

CONFORMATION OF SURFACTANT MOLECULES IN THE INTERLAYER OF MONTMORILLONITE STUDIED BY ^{13}C MAS NMR

HONGPING HE^{1,2,3,*}, RAY L. FROST², FENG DENG³, JIANXI ZHU^{1,3}, XIAOYAN WEN³ AND PENG YUAN^{1,3}

¹ Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China

² Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia

³ National Laboratory of Magnetic Resonance and Atom and Molecular Physics, Wuhan Institute of Physics, Chinese Academy of Sciences, Wuhan 430071, China

Abstract—The ordering conformation of surfactant molecules in intercalated montmorillonite prepared at various concentrations was investigated by ^{13}C MAS NMR. The ^{13}C MAS NMR study demonstrates the coexistence of ordered and disordered chain conformations. Two main resonance peaks are associated with the backbone alkyl chains: the resonance at 33 ppm corresponds to the ordered conformation (all-*trans*), and the resonance at 30 ppm corresponds to the disordered conformation (mixture of *trans* and *gauche*). Deconvolution of ^{13}C MAS NMR spectra indicates that the ordering conformation of surfactant molecules within the gallery of montmorillonite depends very much on their orientation and packing density. When amine chains are oriented parallel to the silicate layers, the amount of all-*trans* conformer decreases with the increase of amine concentration. However, the amount of all-*trans* conformer increases with the increase of amine concentration when amine chains radiate from the silicate layers. Furthermore, ^{13}C MAS NMR spectra show that the intercalated surfactant molecules in the clay minerals never attained the complete liquidlike or solidlike behavior.

Key Words— ^{13}C MAS NMR, Conformation, Montmorillonite, Surfactant.

INTRODUCTION

Clay-surfactant hybrids are employed in a wide variety of industrial and scientific applications, such as adsorbents for organic pollutants (Stackmeyer, 1991; Meier *et al.*, 2001), catalysts (Pinnavaia, 1983; Meier *et al.*, 2001), rheological control agents (Manias *et al.*, 1996), reinforcing fillers for plastics (Wang and Pinnavaia, 1998), electric materials (Wu and Lerner, 1993) and mesoporous materials (Wang *et al.*, 2000). In these applications, the behavior and properties of the organo/clay hybrids depend largely on the structure and the molecular environment of the organic molecules within the galleries.

The most widely used technique to characterize the clay-surfactant hybrids is X-ray diffraction (XRD), which gives the basal *d* spacing of the clay minerals in the hybrids. On the basis of XRD results, various models have been proposed for the molecular arrangement of the surfactant, including lateral monolayer, lateral bilayer, paraffin monolayer, paraffin bilayer and pseudotrilayer (Lagaly, 1981; Tamura and Nakazawa, 1996; Klapyta *et al.*, 2001; Yui *et al.*, 2002; Zhu *et al.*, 2003). However, XRD does not provide the detailed information on the local conformation of surfactant molecules. This information is critical for understanding the surfactant role in the formation of nanocomposites and the effectiveness of the surface treatment. Over the last decade, Fourier

transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) have been used in the study of the fine structure of the confined amine under different conditions (Vaia *et al.*, 1994; Venkataraman and Vasudevan, 2001; Barman *et al.*, 2003; Li and Ishida, 2002, 2003; Madejová, 2003). The detailed information on the molecular conformation was first obtained by Vaia *et al.* (1994) 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. However, recent studies show that the ordering of conformation 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 (Venkataraman and Vasudevan, 2001; Li and Ishida, 2003). The FTIR results are based on small vibrational-frequency variations assigned to absorption bands of the methylene groups on the surfactants. The decrease of frequency reflects the introduction of ordered conformation (all-*trans*) while a shift to high frequency is characteristic of disordered conformation (*gauche*).

