

## INTERLAYER CONFORMATIONS OF INTERCALATED DODECYLTRIMETHYLAMMONIUM IN RECTORITE AS DETERMINED BY FTIR, XRD, AND TG ANALYSES

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**Abstract**—Intercalation of a wide variety of alkylammonium cations into the interlayer spaces of swelling clay minerals leads to many different applications, ranging from surface-charge measurements to rendering the clay compatible for the preparation of clay nanocomposites, but knowledge of the exact conformation of the intercalated organic species is still incomplete, thus preventing a full understanding of this process. The purpose of this study was to investigate the interlayer conformation of dodecyltrimethylammonium (DDTMA) bromide in rectorite as affected by the amounts of DDTMA intercalated, using a battery of physical and spectroscopic methods. The capacity of rectorite to intercalate DDTMA was equivalent to 1.67 times the cation exchange capacity (1.67 CEC) of the mineral even though the initial input was as much as 5.00 CEC. When the DDTMA intercalated was <0.50 CEC of the mineral, minimal counterion sorption was associated with DDTMA intercalation. Derivative thermogravimetric (DTG) analyses revealed a single-peak decomposition temperature ( $T_{\text{peak}}$ ) at 430°C. X-ray diffraction (XRD) analyses indicated a flat-lying monolayer of the intercalated molecules, while shifts in Fourier Transform infrared (FTIR) bands confirmed *gauche* conformation. These results suggested that cation exchange was the dominant mechanism. At the maximum intercalation, the DDTMA adopted a horizontal trilayer arrangement with mainly *gauche* conformation as determined by FTIR and XRD. Meanwhile a second  $T_{\text{peak}}$  appeared at 255°C, similar to the  $T_{\text{peak}}$  of solid DDTMA. Counterion bromide sorption accompanying DDTMA intercalation reached a capacity of 310 mmol/kg. The results indicated that van der Waals interaction was responsible for the DDTMA uptake at the amount beyond 0.50 CEC. When the amount of DDTMA intercalated was between 0.5 and 1.67 CEC, the XRD patterns showed non-integrality, *i.e.* the 002 reflection was split into two non-integral peaks with  $2 \times d_{002} < d_{001}$  and  $3 \times d_{003} > d_{001}$ . They became integral at 1.67 CEC. The results suggest that the mineral might be composed of mixed layers of a monolayer intercalated rectorite and a trilayer intercalated rectorite, without a bilayer as intermediate, when the amount of DDTMA intercalated was between 0.5 and 1.67 CEC.

**Key Words**—DDTMA, FTIR, Intercalation, Organo-clay, TG, XRD.

### INTRODUCTION

Studies of the intercalation of organic molecules into swelling clays have, to date, mainly focused on two different aspects: the first geared toward the determination of layer charges of clay minerals (Lagaly *et al.*, 1976; Ruehlicke and Kohler, 1981; Mermut and Lagaly, 2001); and the second concentrating on elucidation of the mechanism of intercalation (Vaia *et al.*, 1994; Xu and Boyd, 1995; Lee and Kim, 2003; Xi *et al.*, 2004; He *et al.*, 2004; Lee *et al.*, 2005; Xue *et al.*, 2007). Conflicting results have often been found because of different foci. For the purpose of layer-charge determination, the clays were reacted with an aqueous solution of primary *n*-alkylammonium salts at initial input much greater than the cation exchange capacity (CEC) of the minerals, and the excess organic cations were removed by washing with a mixture of alcohol and water (Mermut

and Lagaly, 2001). The intercalated alkylammonium could adopt a flat-lying monolayer, bilayer, trilayer, or even tilted paraffin-like conformation depending on the chain length of the organic molecule (Lagaly *et al.*, 1976). The  $d_{001}$  spacing reported for a high-charge montmorillonite, SAz-1, after intercalation with organic cations that had 16 carbons on the tail group was only 18.0 Å (Mermut and Lagaly, 2001). On the contrary, with excess organic cations, the same montmorillonite SAz-1 expanded to 40 Å after intercalation with hexadecyltrimethylammonium (HDTMA) in the amount corresponding to 2.5 CEC (Lee *et al.*, 2005). In contrast to the large differences found for SAz-1, a low-charge Wyoming montmorillonite, SWy-2, expanded to 17.6 Å after intercalation with *n*-alkylammonium, with C16 as the tail group (Mermut and Lagaly, 2001), and to 20 Å after intercalation by HDTMA (Lee *et al.*, 2005). These contradictions indicate that an investigation of the interlayer conformations of intercalated organic cations in clays as affected by the actual amounts intercalated is necessary.

The conformations of intercalated organic cations may be determined by several methods. Measuring the

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$d_{001}$  spacing by means of X-ray powder diffraction (XRD) has been the most commonly used method (Xi *et al.*, 2004; Zhou *et al.*, 2007). Inspection of fringe images from transmission electron microscopy (TEM) also permitted direct measurement of the  $d$  spacing (Lee *et al.*, 2003, 2005). Analyses by Fourier-transform infrared (FTIR) spectroscopy were used to deduce the arrangement of the organic tail groups adsorbed on mineral surfaces (Kung and Hayes, 1993; Li and Gallus, 2005) and in the interlayer (Vaia *et al.*, 1994; He *et al.*, 2004; Xue *et al.*, 2007; Li *et al.*, 2008). Thermogravimetric (TG) analyses could also provide conformational information of intercalated organic cations as well as the binding between the organic cations and the surface (Xie *et al.*, 2001; Xi *et al.*, 2005; Zhou *et al.*, 2007; Li *et al.*, 2008).

Although extensive studies of surfactant intercalation into smectites have been conducted, no detailed study of dodecyltrimethylammonium (DDTMA) intercalation into rectorite has been reported. Furthermore, because of the presence of two distinct types of component, the sorption, intercalation, and interlayer conformations of long-chain alkylammonium molecules in rectorite are also of interest. The purpose of the present study was to elucidate the interlayer conformations of DDTMA in rectorite as affected by the amount of DDTMA intercalated, using batch sorption, XRD, FTIR, TG, and DTG analyses.

## MATERIALS AND METHODS

The rectorite used was obtained from Zhongxiang, Hubei, China. The clay fraction (<2  $\mu\text{m}$ ) was isolated by sedimentation. Observation by XRD and scanning electron microscopy showed a pure, regularly interstratified rectorite with a CEC of 410 mmol/kg (Hong *et al.*, 2008). The surface area, measured by the BET method after outgassing at 120°C for 3 h, was 10 m<sup>2</sup>/g.

