Modification of Wyoming Montmorillonite Surfaces Using a Cationic Surfactant

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Surfaces of Wyoming SWy-2-Na-montmorillonite were modified using ultrasonic and hydrothermal methods through the intercalation and adsorption of the cationic surfactant octadecyltrimethylammonium bromide (ODTMA). Changes in the surfaces and structure were characterized using X-ray diffraction (XRD), thermal analysis (TG), and electron microscopy. The ultrasonic preparation method results in a higher surfactant concentration within the montmorillonite interlayer when compared with that from the hydrothermal method. Three different molecular environments for surfactants within the surface-modified montmorillonite are proposed upon the basis of their different decomposition temperatures. Both XRD patterns and TEM images demonstrate that SWy-2-Na-montmorillonite contains superlayers. TEM images of organoclays prepared at high surfactant concentrations show alternate basal spacings between neighboring layers. SEM images show that modification with surfactant reduces the clay particle size and aggregation. Organoclays prepared at low surfactant concentration display curved flakes, whereas they become flat with increasing intercalated surfactant. Novel surfactant-modified montmorillonite results in the formation of new nanophases with the potential for the removal of organic impurities from aqueous media.

1. Introduction

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface areas, and consequential strong adsorption/absorption capacities.[1−5] Among the swelling clays, the most common dioctahedral smectite is montmorillonite, which has two siloxane tetrahedral sheets sandwiching an aluminum octahedral sheet. Because of an isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} in the octahedral sheet and Si^{4+} replaced by Al^{3+} in the tetrahedral sheet), the clay layer is negatively charged, which is counterbalanced by exchangeable cations such as Na^+ and Ca^{2+} in the interlayer. The hydration of inorganic cations on the exchange sites causes the clay mineral surface to be hydrophilic. Thus, natural clays are ineffective sorbents for organic compounds.[6−8] However, such a difficulty can be overcome by ion exchange of the inorganic cations with organic cations. Organomontmorillonites are synthesized by intercalating cationic surfactants such as quaternary ammonium compounds into the interlayer space through ion exchange.[9−11] When using long-chain alkylammonium cations, a hydrophobic partition medium within the clay interlayer can form and function analogously to a bulk organic phase. The interlayer height of clay before modification is relatively small, and the interlayer environment is then hydrophilic. The intercalation of a cationic surfactant not only changes the surface properties from hydrophilic to hydrophobic but also greatly increases the basal spacing of the layers. Such surface-property changes effect the applications of the organoclay. In particular, the hydrophobic nature of the organoclay implies that the material can be used as a filter material for water purification.

At present, there are many applications of organoclays used as sorbents in pollution prevention and environmental remediation such as the treatment of spills, in wastewater and hazardous waste landfills, and others. Some studies[10,12−14] have shown that replacing the inorganic exchangeable cations of clay minerals with organic cations can result in a greatly enhanced capacity of these materials to remove organic contaminants. Organoclay-based nanocomposites exhibit a remarkable improvement in properties when compared with untreated polymer or conventional micro- and macro-composites. These improvements include increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers.[15] All of these applications and improvements mentioned above strongly depend on the structure and properties of the organoclays. Understanding the structure and properties of organoclays is essential for their industrial applications.

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The objective of this study is to investigate the structural changes of octadecyltrimethylammonium (ODTMA) bromide-modified montmorillonite (MMT) with different surfactant loadings. Two methods of preparation using hydrothermal and ultrasonic methods are used to determine the most effective preparation method. High-resolution thermogravimetric analysis (HRTG) was used to evaluate the surfactant loading, thermal stability, and chemical nature of the surfactant-modified organoclay prepared by two different methods. X-ray diffraction (XRD), using oriented samples and ethylene glycol expansion, was used to study the surface structure of montmorillonite before and after modification with the cationic surfactant.

The morphology and microstructure of the synthesized organoclays were studied using scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). These techniques have proven to be most useful for the study of the modification of clay surfaces.[16−19] This study provides new insights into the structure and properties of organoclays prepared using ultrasonic and hydrothermal methods from an unusual Wyoming montmorillonite. Such a study is of high importance for understanding the structure, properties, and potential applications of organoclays.