Nuclear magnetic resonance (NMR) has been proven to be one of the most powerful techniques for probing structure and conformation (Gao and Reven, 1995; Badia *et al.*, 1996; Wang *et al.*, 1996, 2000; Venkataraman and Vasudevan, 2000). It has been shown that the carbon

* E-mail address of corresponding author:

hehp@gig.ac.cn

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atoms of *n*-alkanes gave a resonance at 30 ppm in solution where equilibrium populations of *trans* and *gauche* conformations exist, but in the crystalline solid a downfield shift of ~3–4 ppm is observed for an all-*trans* conformation (Earl and Vanderhart, 1979; Tonelli and Schilling, 1981). Gao and Reven (1995) have reported that well oriented monolayers display an intense peak at 33 ppm which is a characteristic ^{13}C chemical shift for the interior methylene carbons of the alkane chains in an all-*trans* conformation. Wang *et al.* (2000) reported the coexistence of ordered and disordered chain conformations in 1-octadecylamine/montmorillonite based on the study of two samples, fully ion exchanged and partially ion exchanged, respectively. Furthermore, the resonance at 33 ppm corresponds to the ordered conformation whereas that at 30 ppm corresponds to the disordered. To the best of our knowledge, the detailed ^{13}C magic angle spinning (MAS) NMR study of surfactant conformation within the surfactant/montmorillonite hybrids prepared at various concentrations has not been reported.

In this paper, the ordering conformation of surfactant molecules in intercalated montmorillonite at various concentrations has been investigated using ^{13}C MAS NMR. It is useful to understand the detailed conformation of surfactant in the organo/clay hybrids.

MATERIALS AND METHODS

The montmorillonite (HM) was obtained from Hebei, China. The sample was purified by sedimentation and the <2 μm fraction was collected and dried at 90°C. The sample was ground through a 200 mesh sieve and sealed in a glass tube. As shown by XRD (Figure 1), the montmorillonite contains minor illite and kaolinite, as indicated by the lack of intensity on the reflections at 1.01 and 0.72 nm. The cation exchange capacity (CEC) is 57.9 mEq/100 g and the structural formula is $[\text{Na}_{0.05}\text{Ca}_{0.18}\text{Mg}_{0.10}][\text{Al}_{1.58}\text{Fe}_{0.03}\text{Mg}_{0.39}][\text{Si}_{3.77}\text{Al}_{0.23}]\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. 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. 10 g of the mixture of montmorillonite and Na_2CO_3 in the ratio of 94:6 were added to 100 cm^3 of deionized water and stirred at 80°C for 3 h. The 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 mesh sieves and kept in a sealed bottle.

The syntheses of surfactant-clay hybrids were performed by the following procedure: 2.5 g of Na-mont were first dispersed in ~300 cm^3 of deionized water and then the desired amount of hexadecyltrimethylammonium bromide was added slowly. The concentrations of HDTMA $^+$ varied from 0.2 CEC 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 a concentration of 0.2 CEC was marked as HM $_{0.2\text{CEC}}$ and the others were marked in the same way.

The method of measuring the CEC of montmorillonite has been reported elsewhere (He *et al.*, 2001). X-ray diffraction (XRD) patterns were recorded between 1.5 and 20 $^\circ$ 2 θ at a scanning speed of 2 $^\circ$ /min, using Rigaku D/max-1200 diffractometer with $\text{CuK}\alpha$ radiation. All samples were analyzed as oriented films prepared by the evaporation of clay suspensions on glass microscope slides. The ^{13}C MAS NMR experiment was carried out with a Varian Infinity-Plus 400 NMR spectrometer with a 7.5 mm ZrO_2 rotator at room temperature. Spectra were collected using a single-pulse (SP) excitation Blochdecay method with a 4.5 μs (90 $^\circ$) ^{13}C pulse and a repetition delay of 70 s. Rotors were spun in air at 4.5 kHz. Spectral manipulation such as baseline adjustment, smoothing and normalization were performed using the spectral software package GRAMS (Galactic Industries Corporation, NH, USA). Peak component analysis was undertaken using the Jandel 'PEAKFIT' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Peak fitting was done