The intercalation of DDTMA into rectorite was performed in batch experiments in duplicate. To each 50 mL centrifuge tube, 1.00 g of rectorite and 20 mL of DDTMA solution at initial concentrations of 5 to 50 mmol/L with a 5 mmol/L increment, or 0.50 g of rectorite and 20 mL of DDTMA solution at initial concentrations of 30 to 50 mmol/L with a 5 mmol/L increment, were added. The initial amounts corresponded to 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 3.00, 3.50, 4.00, 4.50, and 5.00 CEC of the mineral using a CEC value of 400 mmol/kg for easy calculation. The mixtures were shaken at 150 rpm for 24 h and centrifuged at 3000 rpm for 30 min. The supernatant was filtered through 0.45  $\mu\text{m}$  filter discs before analysis for equilibrium DDTMA and counterion bromide solution concentrations.

The DDTMA solution concentrations were determined by a high-performance liquid chromatography (HPLC) method using a Shimadzu 9-A auto-injector, a

Supelco C-18 column, and a Linear 100 UV-Vis detector at a wavelength of 254 nm. The mobile phase was 5 mM *p*-toluenesulfonate in 45% water and 55% methanol. The retention time was 2.2 min at a flow rate of 1 mL/min. For concentrations of >2 mmol/L, a dilution ratio of 1/10 was used. Bromide analysis was performed by another HPLC system using a Shimadzu 9-A auto-injector, a Hamilton PRP-X100 anion chromatographic column, and an Alltech electrical conductivity detector. The mobile phase was 2 mM potassium phthalate at pH 6 adjusted by NaOH. The retention time was 3.1 min at a flow rate of 2 mL/min. For concentrations >10 mmol/L a dilution ratio of 1/10 was used. The amount of DDTMA and bromide sorbed was determined by the difference between the initial and equilibrium concentrations.

The FTIR spectra were acquired using a Perkin Elmer Spectra One Spectrometer equipped with an attenuated total reflection (ATR) accessory. The spectra were obtained by accumulating 256 scans at a resolution of 4 cm<sup>-1</sup>.

Powder XRD patterns were recorded using a Rigaku D/Max-IIIa diffractometer with Ni-filtered CuK $\alpha$  radiation at 35 kV and 20 mA. Orientated samples were prepared by depositing rectorite suspension onto glass slides and drying in air. The samples were scanned from 2 to 15°2 $\theta$  at 2°/min with a 0.01° step size.

The TG analysis was performed on a TGA 2950 device manufactured by TA Instruments. The heating rate was 20°C/min under air. The initial sample mass was between 11 and 15 mg.

## RESULTS AND DISCUSSION

### Sorption isotherms

At the initial loading level of <0.50 CEC, the input DDTMA was completely sorbed onto rectorite (Figure 1), resulting in an equilibrium concentration of <0.1 mmol/L. In contrast, counterion bromide sorption (Figure 1) was minimal. As the initial DDTMA amount increased to

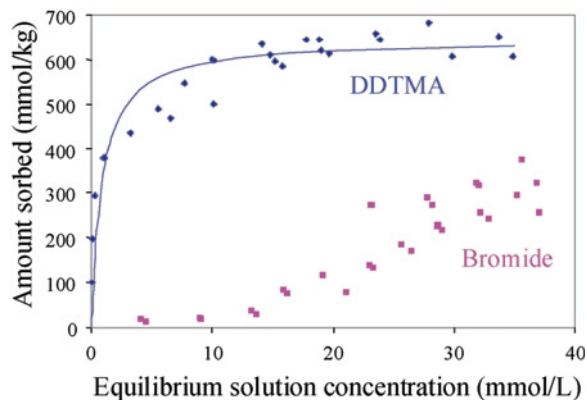


Figure 1. Sorption isotherms of DDTMA and counterion bromide on rectorite. The line is a Langmuir fit to the observed data.

>0.50 CEC, greater bromide sorption was achieved. The DDTMA reached a sorption plateau of  $625 \pm 28$  mmol/kg, at which point counterion bromide sorption was  $313 \pm 37$  mmol/kg. Note that at the greatest DDTMA, corresponding to 5.00 CEC of the mineral, the amount of DDTMA sorbed was only 1.67 CEC (Table 1). The trend for DDTMA sorption was completely different from that for HDTMA sorption on the same rectorite: the HDTMA sorption capacity reached 3.20 CEC with an initial input of 5.00 CEC (Li *et al.*, 2008).

#### FTIR analyses

The full FTIR spectra of raw rectorite and rectorite intercalated with different amounts of DDTMA in the range  $450\text{--}4000$   $\text{cm}^{-1}$  (Figure 2) revealed a sharp, strong vibration band at  $3640$   $\text{cm}^{-1}$ , which is due to the OH-stretching vibration of the structural OH groups (Kloprogge *et al.*, 1999). Although the location of this band is somewhat insensitive to the intercalation of DDTMA, the absorbance was in fact affected by the amount of DDTMA intercalated. The absorbance of raw rectorite was 0.13, but decreased to 0.11 when the DDTMA intercalation was 0.25 CEC and further decreased to 0.09 with intercalation of 0.74 CEC. After that, it increased to 0.11 at 1.31 CEC and finally back to 0.13 at 1.56 CEC (Figure 2). Similarly, the intercalated DDTMA also affected the adsorbed water in the interlayer as revealed by the broad band at  $3200\text{--}3560$   $\text{cm}^{-1}$  with a peak maximum at  $3400$   $\text{cm}^{-1}$ . For raw rectorite, the absorbance of this adsorbed water band was 0.07 but decreased to 0.05 and 0.02 at 0.25 and 0.74 CEC, respectively. At 1.09 and 1.31 CEC intercalation, the absorbance increased to 0.03 and 0.04 and remained at 0.04 thereafter, until 1.67 CEC loading (Figure 2). The absorption band at  $1634$   $\text{cm}^{-1}$ , designated the  $\nu_2(\text{H}\text{--}\text{O}\text{--}\text{H})$  bending vibration of water molecules sorbed on rectorite, displayed an absorbance value of 0.045 in raw rectorite, which decreased to 0.015 at the 0.74 CEC DDTMA intercalation level then

increased to 0.025 at 1.67 CEC. In addition to the variation in absorbance, the frequency located initially at  $1634$   $\text{cm}^{-1}$  for rectorite increased progressively by as much as  $15$   $\text{cm}^{-1}$  with increased DDTMA intercalation (Figure 3). The decrease in absorbance suggested that the amount of water in the interlayer was reduced as the amount of DDTMA intercalation increased, which was confirmed by thermogravimetric (TG) analysis (see below), while the shift to a greater frequency indicated that the residual water molecules were held more tightly due to stronger interactions. Similar results were observed for HDTMA adsorption on Al-montmorillonite (Xue *et al.*, 2007) and on rectorite (Li *et al.*, 2008).