2. Experimental Section

2.1. Materials. The montmorillonite used in this study was supplied by the Clay Minerals Society as source clay SWy-2-Na-montmorillonite (Wyoming). This clay originates from the Newcastle formation (cretaceous), Crook County, Wyoming. The chemical composition of the montmorillonite is 62.9% SiO_2, 19.6% Al_2O_3, 3.35% Fe_2O_3, 3.05% MgO, 1.68% CaO, and 1.53% Na_2O. The formula of the montmorillonite can be expressed as $(Ca_{0.12}-Na_{0.32}K_{0.05})[Al_{3.01}Fe(III)_{0.41}Mn_{0.01}Mg_{0.54}Ti_{0.02}][Si_{7.98}Al_{0.02}]-O_{20}(OH)_4$, as calculated from its chemical composition. The cation-exchange capacity (CEC) is 76.4 mequiv/100 g. The clay was used without further purification. The surfactant selected for this study is octadecyltrimethylammonium bromide ($C_{21}H_{46}NBr$, FW: 392.52) from Sigma-Aldrich.

2.2. Preparation. The synthesis of organoclays was undertaken as follows: (1) SWy-2-Na-montmorillonite (SWy-2-MMT, 4 g) was dispersed in 400 mL of deionized water with a Heidolph magnetic stirrer at about 600 rmp for about 16 h. A predissolved stoichiometric amount of octadecyltrimethylammonium (ODTMA) bromide solution was slowly added to the clay suspension at 60 °C. The reaction mixtures were stirred for 30 min at 60 °C using a Branson Ultrasonics model 250 sonifier with an output of 40 mW.

(2) SWy-2-MMT (3 g) was dispersed in 70 mL of deionized water and stirred with a magnetic stirrer at about 600 rmp for 10 min. Then ODTMA was added to the clay suspension at room temperature. The clay and surfactant mixture was poured into a set of Teflon hydrothermal reaction containers and then hydrothermally treated in a 110 °C oven for 48 h. The concentrations of ODTMA selected for this study are 0.6CEC, 1.5CEC, and 4.0CEC (cation exchange capacity) of the SWy-2-MMT. All organoclays were washed free of the bromide anion, as shown by the lack of chemical reaction with $AgNO_3$, dried at room temperature, ground in an agate mortar, and stored in a vacuum desiccator. The samples are labeled, for example, as 0.6CEC-OMMT-H (OMMT = organomontmorillonite), which defines a 0.6CEC octadecyltrimethylammonium bromide-modified montmorillonite using the hydrothermal preparation route (H). Similarly, the label 1.5CEC-OMMT-U means a 1.5CEC organomontmorillonite prepared using ultrasonic methods.

2.3. Characterization Methods. *2.3.1. Thermogravimetric Analysis.* Thermogravimetric analyses of the surfactant-modified

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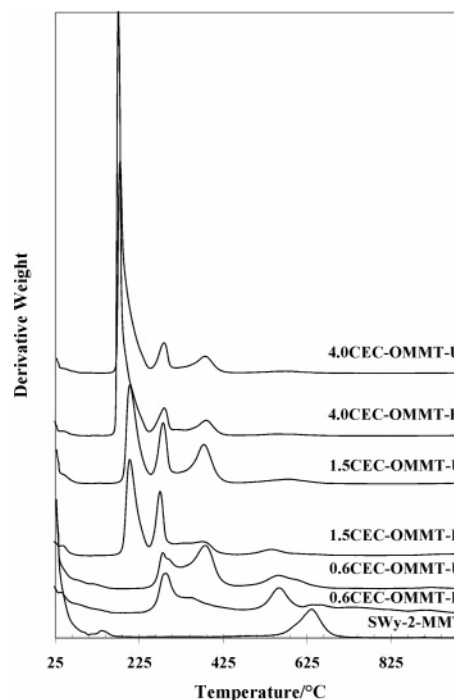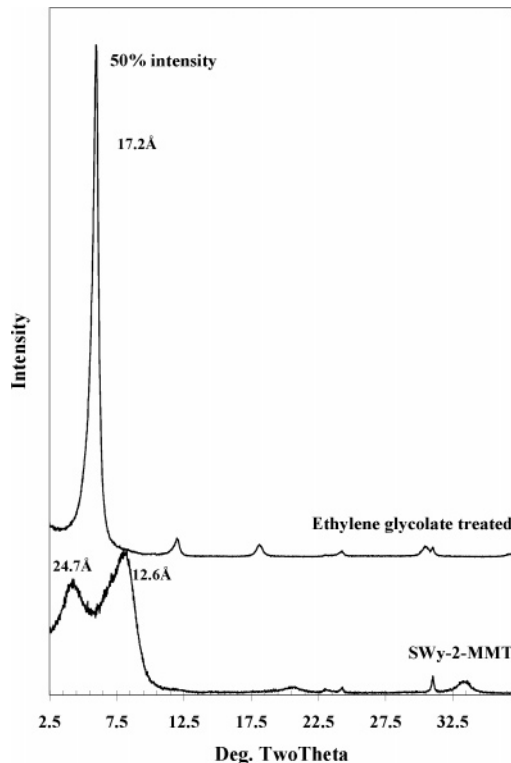(19) Vali, H.; Koester, H. M. *Clay Miner.* **1986**, *21*, 827−859.

