered around exchangeable cations are polarized by the close proximity to the exchangeable cation with the oxygen of the H₂O directed toward the metal cation [12]. Furthermore, the intercalation of HDTMA⁺ will increase such polarization. Thus, a decrease in hydrogen bonding is consistent with isolated hydrated clusters of the residual metal cations within the montmorillonite galleries.

3.2. HDTMA⁺ in montmorillonite interlayer

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 [5,8]. 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.

Fig. 3 shows the FTIR spectra of the HDTMA⁺/montmorillonite composites in the range of 2800–3000 cm⁻¹. As shown in Fig. 3, the intensities of the two intense adsorption

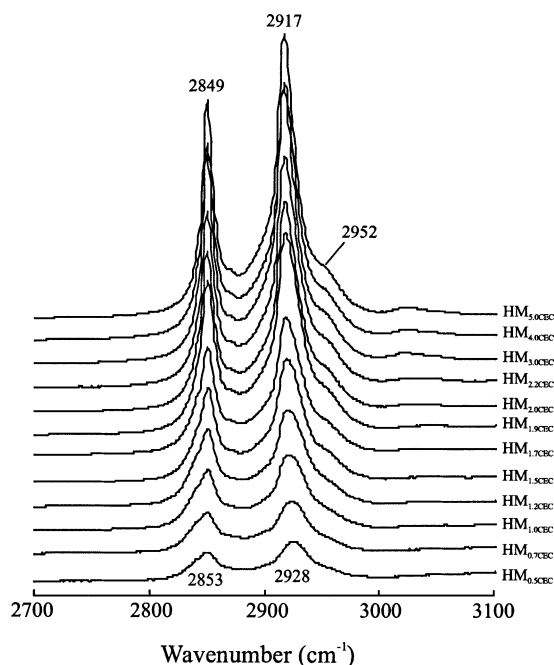


Fig. 3. FTIR spectra of the HDTMA⁺ intercalated montmorillonites at 0.5–5.0 CEC (2800–3000 cm⁻¹).

bands at 2916 and 2848 cm⁻¹, corresponding to the anti-symmetric and symmetric CH₂ stretching modes of amine, respectively, increase gradually with increase of the packing density of amine chains within the montmorillonite galleries. At the same time, the symmetric and anti-symmetric C–H stretching of the terminal –CH₃ groups appear at 2867 and 2952 cm⁻¹, respectively, as a function of the packing density of amine chains. This means that the intensity of the absorption bands strongly depends on the packing density of amine chains within the montmorillonite galleries.

The frequencies of the CH₂ stretching absorption bands of amine chains are extremely sensitive to the conformational changes of the chains [7,8,18,19] and only when the chains are highly ordered (all-trans conformation), the narrow absorption bands appear around 2916 (ν_{as}(CH₂)) and 2848 cm⁻¹ (ν_s(CH₂)) in the infrared spectrum [7].

The frequency and bandwidth of both anti-symmetric and symmetric CH₂ stretching modes for the confined amine strongly depends on the concentration of amine. In the high concentration range, the frequency of the anti-symmetric CH₂ stretching absorption band keeps relatively constant. They are close to the frequency of the pure amine. This means that, in this relatively high concentration range, the confined amine chains adopt an essentially all-trans conformation. However, in the relatively low amine concentration range, the frequency shifts significantly to high wavenumber, indicating that a large number of the gauche conformer is introduced into the amine chain. The wavenumber variation of the anti-symmetric CH₂ stretching absorption band is as much as 11 cm⁻¹ from 2928 cm⁻¹ for HM_{0.2}CEC to 2917 cm⁻¹ for HM_{5.0}CEC as shown in Fig. 3. However, for the sym-

metric CH₂ stretching absorption mode in the present study, there is only a slight shift from 2853 cm⁻¹ for HM_{0.2}CEC to 2849 cm⁻¹ for HM_{5.0}CEC. This means that the symmetric CH₂ stretching absorption mode is less sensitive to the amine chain conformation than the anti-symmetric CH₂ stretching absorption mode does.