The bands near  $2917$  and  $2850$   $\text{cm}^{-1}$  are  $\text{CH}_2$  anti-symmetric ( $\nu_{\text{as}}$ ) and symmetric ( $\nu_{\text{s}}$ ) stretching bands, respectively, and are sensitive to the *gauche/trans* conformer ratio of the hydrocarbon chains. A shift from low frequencies, characteristic of highly ordered, all-*trans* conformations, to higher frequencies and increased width, was accompanied by an increase in the number of *gauche* conformers (the 'disorder' of the chain) (Weers and Scheuing, 1990). At intercalation levels of 0.25 and 0.74 CEC, these bands were located at  $2930$  and  $2855$   $\text{cm}^{-1}$ , respectively, reflecting a large number of *gauche* conformers intercalated into rectorite (Figure 4). A shift toward lower frequencies was seen as the amount of DDTMA intercalated was  $>1.31$  CEC (Table 2), revealing a decrease in the number of *gauche* conformers intercalated into rectorite. At 1.67 CEC, the bands were located at  $2925$  and  $2851$   $\text{cm}^{-1}$  compared to  $2918$  and  $2850$   $\text{cm}^{-1}$  for HDTMA-intercalated rectorite (Li *et al.*, 2008), to  $2917$  and  $2849$   $\text{cm}^{-1}$  for HDTMA-intercalated montmorillonite at 2.00 CEC (He *et al.*, 2004), and to  $2917$  and  $2850$   $\text{cm}^{-1}$  for solid DDTMA. Thus, at the DDTMA sorption maximum, significant amounts of the intercalated DDTMA still maintained a *gauche* conformation compared to an all-*trans* conformation for HDTMA intercalation into rectorite at sorption maxima (Li *et al.*, 2008).

Table 1. Amounts of DDTMA intercalated and counterion bromide sorbed as affected by initial DDTMA loading.

Initial DDTMA loading, equivalent to CEC	DDTMA intercalated, equivalent to CEC	Bromide sorbed, equivalent to CEC	Ratio of bromide to DDTMA sorbed
0	0	0	0
0.25	0.25	0.02	0.08
0.50	0.50	0.04	0.08
0.75	0.74	0.08	0.11
1.00	0.95	0.20	0.21
1.25	1.09	0.25	0.23
1.50	1.20	0.34	0.28
1.75	1.31	0.44	0.34
2.25	1.47	0.60	0.41
3.00	1.56	0.66	0.42
4.00	1.63	0.79	0.48
5.00	1.67	0.84	0.50

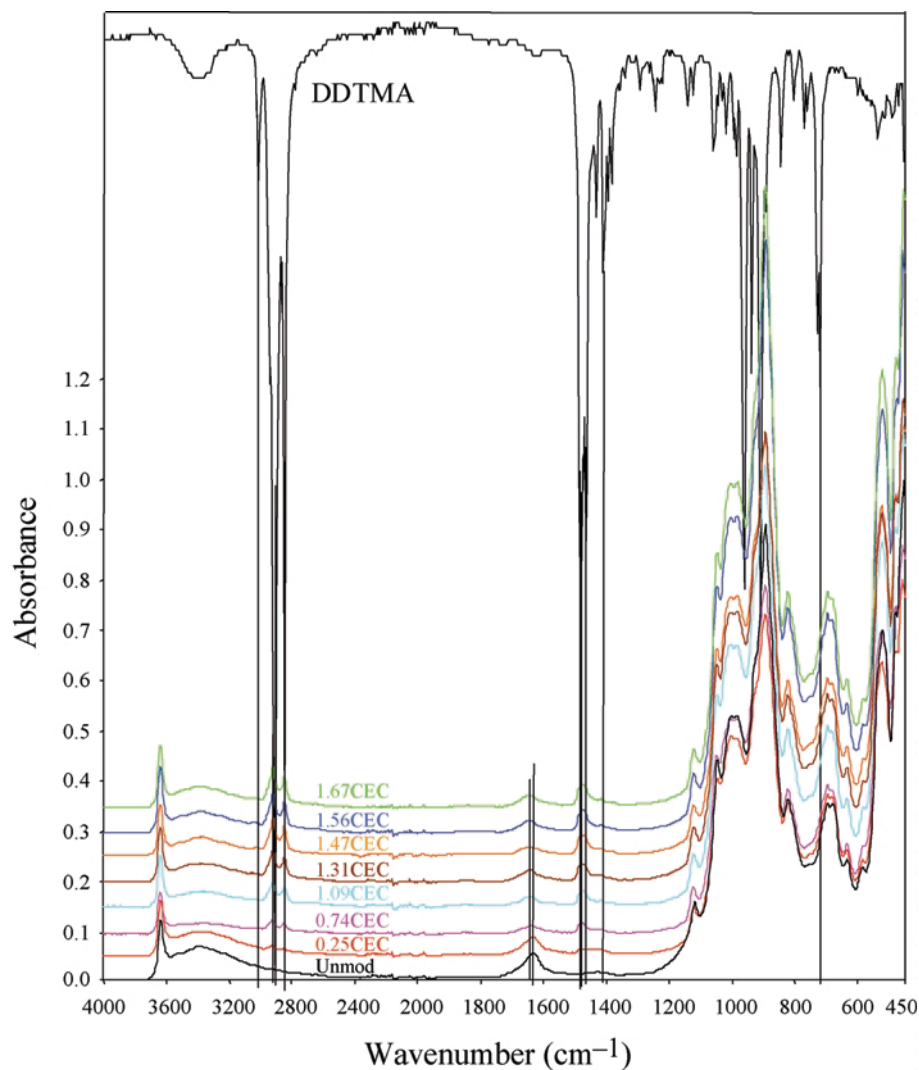


Figure 2. FTIR spectra of rectorite intercalated with different amounts of DDTMA.