Figure 1. High-resolution thermogravimetric analysis of organoclays prepared by hydrothermal and ultrasonic methods.

montmorillonites were obtained using a TA Instruments Inc. Q500 high-resolution TGA operating at a ramp of 10 °C/min with resolution of 6.0 °C from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (80 cm³/min). Approximately 50 mg of the finely ground sample was heated in an open platinum crucible. Repetitive analyses were undertaken.

2.3.2. X-ray Diffraction. X-ray diffraction (XRD) patterns of untreated and ethylene glycol-treated SWy-2-MMT samples were recorded using Co Kα radiation (λ = 1.78897 Å) on a Philips PW1050 diffractometer at 40 kV and 32 mA with a 1° divergence slit and a 1° antiscattter slit between 2.5 and 37° (2θ) at a step size of 0.02° (2θ). Surfactant-modified montmorillonites were pressed in stainless steel sample holders. X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation (λ = 1.5418Å) on a Philips PANalytical X'Pert PRO diffractometer operating at 40 kV and 40 mA with an automatic variable divergence slit and a 0.25° antiscattter slit between 1 and 10° (2θ) at a step size of 0.0167°.

The ethylene glycol-treated SWy-2-MMT sample was prepared as follows: SWy-2-MMT (1 g) was dispersed in 100 mL of deionized water. The solution was dropped on a silicon slide and dried at room temperature, and then the slide was solvated in an ethylene glycol atmosphere overnight at 60 °C to expand the montmorillonite.

2.3.3. Electron Microscopy. An FEI QUANTA 200 scanning electron microscope (SEM) was used for morphological studies. SWy-2-MMT and OMMTs were dried at room temperature and coated with gold under vacuum conditions in an argon atmosphere ionization chamber for the SEM studies. A Philips CM 200 transmission electron microscope (TEM) at 200 KV was used to investigate the microstructure of the organoclays. All samples were dispersed in a 50% ethanol solution and then dropped on carbon-coated films and dried in an oven at 50 °C for 10 min for TEM studies.

3. Results and Discussion

3.1. Thermogravimetric Analysis. The thermal stability of the organoclay can be determined by the use of thermogravimetric techniques. The high-resolution thermogravimetric analyses (HRTG) of organoclays prepared by the ultrasonic and hydrothermal methods are shown in Figure 1. This Figure shows the differential mass

Table 1. HRTG Results of Prepared Organoclays via Different Methods

samples	desurfactant (1)		desurfactant (2)		desurfactant (3)	
	% mass loss	temp (°C)	% mass loss	temp (°C)	% mass loss	temp (°C)
0.6CEC-OMMT-U	not determined	not determined	3.83	280.9	6.34	381.2
0.6CEC-OMMT-H	not determined	not determined	4.39	289.3	2.41	351.5
1.5CEC-OMMT-U	12.98	202.3	7.28	281.4	9.53	379.2
1.5CEC-OMMT-H	12.54	202.1	7.01	274.8	5.71	374.3
4.0CEC-OMMT-U	33.79	178.7	6.28	283.5	7.44	382.3
4.0CEC-OMMT-H	41.81	175.0	6.57	285.0	6.33	385.1