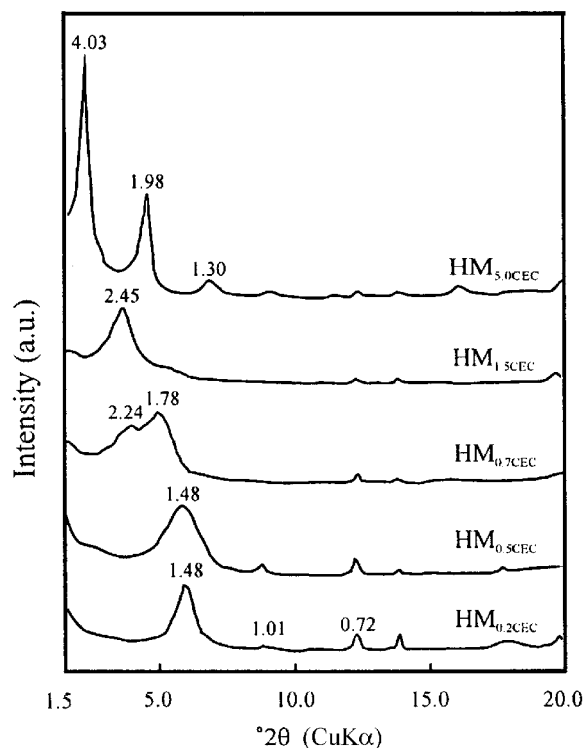


Figure 1. XRD patterns of HDTMA $^+$ /montmorillonite hybrids with surfactant concentration at 0.2, 0.5, 0.7, 1.5 and 5.0 CEC. Spacings in nm.

using a Lorentzian-Gaussian cross-product function with the minimum number of component peaks used for the fitting process. The Lorentzian-Gaussian ratio was maintained at values >0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of $R^2 >0.995$.

RESULTS AND DISCUSSION

Our previous study (Zhu *et al.*, 2003) has shown that, with the increase of the concentration of surfactant, the arrangement of surfactant in the clay interlayer will vary from lateral-monolayer, to lateral-bilayer, then to paraffin-type monolayer and finally to paraffin-type bilayer, based on their XRD patterns (Figure 1). 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 (not shown). However, it is difficult to obtain detailed information on the conformation of surfactant molecules in the interlayer of montmorillonite based on XRD results. ^{13}C NMR has proven to be a powerful technique for probing the conformation of surfactants in clay-surfactant hybrids. The ^{13}C resonance for long carbon-chain surfactant molecules is sensitive to the difference in conformation and packing in addition to the chemical structure.

Figure 2 shows single-pulse (SP) ^{13}C MAS NMR spectra of HDTMAB and the HDTMA⁺/montmorillonite hybrids prepared at various surfactant concentrations. The ^{13}C MAS NMR spectrum of crystalline HDTMAB exhibits one intense resonance at 33 ppm, indicating the methylene carbons of the alkane chains in all-*trans* conformation (Earl and Vanderhart, 1979; Tonelli and Schilling, 1981). However, an intense resonance at 30 ppm in addition to the shoulder centered at 33 ppm was recorded in the ^{13}C MAS NMR spectra of $HM_{0.2CEC}$ and $HM_{0.5CEC}$, corresponding to the disordered and the ordered conformation, respectively, based on the previous NMR spectrum assignment for surfactant/clay hybrids (Wang *et al.*, 2000). The resonances associated with the amine chain can be deconvoluted and quantified using two fitting peaks at 33 and 30 ppm. The area ratios of the ordered conformation at 33 ppm to the disordered conformation at 30 ppm are $\sim 32:68$ in $HM_{0.2CEC}$ and $20:80$ in $HM_{0.5CEC}$, respectively, indicating the coexistence of all-*trans* and *gauche* conformations. As shown by the XRD patterns (Figure 1), both $HM_{0.2CEC}$ and $HM_{0.5CEC}$ have the same basal *d* spacing of 1.48 nm. This value corresponds to an interlayer height (gallery height) of 0.51 nm, assuming the thickness of the montmorillonite's TOT layer to be 0.97 nm (Harris *et al.*, 1999). Therefore, it is reasonable to assume that in $HM_{0.2CEC}$ the surfactants adopt a lateral orientation as shown in Figure 3a. Here, it may be concluded that surfactants have a significant degree of *gauche* conformation in addition to a small amount of all-*trans*