Several vibration bands were observed in the  $1350\text{--}1500\text{ cm}^{-1}$  range, and their assignments are identified in Figure 3. The location of the anti-symmetric scissoring mode of  $\text{CH}_3\text{-N}$  ( $\delta_{\text{as}}$ ,  $\text{CH}_3\text{-N}$ ) was the least sensitive to the amount of DDTMA intercalated. On the other hand, the FTIR absorption bands at  $1450\text{--}1480\text{ cm}^{-1}$ , corresponding to the methylene scissoring mode, were sensitive to the interchain interactions and were diagnostic of the packing arrangements in alkyl-chain assemblies (Casal *et al.*, 1982; Venkataraman and Vasudevan, 2001). The band could be a singlet or split into a doublet depending on the conformation of methylene tail groups. A doublet at  $1463$  and  $1473\text{ cm}^{-1}$  for the DDTMA solid indicated an orthorhombic subcell (Weers and Scheuing, 1990). However, for DDTMA-intercalated rectorite, a shoulder appeared at  $1472\text{ cm}^{-1}$  at  $1.09\text{ CEC}$  intercalation and remained a singlet as the amount of DDTMA intercala-

tion increased. This singlet was different from the doublet of the DDTMA solid, reflecting different conformations between the solid and intercalated DDTMA. The significant difference in band locations between solid DDTMA and DDTMA intercalated in rectorite also suggested more *gauche* DDTMA conformations compared to more *all-trans* conformations in HDTMA-intercalated rectorite at greater loading levels (Li *et al.*, 2008).

#### XRD analyses

The XRD patterns of raw and DDTMA-intercalated rectorite (Figure 5) yielded a  $d_{001}$  value of  $22.6\text{ \AA}$  for oriented raw rectorite. The  $d_{002}$  and  $d_{003}$  were integral to  $d_{001}$  at  $11.1$  and  $7.3\text{ \AA}$ . For intercalation at  $0.25\text{ CEC}$ , the  $d_{001}$  and  $d_{002}$  values increased to  $24.1$  and  $12.1\text{ \AA}$ , respectively, and were still integral. However, for intercalation at  $0.74\text{ CEC}$ , the  $d_{001}$  revealed further

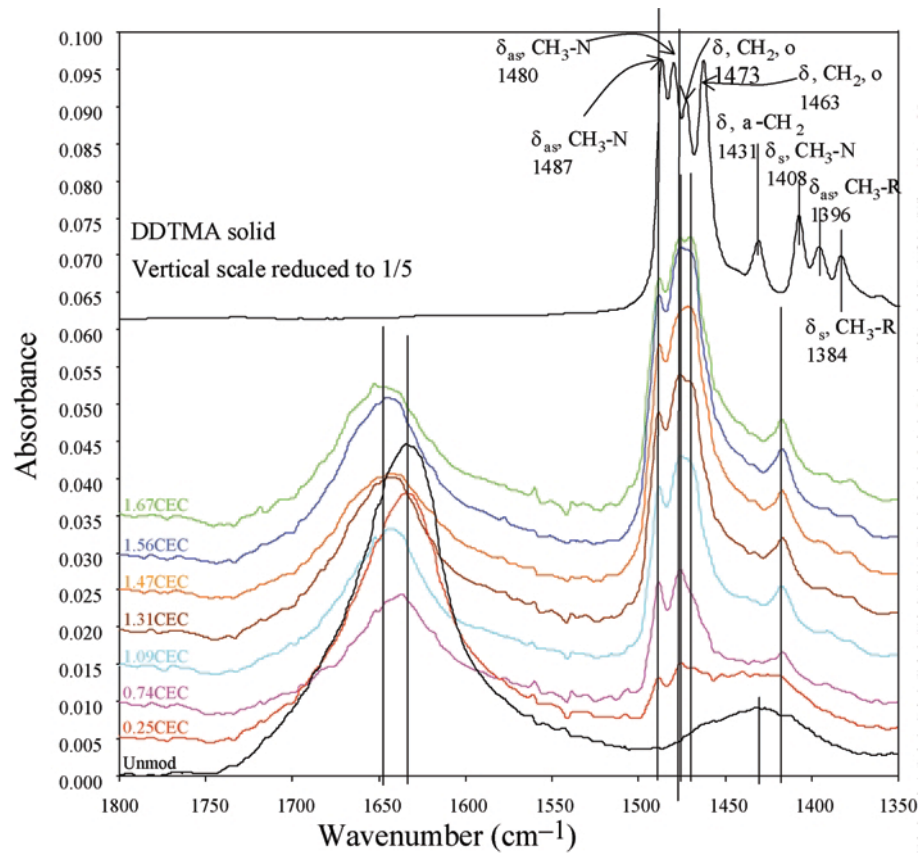


Figure 3. FTIR spectra of rectorite intercalated with different amounts of DDTMA in the wavenumber range 1350–1800  $\text{cm}^{-1}$ .

expansion to only 26.7 Å, while the 002 reflection began to show a broad plateau instead of a sharp peak (Figure 5). At 1.09 CEC intercalation,  $d_{001}$  increased to 31.4 Å. Meanwhile, the broad plateau separated into two reflections. The values for  $d_{002}$  and  $d_{003}$  were 14.2 and 10.8 Å, non-integral to the 001 reflection. Finally, for intercalation at 1.67 CEC,  $d_{001}$  showed expansion to 31.6 Å, with the values for  $d_{002}$  at 15.8 Å and  $d_{003}$  at 10.7 Å again showing the integrality of the three basal reflections (Figure 5). Moreover, the width of the (002)

and (003) reflections became narrower compared to those of the 1.09 CEC intercalation. To further confirm the non-integral feature of the basal reflection from the low to intermediate levels of intercalation, the raw rectorite and 0.50 CEC intercalated rectorite were subjected to ethylene glycol (EG) solvation. The  $d_{001}$  of raw rectorite expanded to 27.2 Å after EG solvation, showing a regular interstratified rectorite. In contrast, the  $d_{001}$  of 0.50 CEC intercalated rectorite only increased from 24.5 to 26 Å, revealing further potential for expansion (Figure 6). In

Table 2. Location and absorbance of C-H anti-symmetric and symmetric stretching vibrations of DDTMA in rectorite as affected by the amount intercalated.

DDTMA intercalated	C-H anti-symmetric stretching		C-H symmetric stretching	
	Location ( $\text{cm}^{-1}$ )	Absorbance	Location ( $\text{cm}^{-1}$ )	Absorbance
0.00 CEC	—	—	—	—
0.25 CEC	2930	0.008	2855	0.004
0.74 CEC	2929	0.018	2854	0.010
1.09 CEC	2929	0.028	2850	0.020
1.31 CEC	2926	0.041	2851	0.028
1.47 CEC	2924	0.052	2851	0.036
1.56 CEC	2925	0.051	2851	0.035
1.67 CEC	2925	0.058	2851	0.037