loss as a function of temperature. Our previous study[20] showed that the decomposition of an organoclay takes place in four steps: (1) water desorption, (2) dehydration, (3) desurfactant, and (4) dehydroxylation of the organoclay. In addition, there are three different molecular environments for the surfactant in the organoclays: (1) surfactant cations intercalated into the clay interlayers through cation exchange and bound to surface sites via electrostatic interaction; (2) surfactant (cations and/or molecules) physically adsorbed on the external surface of the clay; and (3) surfactant molecules located within the clay interlayer.[21-25] Accordingly, the decomposition temperatures for surfactants with different molecular environments will be different from each other. Normally, montmorillonite does not undergo thermally induced changes in the temperature range of 170−500 °C, hence the mass loss in this temperature range should be attributed to the decomposition and/or evaporation of the surfactant.

The results of surfactant mass loss and the corresponding temperature are reported in Table 1. It is found that the content of surfactant in the synthesized organoclays increases with the increasing surfactant concentration in the preparation solutions. This is similar to previous reports.[21,23-25] Meanwhile, all three different molecular environments of the surfactant are observed as shown in Figure 1. The peaks at 170−205, 270−290, and 370−385 °C correspond to the decomposition of the external surface, physically adsorbed surfactant, interlayer-adsorbed surfactant molecules, and intercalated surfactant cations, respectively.[21-26] For organoclay prepared at 0.6CEC, only two peaks corresponding to interlayer-adsorbed surfactant molecules and intercalated surfactant cations were observed. This reflects the fact that all surfactants enter into the montmorillonite interlayer at low surfactant concentration. However, with an increase in surfactant concentration, there are more and more surfactants physically adsorbed on the external surface of the montmorillonite, as indicated by the strong peak at 170−205 °C and the corresponding mass loss.

A comparison of the derivative thermogravimetric (DTG) curves and mass loss among the samples indicates that there are more surfactant cations electrostatically bound within the montmorillonite surfaces in the samples prepared by ultrasonic methods than in those prepared by hydrothermal methods, especially for samples synthesized at 0.6CEC and 1.5CEC concentrations. Meanwhile, for all samples prepared at 1.5CEC and 4.0CEC using the two different methods, three well-resolved peaks

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Figure 2. X-ray diffraction patterns of untreated and ethylene glycol-treated SWy-2-MMT samples.

in the DTG curves are recorded. This is very different from previous studies in which organoclays were prepared by ion exchange at low temperature. In this case, only three poorly resolved peaks were recorded. Intercalated surfactant cations are dominant. The peak at 270−290 °C always occurs as a shoulder.[21,23-26] Both the ultrasonic and hydrothermal methods significantly increase the amount of external-surface adsorbed surfactant compared with those results reported in the literature for other preparation methods. This research demonstrates that the preparation method has a strong influence on the molecular environment of the surfactant within the clays and affects the structure of the resultant organoclays. In our present study, it is found that the organoclays prepared at low surfactant concentration (e.g., 0.6CEC) have better thermal stability than those prepared at high concentration (e.g., 1.5CEC and 4.0CEC). It is proposed that the poor thermal stability of the latter results from the low decomposition temperature of physically adsorbed surfactant on the external surface of montmorillonite. However, these physically adsorbed surfactants on the external surface will improve the hydrophobic property of the organoclays, resulting in good affinity to organic compounds. The potential application is for the removal of organic compounds from water.