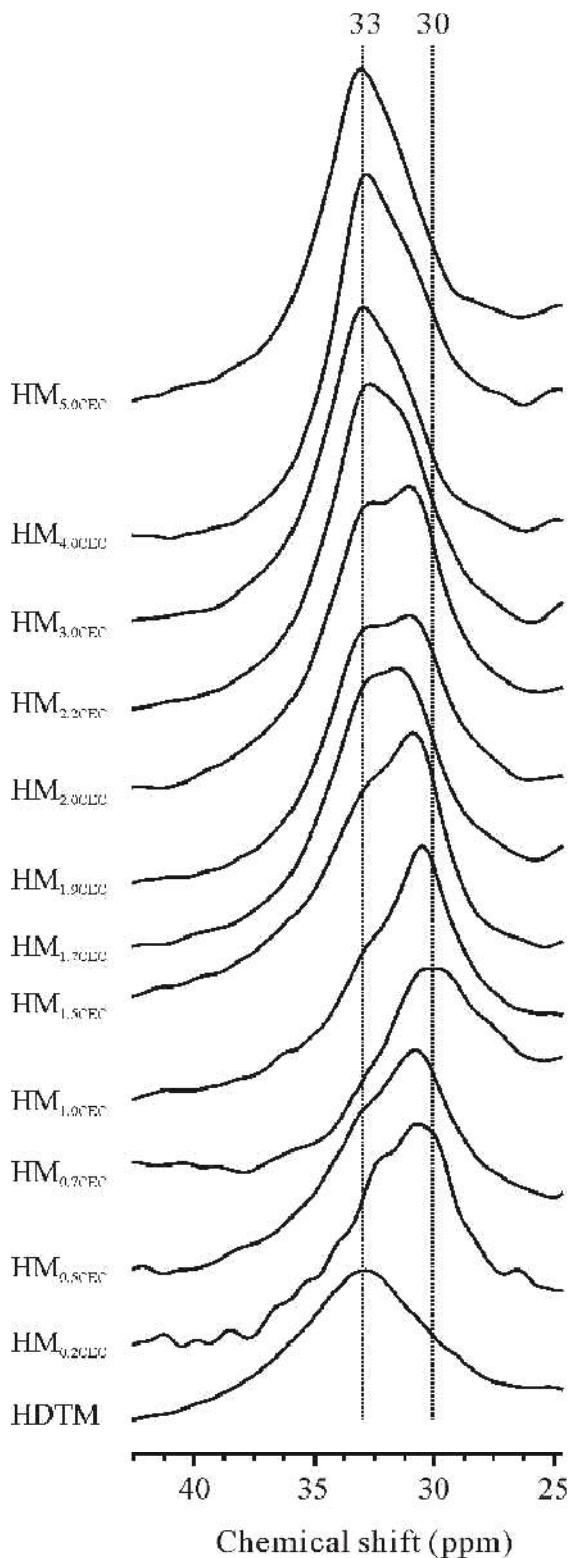


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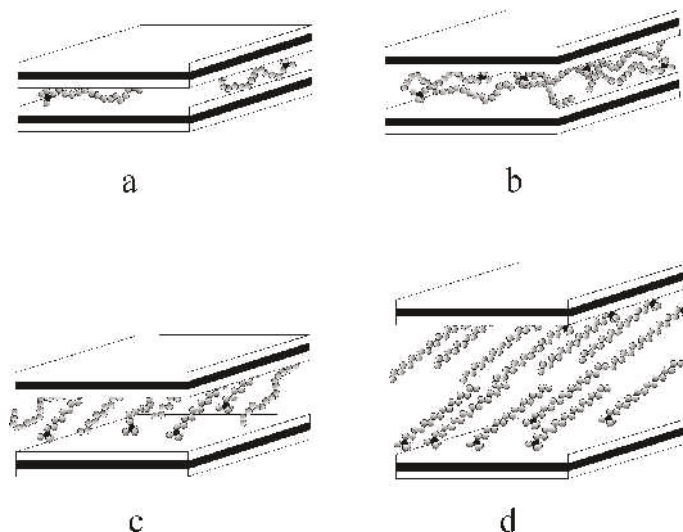