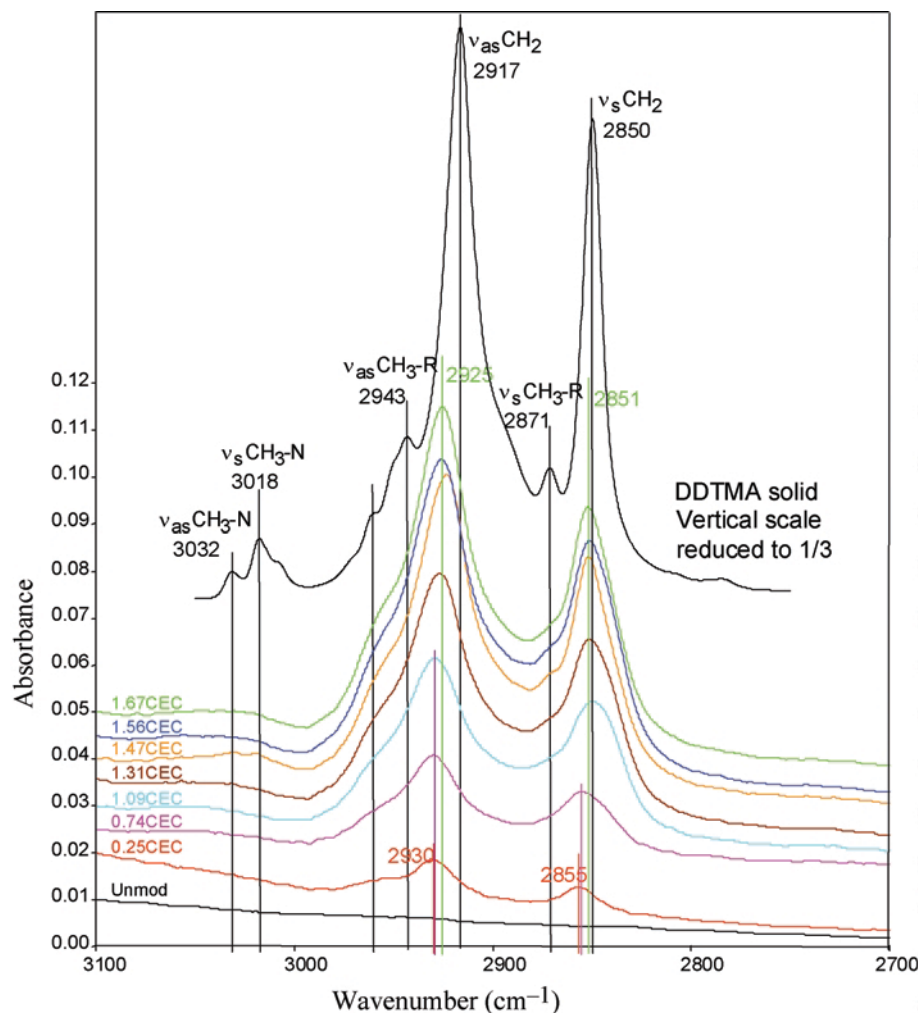


Figure 4. FTIR spectra of the CH<sub>2</sub> stretching bands showing the peak shift and change in intensity as a function of DDTMA intercalated.

addition, the 002 reflection changed from a single reflection at 11.9 Å to a broad plateau, which could be interpreted as consisting of 13.1 and 12.0 Å reflections, again showing non-integrality (Figure 6).

#### TG and DTG analyses

For DDTMA solid, the procedural decomposition temperature ( $T_{\text{onset}}$ ) was at 220°C and the temperature at the maximum rate of decomposition ( $T_{\text{peak}}$ ) was 255°C (Figure 7a). Compared to pure DDTMA, rectorite intercalated with 1.67 CEC of DDTMA showed three steps in mass loss (Figure 7b), corresponding to the removal of water at  $T < 200^\circ\text{C}$  and pyrolyses of organic cations present in different states at 230–280°C and 420–450°C. For the second step of mass loss, the  $T_{\text{onset}}$  and  $T_{\text{peak}}$  were about the same as those of solid DDTMA at 220 and 255°C. The second step of mass loss was minimal at 0.75 CEC loading levels (Figure 7b). The  $T_{\text{peak}}$  of the third step of mass loss was 430°C and was present at both 1.67 and 0.75 CEC loading levels, but

was absent from the unmodified rectorite. Xie *et al.* (2001) obtained  $T_{\text{peak}}$  at 256 and 432°C for montmorillonite intercalated with trimethyl-coco-ammonium chloride, the major component of which is trimethylammonium with the tail group containing 12–15 carbons, and the same temperatures for DDTMA-intercalated montmorillonite. Similar results were observed for HDTMA-intercalated montmorillonite (Kooli and Magusin, 2005) and octadecyltrimethylammonium-intercalated montmorillonite (Hedley *et al.*, 2007). Thus, the absence of a peak at 230–280°C at a 0.75 CEC loading level suggests that the amount intercalated was almost entirely in the interlayer spaces. For 1.67 CEC intercalation, the sorbed DDTMA occurred on both internal and external surfaces.

#### Thermal treatment

The FTIR spectra of rectorite intercalated at 1.67 CEC, then heated to 300 °C, revealed that the absorbance at 2925 and 2851 cm<sup>-1</sup> was greatly reduced (Figure 8a).