3.2. X-ray Diffraction. The modification of the montmorillonite by surface reaction with a cationic surfactant through its incorporation into the structure can be followed through the expansion of the clay. Figure 2 shows the
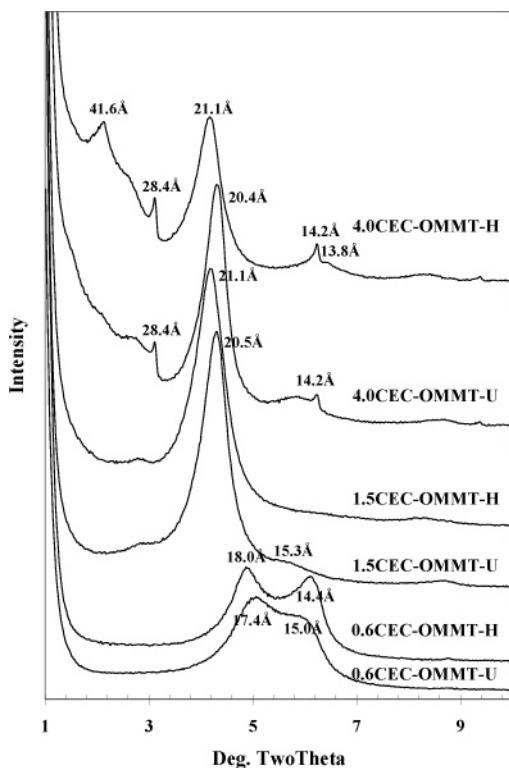
Figure 3. X-ray diffraction patterns of surfactant-modified SWy-2-MMT samples.

XRD patterns of untreated and ethylene glycol-treated SWy-2-MMT samples. The sodium montmorillonite (SWy-2-MMT), supplied by the Clay Minerals Society, is very different from those reported in previous research.[27,28] Two reflections at 24.7 and 12.6 Å were observed. The later should be attributed to the basal spacing of sodium montmorillonite, whereas the former reflects a supercell or superlayer resulting from the packing arrangement of neighboring layers. This is confirmed by the XRD pattern of the ethylene glycol-treated specimen, which clearly displays a reflection at 17.2 Å. This proposal is further supported by the XRD patterns and TEM images of the surfactant-modified samples (see below). Figure 3 displays the XRD patterns of organoclays prepared using ultrasonic and hydrothermal methods with 0.6CEC, 1.5CEC, and 4.0CEC surfactant concentration loadings. With the cation exchange of the sodium ion by the cationic surfactant, expansion of the montmorillonite layers occurs as shown in Figure 3. Both 0.6CEC-OMMT-H and 0.6CEC-OMMT-U show double overlapping peaks at 18.0 and 14.4 Å for the former and at 17.4 and 15.0 Å for the later. Meanwhile, the reflection at 24.7 Å in the original sample disappears. These two phenomena further support our proposal that the reflection at 24.7 Å should be attributed to the supercell or superlattice in the clay.

According to previously experimental and molecular modeling studies,[20,22,29−34] the peaks at 17−18 and 13−15 Å correspond to bilayer and monolayer arrangements of the intercalated surfactant, respectively. The coexistence of bilayer and monolayer arrangements demonstrates property variation (e.g., surface charge density) among montmorillonite layers.[34,35] However, when the surfactant concentration is increased to 1.5CEC, both organoclays display one broad peak at 20.5 Å for 1.5CEC-OMMT-U and one at 21.1 Å for 1.5CEC-OMMT-H, corresponding to a pseudotrilayer arrangement. The basal spacing for organoclays prepared by the hydrothermal method is slightly greater than that prepared by the ultrasonic method, despite the fact that there is more surfactant intercalated into the clay interlayer as shown in Table 1. This observation shows that the loaded quantity of surfactant is not the key factor in controlling the basal spacing of the organoclays. This is consistent with the silane grafting experiment performed by He et al.[35]

One very interesting phenomenon was observed when the surfactant concentration was further increased to 4.0CEC. For sample 4.0CEC-OMMT-H, two series of reflections were observed. A broad peak is observed at 41.6 Å (001), 21.1 Å (002), and 13.8 Å (003), whereas another relatively narrow one is observed at 28.4 Å (001), 14.2 Å (002)... The XRD result is in accord with our TEM observations (see below). The occurrence of the two series of reflections is strong evidence for the regular stacking of two kinds of layers in this clay sample. As shown by TG analysis (Table 1), the loaded surfactant within the montmorillonite interlayer is more than the CEC of the clay, which means that organoclay has a "saturated" state.[21] Thus, the difference in d(001) values between the two series reflects that the property of the clay layer has a significant influence on the organoclay microstructure.[34,35] For organoclay 4.0CEC-OMMT-U, there is no obvious reflection at 41.6 Å, whereas the other reflections for the two series were recorded, reflecting the fact that the preparation method also has an important effect on the structure of organoclays.