Figure 3. Schematics for alkyl-chain aggregation in the interlayer of montmorillonite: (a) lateral-monolayer; (b) lateral-bilayer; (c) paraffin-type monolayer; (d) paraffin-type bilayer. The single open circles (O) represent carbon atoms while nitrogen atoms in cationic head groups are represented by filled circles (●).

conformation in the lateral-monolayer of surfactants in the HDTMA⁺/montmorillonite hybrids. The conformation of HDTMA⁺ lateral-monolayers in the present study is quite different from the situation of octadecylsiloxane and octadecylphosphonate monolayers on non-porous silica (Gao and Reven, 1995). It was reported that well oriented monolayers display an intense peak at 33 ppm, the characteristic ¹³C chemical shift of the interior methylene carbons of the alkane chains in an all-*trans* conformation, in addition to a smaller component at 30 ppm corresponding to conformationally disordered chains. This reflects the surfactant molecules confined within the clay interlayer as distinct from some other environments.

For sample HM_{0.7CEC}, the XRD pattern displays an intense reflection at 1.78 nm in addition to a weak reflection at 2.24 nm (Figure 1). The two reflections indicate the interlayer heights of 0.82 nm and 1.27 nm, corresponding to the arrangements of lateral-bilayer (Figure 3b) and paraffin-type monolayer (Figure 3c), respectively, as proposed by Lagaly (1981). This indicates that amine chains begin to radiate away from the clay surface as shown in previous studies (Li and Ishida, 2002, 2003; Zhu *et al.*, 2003). The ¹³C MAS NMR spectrum of HM_{0.7CEC} displays a wide resonance centered at 30 ppm. The deconvolution shows that the area ratio of the ordered conformation at 33 ppm to the disordered conformation at 30 ppm is 6:94, indicating that the surfactants in the interlayer become more disordered.

As shown by the literature (Klapyta *et al.*, 2001; Li and Ishida, 2003) and our previous work (Zhu *et al.*, 2003), the chain orientation of the confined amine within the silicate galleries depends on the amine concentration. In the present study, the critical concentration for the orientation is ~0.7 CEC. Amine chains are parallel to the

clay surface below 0.7 CEC, whereas they radiate away from the clay surface above 0.7 CEC. Furthermore, in the concentration range of 0.7 and 2.0 CEC, amine chains adopt paraffin-type monolayer while amine chains adopt paraffin-type bilayer (Figure 3d) in the range 2.2–5.0 CEC (Zhu *et al.*, 2003). ¹³C MAS NMR spectra (Figure 2) show that the relative intensities for the resonances at 33 and 30 ppm change as a function of the packing density of the surfactants within the interlayer in the concentration range 0.7–5.0 CEC (Figure 4). As the packing density increases, the number of all-*trans* conformation increases. The area ratios of the ordered conformation at 33 ppm (all-*trans*) to the disordered conformation at 30 ppm (mixed *trans* and *gauche*) are ~1:1 for both HM_{1.9CEC} and HM_{2.0CEC}. With the further increase of surfactant concentration, the maximum peak intensity shifts to 33 ppm in HM_{5.0CEC} from 30 ppm in HM_{0.7CEC}, indicating that surfactant molecules are mostly ordered in HM_{5.0CEC}. The ¹³C MAS NMR spectra in the present study reveal that the number of all-*trans* conformations decreases with the increase of packing density for the lateral model whereas the number of all-*trans* conformations increases with the increase of packing density for the paraffin model. However, the intercalated surfactant molecules confined within montmorillonite interlayer never have the complete all-*trans* or *gauche* conformation, as indicated by ¹³C MAS NMR spectra.