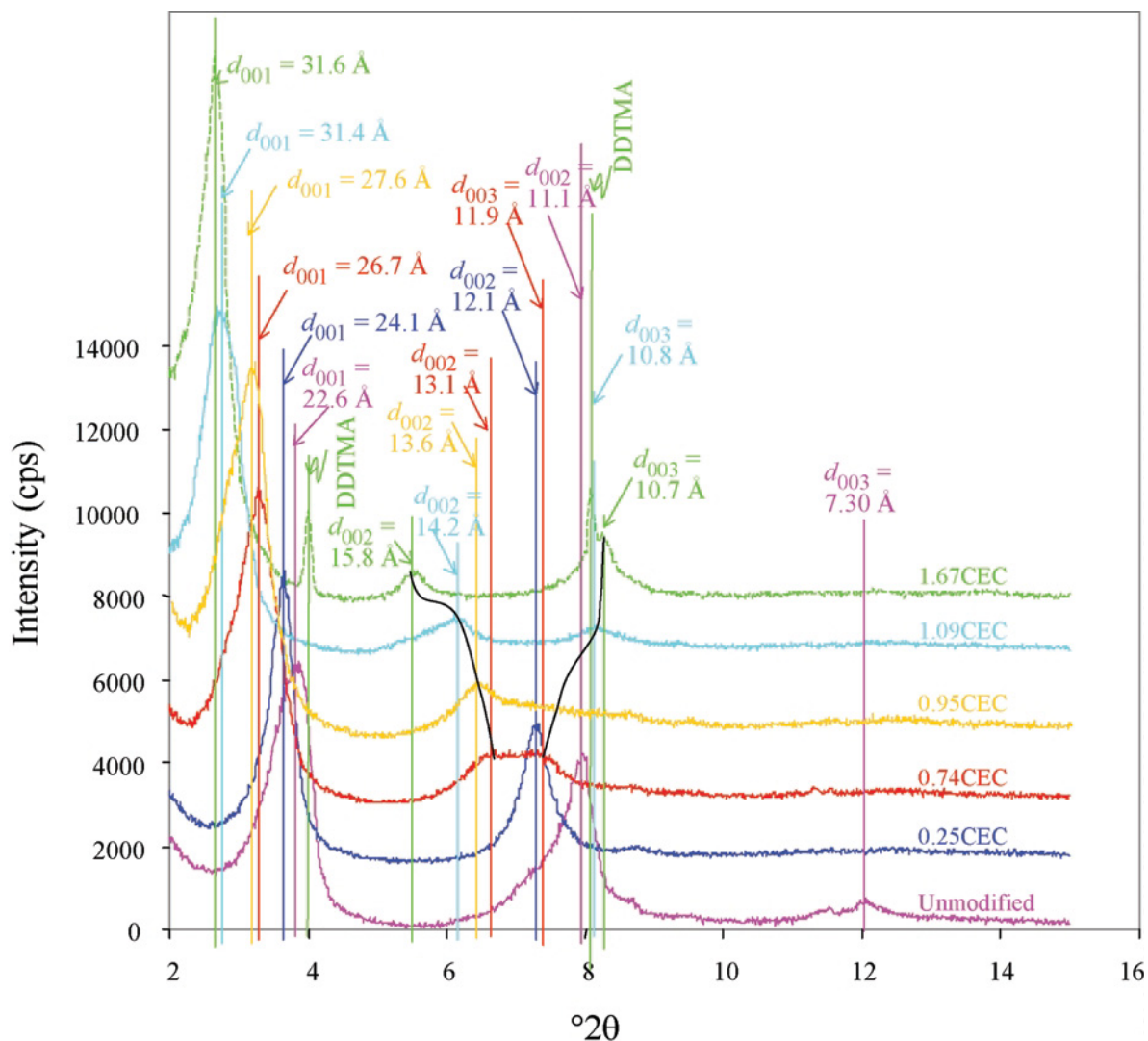


Figure 5. XRD patterns of rectorite intercalated with different amounts of DDTMA. The second reflection is non-integral for the samples intercalated with DDTMA at 0.74 CEC and above and becomes integral again at 1.67 CEC.

Meanwhile, the locations of the bands at 2930 and 2855  $\text{cm}^{-1}$  were similar to those of rectorite intercalated with 0.25 CEC DDTMA (Figure 8a). Furthermore, the vibration bands at 1450–1500  $\text{cm}^{-1}$  after heating to 300°C were almost identical to those of rectorite intercalated with 0.25 CEC of DDTMA (Figure 8b). These results suggested that most of the DDTMA molecules were pyrolyzed at this temperature. The residual DDTMA was only a fraction ( $\sim 0.5$  CEC based on the absorbance at 2930, 2855, and 1450–1500  $\text{cm}^{-1}$ ) of the original intercalated DDTMA and the interlayer conformation of the residual DDTMA was different from that of DDTMA intercalated at 1.67 CEC. This residual DDTMA was thermally stable at 300°C. After the sample was heated to 550°C, the bands at 2930, 2855, and 1450–1500  $\text{cm}^{-1}$  all disappeared (Figure 8), reflecting complete pyrolysis of DDTMA from the interlayer of

rectorite. These results agree with those from alkylammonium-intercalated montmorillonite after heating to 500°C (Xie *et al.*, 2001). Because the electrostatic interactions associated with cation exchange are stronger than van der Waals interactions, one may reasonably speculate that the pyrolyses at 230–280°C and 420–450°C correspond to the decomposition of DDTMA held by van der Waals interaction and by cation exchange in the interlayer, respectively. The mass losses are 2.5, 10, and 5% for the first, second, and third steps, respectively (Figure 7), representing the percentages of water removal, DDTMA held by van der Waals interaction, and DDTMA held by cation exchange.

Batch sorption showed that cation exchange was the dominant mechanism when DDTMA loading was  $< 0.50$  CEC and van der Waals interaction became more important as the amount of DDTMA intercalation

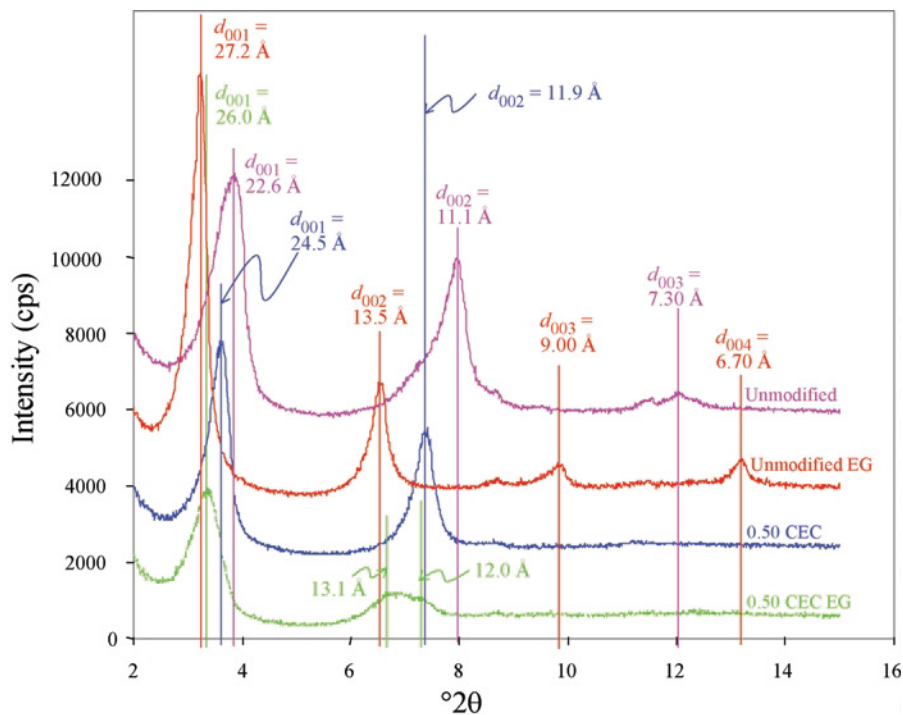


Figure 6. XRD for raw rectorite and rectorite intercalated with DDTMA at 0.50 CEC before and after EG solvation.