3.3. Scanning Electron Microscopy (SEM). SEM is used to study the changes in morphology of SWy-2-MMT upon intercalation. Importantly, there are not many morphologic differences observed between organoclays prepared by ultrasonic and hydrothermal methods, despite the variation in surfactant loading and basal spacing as demonstrated by TG and XRD analyses. Consequently, only the SEM images of organoclays prepared by the hydrothermal reaction method are shown. Figure 4 shows the morphology of montmorillonites before and after modification. The unmodified SWy-2-MMT (Figure 4a) shows massive, aggregated morphology, and in some instances, there are some large flakes. Figure 4b shows the morphology of 0.6CEC-OMMT-H; compared with SWy-2-MMT, 0.6CEC-OMMT has more fragments of smaller size, and they are formed with irregular shapes. For 1.5CEC-OMMT-H, as shown in Figure 4c, nonaggregated morphology is observed, and there is a large number of small flakes with severely curled or crumpled structures. When the concentration of surfactant was increased to 4.0CEC, the flakes of the organoclay became flat, as shown in Figure 4d.

3.4. Transmission Electron Microscopy (TEM). TEM images of the two series of organoclays prepared using the ultrasonic and hydrothermal routes have been obtained. TEM permits the direct observation of microstructural features resulting from the transformation of clays to organoclays. Unfortunately, the layer-structure

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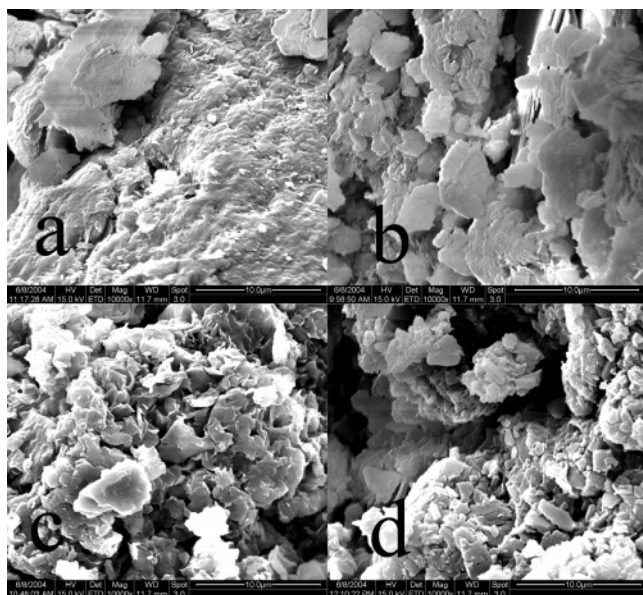
Figure 4. SEM images of SWy-2-MMT and the resultant organoclays. (a) SWy-2-MMT with massive, aggregated morphology, (b) 0.6CEC-OMMT-H, (c) 1.5CEC-OMMT-H, and (d) 4.0CEC-OMMT-H with organoclay fragments.

Figure 5. TEM images of the resultant organoclays. (a) 0.6CEC-OMMT-U and (b) 0.6CEC-OMMT-H show very clear layer structure with some curved layers and extremely large basal spacing (shown by the black arrow). (c) 1.5CEC-OMMT-U and (d) 1.5CEC-OMMT-H show the alternate basal spacings for the neighboring layers located at 17−24 Å. (e) 4.0CEC-OMMT-U and (f) 4.0CEC-OMMT-H with alternate layer heights.

images of untreated SWy-2-MMT were not observed with TEM. It is supposed that for untreated SWy-2-MMT there is water adsorbed on exchangeable cations such as Na^+ and Ca^{2+}. Therefore, the high vacuum of TEM and the high-energy beam can remove the water that makes the layer structures collapse and prohibits the structures from being readily observed. In fact, even for OMMTs, extra exposure time during TEM observation also destroys the layer structure, making the image of the layer structure blurry and difficult to observe. Therefore, with the current TEM sample preparation method, one must take photographs as soon as possible to obtain clear, real images.