When the amine chains of surfactants radiate away from the silicate surface, the conformational ordering information indicated by ¹³C MAS NMR spectra is similar to that shown by FTIR (Vaia *et al.*, 1994; Li and Ishida, 2003). However, for the surfactant/montmorillonite hybrids in which amine chains are oriented parallel to the silicate layer, the conformational ordering information indicated by ¹³C MAS NMR spectra in the

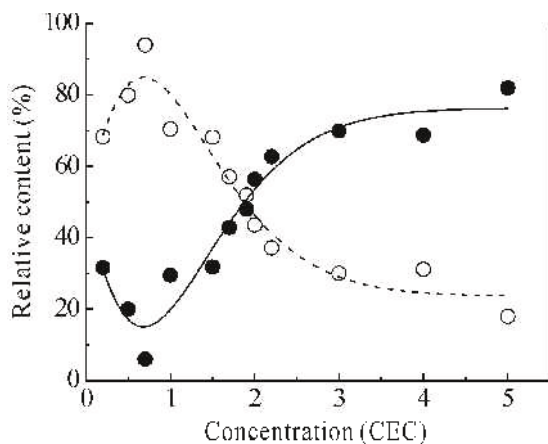


Figure 4. Change of the relative contents of the ordered (●) and the disordered (○) conformations as a function of amine concentration.

present study is quite different from that reported in the literature (Vaia *et al.*, 1994; Li and Ishida, 2003). It was reported that, when amine chains have orientation parallel to the silicate layers, a disordered *gauche* conformer is introduced to the chain with the amount of *gauche* conformer increasing as amine concentration decreases.

For amine molecules confined within the silicate layers, since the positive charge of the amine chain locates at the 'head' which holds three methyls, the 'head' of the amine will be fixed on the silicate surface through the electronic interaction between amine chain and the clay mineral. Meanwhile, they face the competition of interactions between the amine molecule–silicate surface and the amine–amine molecules. Theoretical calculation (Tasi and Mizukami, 1999) and experimental results (Okamura *et al.*, 1985) indicate that the most important factors governing the conformational behavior of free *n*-alkanes are the non-bonded van der Waals interactions between the hydrogen atoms. On the other hand, since the silicate surface of clay is relatively hydrophilic whereas the hydrocarbon chains of amine molecules are hydrophobic, the silicate surface–hydrocarbon chain interaction is of repulsive nature. Therefore, such repulsive force from the silicate surface would increase the mobility of amine molecules, resulting in an increased number of *gauche* conformers. The force between the silicate wall and the confined amine molecules is limited by the distance. Through computer simulation, Gupta *et al.* (1994) found that the surface effect is only restricted to the layer in contact with the surface. At the same time, the interaction among amine molecules is a function of amine concentration.

Hence, in a sample with very low amine concentration, *e.g.* sample HM_{0.2CEC}, the amine molecules are parallel to the interlayer and individually separated (Li

and Ishida, 2003). The interaction among amine molecules is very weak. This dilution effect causes the formation of *gauche* conformer. For sample HM_{0.5CEC}, in which the amine chains are still parallel to the interlayer, the interaction among the amine chains is obviously increased with the increase of the amine concentration within the interlayer. This kind of inter-chain interaction will introduce the *gauche* conformer into the amine chain. This is reflected by the increase of the signal at 30 ppm on the ¹³C MAS NMR spectrum.