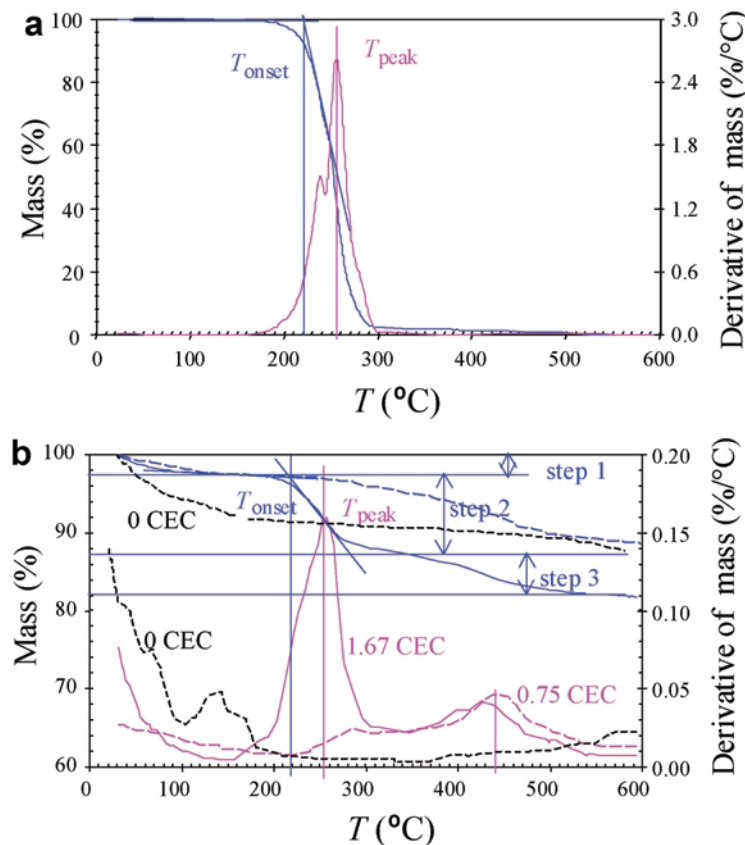


Figure 7. TG and DTG curves for DDTMA solid (a) and rectorite intercalated with DDTMA (b) at 1.67 CEC (solid lines), 0.75 CEC (dotted lines), and 0 CEC (dashed line).

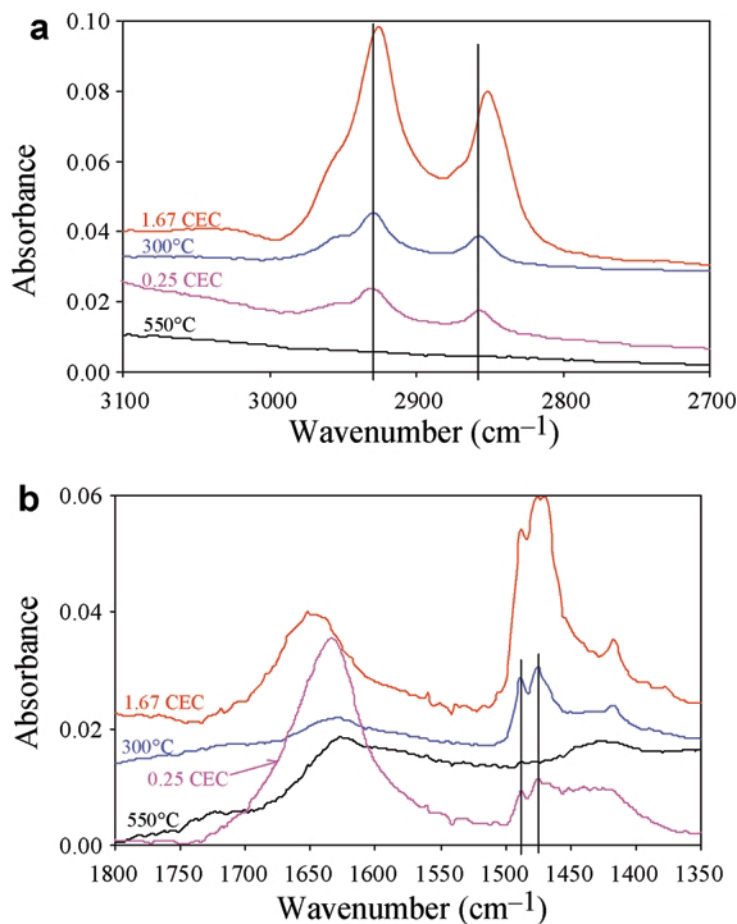


Figure 8. FTIR spectra in the wavenumber ranges 2700–3100  $\text{cm}^{-1}$  (a) and 1350–1800  $\text{cm}^{-1}$  (b) after the rectorite intercalated with DDTMA at 1.67 CEC was heated to 300 and 550°C. For comparison, a spectrum of rectorite intercalated with 0.25 CEC of DDTMA is also shown.

increased. The percentage of mass loss in TG analyses agreed well with the batch study as well as the absorbance values determined from FTIR.

#### Deduction of DDTMA interlayer conformations

From the batch sorption isotherm, and from the FTIR, XRD, TG, and DTG analyses, the DDTMA in the interlayer of rectorite clearly can adopt two different states. The first is observed when the amount of DDTMA intercalated is between 0.25 and 0.50 CEC. The uptake of DDTMA by rectorite to these states is more complete, as supported by sorption isotherms. The sorbed DDTMA is held by a strong interaction, and thus requires a greater temperature to decompose as revealed by TG and DTG analyses. The sorbed DDTMA adopted a more *gauche* conformation as indicated by FTIR, with a flat-lying monolayer orientation confirmed by XRD (Figure 9). When the amount of DDTMA intercalated is between 0.75 and 1.67 CEC, the DDTMA conformations may change gradually from a monolayer to a trilayer, bypassing a bilayer. Accompanying the change, a non-

integral (00 $l$ ) reflection begins to appear, which explains the continuous increase in  $d_{001}$  spacing as the surfactant loading increased. Meanwhile, most of the DDTMA molecules in the trilayer conformation are held by tail-tail van der Waals interaction (Figure 9). This is confirmed by the significant uptake of counterion bromide accompanying DDTMA intercalation, by the same pyrolysis temperature as that of DDTMA solid, by the shift of the  $\text{CH}_2$ - anti-symmetric and symmetric stretching vibrations to lower frequencies, and finally by the integral (00 $l$ ) reflections with  $d_{001} = 31.6 \text{ \AA}$ , suggesting a horizontal trilayer conformation.