Unlike untreated MMT, both 0.6CEC-OMMT-H and 0.6CEC-OMMT-U show very clear layer structures (Figure 5a and b), and the d(001) basal spacings are 14 to 18 Å. This is in a general agreement with the XRD results. Unfortunately, it is difficult to find regularly alternating basal spacings between 14 and 17−18 Å as indicated by the XRD patterns. In some places, there are some curved layers for both in the same samples. Meanwhile, some very large basal spacings can be observed as shown by the black arrow in Figure 5a, but they are not pervasive. This is in agreement with the observation of Lee and Kim.[17,18]

The TEM images of organoclays prepared at 1.5CEC reveal that with an increase in surfactant concentration the d(001) basal spacing increases further. For 1.5CEC-OMMT-U, as shown in Figure 5c, the basal spacings are mainly from 17 to 24 Å, and in some places, the basal spacing even reaches 30−40 Å. This explains the broad XRD peak and reflects the fact that various surfactant arrangements (e.g., bilayer, pseudotrilayer, and paraffin monolayer) may be adopted. A similar structure characteristic is also observed in 1.5CEC-OMMT-H (Figure 5d). In both TEM images of 1.5CEC-OMMT-U and 1.5CEC-OMMT-H, some ordered alternate layer heights can be found. This phenomenon can be observed in the organoclays prepared at 4.0CEC as shown in the TEM images of 4.0CEC-OMMT-U and 4.0CEC-OMMT-H (Figure 5e and f). The alternate layer height observed can well explain the two series of (001) reflections in the XRD patterns. Meanwhile, some exfoliation structures have been observed. Our TEM images of organoclays clearly demon-
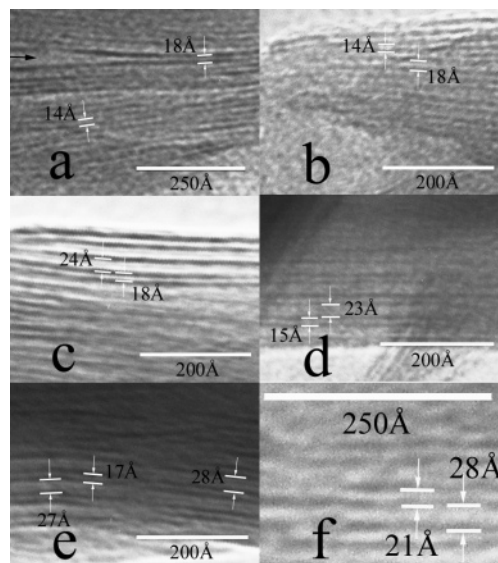
strate that clay layer characteristics have a significant effect on the interlayer structure of surfactant-modified clays. This results from the charge density as demonstrated by molecular modeling.[30,33]

4. Conclusions

Organoclays intercalated with octadecyltrimethylammonium bromide and SWy-2-Na-montmorillonite (Wyoming) were prepared by hydrothermal and ultrasonic methods. Both XRD patterns of the original clay and TEM images of surfactant-modified clays demonstrate that Wyoming SWy-2-Na-montmorillonite contains superlayers. The superlayer results from the variation of the surface-layer charge density, which influences the swelling ability of the corresponding layer. As shown by TEM images and XRD patterns, two different models of intercalated surfactants in the neighboring layers are observed. SEM images of the untreated SWy-2-MMT show massive, aggregated morphology. However, modification with surfactant reduces the clay particle size and aggregation. Organoclays prepared at low surfactant concentration display curved flakes, whereas they become flat with increasing intercalated surfactant.

HRTG analysis clearly shows that there are three different molecular environments for surfactants in organoclays: (1) surfactant cations intercalated into clay interlayers through cation exchange and bound to surface sites via electrostatic interaction; (2) surfactant (cations and/or molecules) physically adsorbed on the external surface of clay; and (3) surfactant molecules located within the clay interlayer. The organoclays prepared at low surfactant concentration has better thermal stability than those prepared at high surfactant concentration, and their thermal stability strongly depends on the surfactant adsorbed on external surfaces of the montmorillonite. Meanwhile, there are more surfactant cations electrostatically bound to the montmorillonite interlayer surface in the samples prepared by the ultrasonic method than those prepared by the hydrothermal method.

This study provides some new insights into the microstructure and thermal stability of organoclays and is important for preparing organoclay-based nanocomposites.