The infrared absorption bands between 1475 and 1420 cm⁻¹, due to the methylene scissoring modes, are quite similar to the 735–715 cm⁻¹ methylene rocking modes in the disposition and shape of the bands. Doublets are observed for the pure crystalline HDTMA, similar to the previous reports [7]. These doublets appear at 1473 and 1463 cm⁻¹ for the scissoring modes and 730 and 720 cm⁻¹ for the rocking modes, respectively. The splitting of 10 cm⁻¹ of the CH₂ scissoring and rocking bands is due to the intermolecular interaction between the two adjacent hydrocarbon chains in a perpendicular orthorhombic subcell [20,21] and further requires an all-trans conformation for its detection [22]. Since both our present study and previous research [7,8] proposed that the confined amine chains adopt an essentially all-trans conformation in the relatively high concentration range, two doublets at 1463–1473 cm⁻¹ and 720–730 cm⁻¹, corresponding to the methylene scissoring and rocking modes, respectively, should be observed. However, both our FTIR study using (ATR) technique and previous studies [7,8] only display singlets at 1468 and 720 cm⁻¹ as shown in Fig. 4. The frequencies of the two bands are almost independent of the chain conformation while their intensities increase with the increase of the confined amine concentration. Venkataraman and Vasudevan [8] attributed the absence of the splitting bands to the weak interchain interactions while Li and Ishida [7] proposed that the alkyl tails of confined hexadecylamine are poorly packed within the silicate layers, i.e., the confined amine does not have the same three-dimensional order as the pure amine. Their suggestions can not explain the FTIR results for the organo-clays with higher concentration, in which the surfactant ions are highly ordered and adopt an essentially all-trans conformation indicated by the anti-symmetric and symmetric CH₂ stretching modes.

To get more information, KBr pressed disk technique was used in the present study. Fig. 5 shows the FTIR spectra of organo-clays at 1440–1480 cm⁻¹ and 700–750 cm⁻¹, corresponding to the CH₂ scissoring and the rocking modes, respectively. As shown in Fig. 5, both the FTIR spectra of the CH₂ scissoring and rocking modes strongly depend on the amine concentration, chain packing and conformational ordering. For sample HM_{0.5}CEC, which adopts lateral-monolayer for the arrangement of surfactant in the clay interlayer [15], the FTIR spectrum only displays broad singlets at 1472 and 723 cm⁻¹ for the CH₂ scissoring and the rocking modes, respectively. These broad single absorption bands are related to a liquid-like structure [7] and weak interchain interaction [8]. In other words, a number of disordered gauche conformers are introduced into the amine chains. The spectrum of sample HM_{0.7}CEC, which adopts