Many have investigated the change in  $d$  spacing as affected by alkylammonium loading. Studies of intercalation of alkylammonium into smectite have shown that a flat-lying orientation was adopted with a surfactant chain length of <8 carbons, resulting in an increase in  $d$  spacing to 13.5  $\text{\AA}$ , comprising a dehydrated montmorillonite layer (the same as an illite layer) of 10  $\text{\AA}$  and a flat-lying monolayer of 3.5  $\text{\AA}$  (Lagaly *et al.*, 1976; Vaia *et al.*, 1994). As the surfactant loading increased, the inter-

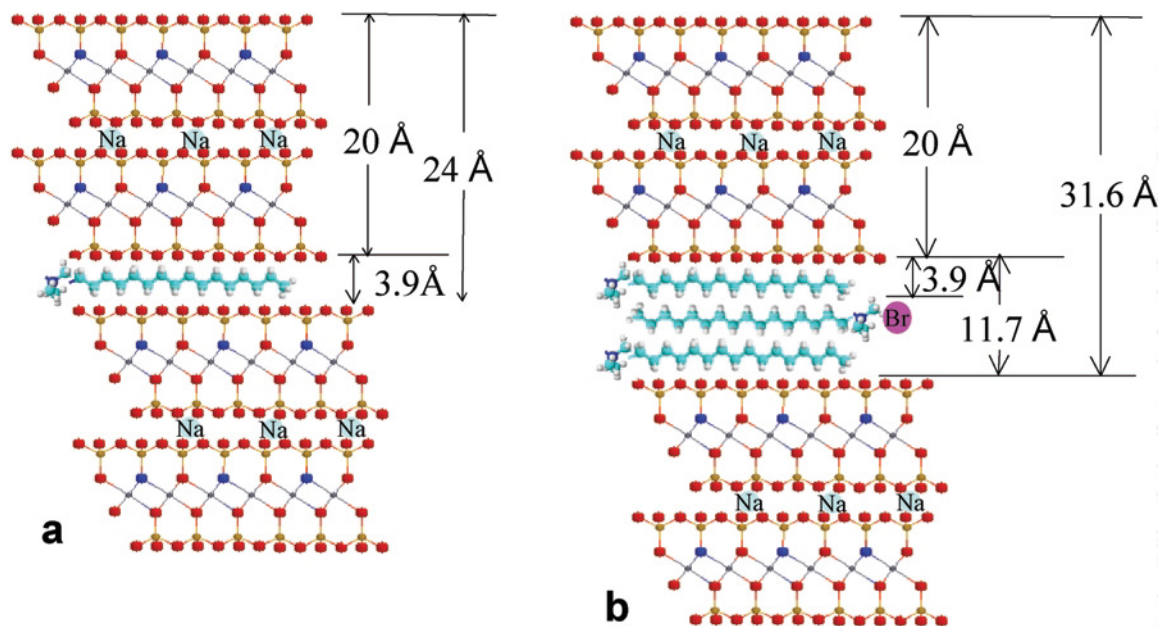


Figure 9. Illustration of horizontal monolayer (a) and trilayer (b) conformations of DDTMA molecules intercalated in the interlayer space of the smectite component in rectorite.

calated alkylammonium could adapt to horizontal bilayer and horizontal trilayer conformation, resulting in  $d$  spacings of 17 and 21.5 Å, respectively (Lagaly *et al.*, 1976; Xi *et al.*, 2004). In many of the XRD patterns of intercalated montmorillonite, however, only the strongest (001) reflection was observed, even though the XRD was scanned to  $10^\circ 2\theta$  and beyond (He *et al.*, 2004; Xi *et al.*, 2004; Lee *et al.*, 2005; He *et al.*, 2006; Xue *et al.*, 2007). On the other hand, TEM lattice-fringe images revealed mixed layers of different layer thickness after intercalation of HDTMA into a Na- and a Ca-montmorillonite at amounts  $>$ CEC (Lee *et al.*, 2005). He *et al.* (2006) also noticed the co-existence of layer spacings of 20.1 and 23.2 Å in a single TEM image.

The observation of the non-integral (00 $l$ ) reflection in this study strongly supports the TEM observation. The intercalation might well lead to a mixed layer consisting of raw rectorite and monolayer-intercalated rectorite, as well as consisting of monolayer and trilayer intercalated rectorite. Due to the similar  $d$  spacings, however, between the raw rectorite and monolayer intercalated rectorite, broadening of the (002)/(003) reflections at lower intercalation levels is difficult. The difference in  $d$  spacings between a horizontal monolayer and a horizontal trilayer is large enough to result in a significant broadening of the (002)/(003) reflections as seen in this study. Thus, the continuous change in  $d_{001}$  spacing with increase in the amount of DDTMA intercalated suggests a transition from horizontal monolayer to horizontal trilayer *via* a mixed-layer process rather than *via* a horizontal bilayer as the intermediate phase. In fact, development of a horizontal bilayer DDTMA conformation in the transition from a monolayer to trilayer intercalation as

the uptake of the DDTMA molecules beyond monolayer is unlikely *via* van der Waals interaction. As the intercalation of surfactant is in the smectite component of rectorite, a similar result would be anticipated for smectite intercalation, compared to the traditional belief that an abrupt change of  $d$  spacing from monolayer, to bilayer, then to trilayer without any transition.

## CONCLUSIONS

The interlayer conformations of intercalated DDTMA in rectorite were affected by initial surfactant input, and thus, the amount of surfactant intercalated. When the amount of DDTMA intercalated was  $<0.75$  CEC of the minerals, the intercalated surfactant adopted a more *gauche* arrangement in the interlayer as revealed by the shift of symmetric and anti-symmetric stretching vibrations of the methylene tail group, and a flat-lying monolayer DDTMA interlayer conformation was adopted as confirmed by XRD. A greater pyrolysis temperature and a minimal sorption of counterion bromide indicated that the DDTMA held at this level was *via* a strong interaction between the DDTMA molecules and the interlayer surface, mainly by electrostatic interaction. As the amount of DDTMA intercalated was  $>0.75$  CEC, a transition from monolayer to trilayer of the intercalated DDTMA was seen by the non-integral (002)/(003) reflection together with a continuous increase in  $d_{001}$  spacing in XRD analyses. The FTIR showed that DDTMA adopted a mainly *gauche* conformation. At the DDTMA intercalation maximum of 1.67 CEC, the flat-lying trilayer conformation of DDTMA in the interlayer was well developed and the (002) and (003) reflections in XRD

became integral. More counterion sorption suggested that van der Waals interaction was responsible for the additional uptake of DDTMA in the interlayer. The DDTMA held *via* van der Waals interaction had a peak pyrolysis temperature of 255°C, much less than that of 430°C due to cation exchange.

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