Molecules have the tendency to take more ordered *trans* conformer and a more dense packing structure to minimize the energy (Li and Ishida, 2003). At the same time, previous study shows that the interaction among amine molecules is a function of amine concentration (Gupta *et al.*, 1994). Hence, when the concentration of surfactant increased, the increased interchain interaction competes with the silicate surface–amine chain interaction. When the interchain interaction among amine molecules overcomes the repulsive forces from the silicate surface, the orientation of the hydrocarbon tail changes from being parallel to radiating away from the silicate surface. As shown by the XRD pattern of HM_{0.7CEC} (shown in Figure 1), two broad basal reflections at 2.24 nm and 1.78 nm are observed, corresponding to paraffin-type monolayer and lateral-bilayer arrangements, respectively (Lagaly, 1981; Yui *et al.*, 2002; Zhu *et al.*, 2003). This indicates that there is a transitional stage between all the amine chains being parallel to and radiating away from the interlayer, despite the previous proposal of a sudden change from parallel to radiating away from the silicate surface (Li and Ishida, 2003). Hence, it is reasonable that a number of *gauche* conformers exist as indicated by ¹³C MAS NMR. Since the positive charge of the amine chain locates at the 'head' which holds three methyls, the 'head' will be fixed on the silicate surface through the electronic interaction between amine chain and the clay mineral when the tail of the amine chain radiates away. The amine tail with orientation radiating away from the silicate surface is rarely involved in the interaction between the silicate surface and amine chain, while the van der Waals forces among amine tails maintain the fully ordered *trans* conformation. At this stage, amine concentration may be the most important factor affecting the conformation of amine chains as indicated by the ¹³C MAS NMR result. However, even in the sample HM_{5.0CEC} with the most ordered conformation, there is still a proportion of disordered conformation as indicated by the deconvolution of the ¹³C MAS NMR spectrum. This may be due to the interaction between the amine head and silicate surface (Li and Ishida, 2003) and/or the insertion of methyl in the 'head' of amine chain into the silicate ring (Vahedi-Faridi and Guggenheim, 1997). In the latter case, since the methyl in the 'head' of the amine chain is keyed into the silicate ring and there is a tilt angle between the amine chain and the basal plane of

layer silicate, this will result in the variation of the forces acting on different parts of the amine chain, which are from the interactions between the amine molecule–silicate surface and the amine–amine molecules. The amine chains have to adjust their own conformation to reach a stable state. Accordingly, this sort of modification will introduce the *gauche* conformer into the amine chain.

In the present study, ^{13}C MAS NMR result shows that, generally, the ordering of conformation of amine chain within the galleries will be increased with the increase of surfactant concentration in spite of the slight difference indicated by ^{13}C MAS NMR in the present study and FTIR in a previous study (Li and Ishida, 2003) in the samples with a lateral orientation of surfactant. This difference may result from the different information they provide. The FTIR study provides an average estimate of conformational states and different molecular conformations lead to the breadth of the absorption band while the two NMR resonances at 30 and 33 ppm are associated with backbone methylene groups with two distinct structures of the nearest chemical repeat unit (Holler and Callis, 1989; Wang *et al.*, 2000).

CONCLUSIONS

The ordering conformation of surfactant molecules in intercalated montmorillonite at various concentrations has been investigated using ^{13}C MAS NMR and XRD. The ^{13}C MAS NMR result is not only complementary to that of FTIR but also give new insights into the conformational ordering of the surfactants in the interlayer of montmorillonite. The ^{13}C MAS NMR study demonstrates the coexistence of ordered and disordered chain conformations. Two main resonance peaks are associated with the backbone alkyl chains: the resonance at 33 ppm corresponds to the ordered conformation (all-*trans*), and the resonance at 30 ppm corresponds to the disordered conformation (mixture of *trans* and *gauche*). The deconvolution of ^{13}C MAS NMR spectra indicates that the ordering conformation of surfactant molecules within the gallery of montmorillonite depends very much on their orientation and packing density. When amine chains have orientation parallel to the silicate layers, the amount of all-*trans* conformer decreases with the increase of amine concentration. However, the amount of all-*trans* conformer increases with the increase of amine concentration when amine chains radiate from the silicate layers. Furthermore, the intercalated surfactant molecules in the clay minerals never attain the complete liquid-like or solid-like behavior.

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