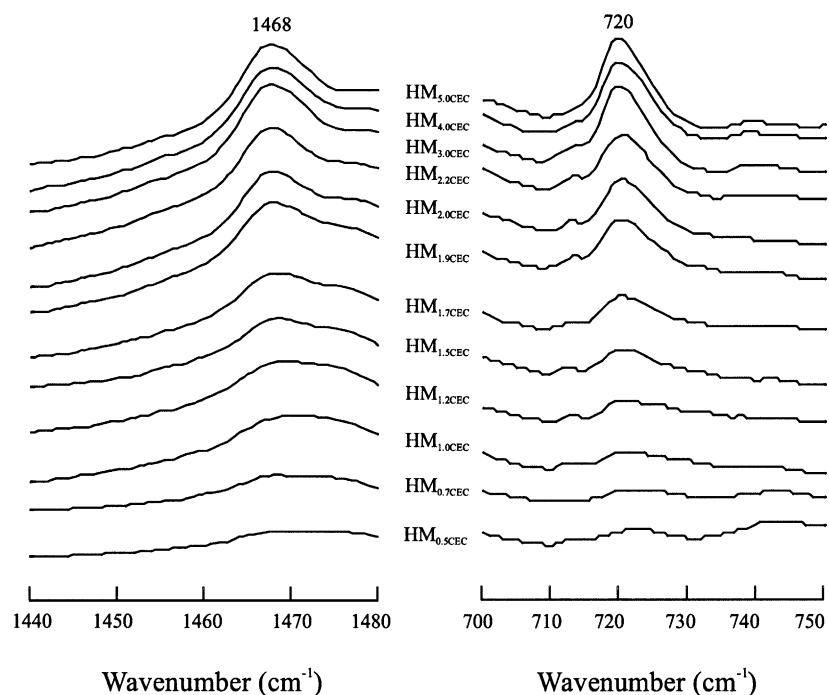


Fig. 4. FTIR spectra of the methylene scissoring and rocking vibrations for organo-clays (using ATR technique).

lateral-bilayer for the arrangement of surfactant in the clay interlayer, is similar to that of sample HM_{0.5}CEC. However, when the concentration is above 1.0 CEC, a shoulder occurs on the main absorption band at ca. 720 cm⁻¹ for the CH₂

rocking mode while the absorption band at ca. 1472 cm⁻¹, corresponding to the CH₂ scissoring mode, begins to split into two bands with similar intensity. And, with the further increase of surfactant concentration (especially for samples

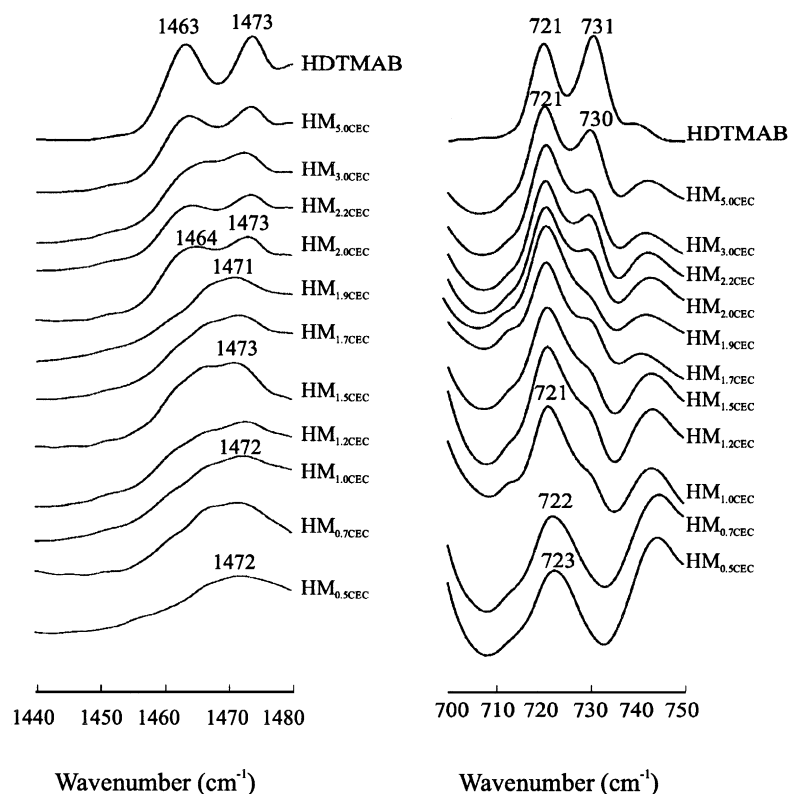


Fig. 5. FTIR spectra of the methylene scissoring and rocking vibrations for organo-clays (using KBr pressed disk technique).

adopt paraffin-type bilayer), two well resolved absorption bands at 730 and 720 cm^{-1} , and at 1473 and 1463 cm^{-1} , are observed, corresponding to the CH_2 rocking and scissoring modes, respectively. These modes are split due to interchain interaction between contiguous CH_2 groups of adjoining chains [21]. Here, we can find that the FTIR spectroscopy with KBr pressed disk technique is suitable to probe the conformational ordering of confined amine chains within the clay interlayers.

Casal et al. [21] proposed that the splitting of the CH_2 rocking and scissoring bands strongly depend on temperature and chain length, and the conformational disorder does not much affect the doubling of 1460 and 720 cm^{-1} bands. However, in the present study, only one kind of surfactant has been used and all the experiments are conducted at the same temperature. The chain packing of surfactants within the montmorillonite galleries is the only different thing for the series of organo-clays, which will result in the different chain conformation. As we know, for amine molecules confined within the silicate layers, they face the competition of interactions between the amine ions–silicate surface and the amine–amine ions. Theoretical calculation [23] and experimental results [24] indicate that the most important factors governing the conformational behavior of free *n*-alkanes are the nonbonded van der Waals interactions between the hydrogen atoms. Hence, in the sample with low amine concentration, the amine ions are parallel to the interlayer and individually separated [7]. The interaction among amine molecules is very weak. This dilution effect causes the formation of gauche conformers. However, the increase of amine concentration will result the increased interchain interaction and also restrict the room for the movement of the amine tail. This will lead to the increase of the number of the ordered conformers, reflected by the antisymmetric and symmetric CH_2 stretching modes in the region of 2800–300 cm^{-1} in the present and previous studies [7,8]. Also, Casal et al. [21] proposed that these modes are split due to interchain interaction between contiguous CH_2 groups of adjoining chains. Hence, based on our experimental result and the proposal in the literature, we can make the conclusion that the splitting of the CH_2 rocking and scissoring bands strongly depends on the conformational ordering of surfactants within the montmorillonite galleries, i.e., the splitting of the bands at 1460 and 720 cm^{-1} results from the increase of all-trans conformers. At the same time, our present study shows that the probing technique is very important as demonstrated in the present study: the FTIR spectra with ATR technique only show singlets at 720 and 1470 cm^{-1} whereas the FTIR spectra with KBr pressed disk technique show doublets at 1473 and 1463 cm^{-1} for the CH_2 scissoring mode, and at 730 and 720 cm^{-1} for the CH_2 rocking mode at higher surfactant concentration. In other words, the FTIR spectrum with KBr pressed disk technique is more sensitive to the conformational ordering than that with ATR technique does.

4. Conclusions

In this paper, FTIR spectroscopy using ATR and/or KBr pressed disk techniques has been used to characterize water and HDTMA⁺ in montmorillonite. Sorbed water content decreases with the intercalation of HDTMA⁺, resulted from the replacement of hydrated cations by HDTMA⁺ ions. The position and line shape of FTIR spectra corresponding to sorbed water are strongly depend on the water content residing within the interlayer. With the decrease of the water content, the shift of the ν_2 mode shifts to higher frequency dramatically while the stretching vibration shifts to lower frequency slightly, indicating that H_2O is less hydrogen bonded. This might be resulted from the polarization of H_2O molecules by the changeable cations and HDTMA⁺ ions.

FTIR spectra show that both antisymmetric and symmetric CH_2 stretching absorption bands shift to lower frequencies with increase of amine concentration within the galleries of montmorillonite, elucidating the increase of ordered conformation. Also, the present study demonstrates that the antisymmetric CH_2 stretching mode is more sensitive to the conformational ordering while both antisymmetric and symmetric CH_2 stretching modes show strong dependence on the amine concentration and orientation. FTIR spectra using ATR technique only display singlets at 1468 and 720 cm^{-1} due to the methylene scissoring and rocking mode, respectively, and they are independent of chain conformation. However, FTIR spectra using KBr pressed disk technique clearly show that the splitting of the scissoring and rocking absorption bands strongly depend on amine concentration and chain conformation. Two well resolved absorption bands at 730 and 720 cm^{-1} , and at 1473 and 1463 cm^{-1} could be observed in the samples with relative higher concentration of surfactant, in which the confined amine chains adopt an essentially all-trans conformation. Our present study demonstrates that FTIR spectroscopy using KBr pressed disk technique is more suitable to probe the conformational ordering of surfactant in organo-clays than that using ATR technique does.

Acknowledgements

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