

# Structure of organoclays—an X-ray diffraction and thermogravimetric analysis study

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## Abstract

X-ray diffraction has been used to study the changes in the surface properties of a montmorillonitic clay through the changes in the basal spacings of montmorillonite (SWy-2) and surfactant-intercalated organoclays. Variation in the *d*-spacing was found to be a step function of the surfactant concentration. High-resolution thermogravimetric analysis (HRTG) shows that the thermal decomposition of SWy-2-MMTs modified with the surfactant octadecyltrimethylammonium bromide takes place in four steps. A mass-loss step is observed at room temperature and is attributed to dehydration of adsorption water. A second mass-loss step is observed over the temperature range 87.9 to 135.5 °C and is also attributed to dehydration of water hydrating metal cations such as Na<sup>+</sup>. The third mass loss occurs from 178.9 to 384.5 °C and is assigned to a loss of surfactant. The fourth mass-loss step is ascribed to the loss of OH units through dehydroxylation over the temperature range 556.0 to 636.4 °C. A model is proposed in which, up to 0.4 CEC, a surfactant monolayer is formed between the montmorillonitic clay layers; up to 0.8 CEC, a lateral-bilayer arrangement is formed; and above 1.5 CEC, a pseudotrimolecular layer is formed, with excess surfactant adsorbed on the clay surface.

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## 1. Introduction

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface area, and resulting strong adsorption/absorption capacities [1–4]. In expanding clays, the most common dioctahedral smectite is montmorillonite, which has two silica–oxygen tetrahedral sheets sandwiching an aluminum or magnesium octahedral sheet, where an aluminum or magnesium ion is octahedrally coordinated to six oxygens or hydroxyls. Because of replacement of silicon by aluminum in the tetrahedral layers or similar replacement of aluminum ions by magnesium ions montmorillonite layers are negatively charged. Thus, cations such as sodium, potassium, and calcium are attracted to the mineral surface to neutralize the negative layer charges. Because of

the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature, which make natural clays ineffective sorbents for organic compounds [5–7]. Organomontmorillonites are synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer space [8–10]. When long-chain alkylammonium cations are used, a hydrophobic partition medium can form within the clay interlayer and function analogously to a bulk organic phase. The intergallery distance of the *d* (001) plane of the clay, which has not been organically modified, is relatively small, and the intergallery environment is hydrophilic. Intercalation of organic surfactant between layers of clays not only changes the surface properties from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers. At present, there are many applications of organoclays as sorbents in pollution prevention and environmental remediation, such as treatment of spills, waste water, and hazardous waste landfills. Some studies [11–14] have shown that replacing the

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inorganic exchange cations of clay minerals with organic cations can result in greatly enhanced capacity of the materials to remove organic contaminants.

This paper reports changes in the structure of a montmorillonitic clay which has been intercalated with a long-chain organic surfactant. X-ray diffraction and high-resolution thermogravimetric analyses are used to study the changes in the surfactant concentration-dependent organoclays. The objective of the research is the study of the change in structure of the organoclays with surfactant concentration.

## 2. Experimental

### 2.1. Materials

The montmorillonite used in this study as source clay, SWy-2-Na-Montmorillonite (Wyoming), was supplied by the Clay Minerals Society. This clay originates from the Newcastle formation (Cretaceous), county of Crook, state of Wyoming, USA. The cation exchange capacity (CEC) is 76.4 meq/100 g (according to the specifications of its producer). The surfactant used in this study is octadecyltrimethylammonium bromide ( $C_{21}H_{46}NBr$ , FW: 392.52) from Sigma–Aldrich.

### 2.2. Preparation

The synthesis of surfactant–clay hybrids was undertaken by the following procedure: 4 g of SWy-2-Na-montmorillonite was first dispersed in 400 ml of deionized water under stirring with a Heidolph magnetic stirrer at about 600 rpm for about 16 h. A predissolved stoichiometric amount of octadecyltrimethylammonium (ODTMA) bromide solution was slowly added to the clay suspension at 60 °C. The concentrations of ODTMA<sup>+</sup> used are 0.2 CEC (cation exchange capacity), 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3.0, and 4.0 CEC of the SWy-2-montmorillonite, respectively. The reaction mixtures were stirred for 30 min at 60 °C using a Branson Ultrasonics Model 250 sonifier with an output of 40 mW. All organoclay products were washed free of bromide anions as determined by the use of  $AgNO_3$ , dried at room temperature, ground in an agate mortar, and stored in a vacuum desiccator for about seven days.

### 2.3. Characterization methods

#### 2.3.1. Methods for X-ray diffraction

The SWy-2-montmorillonite and surfactant montmorillonite hybrids were pressed in stainless steel sample holders. X-ray diffraction (XRD) patterns were recorded using  $CuK\alpha$  radiation ( $n = 1.5418 \text{ \AA}$ ) on a Philips PANalytical X'Pert PRO diffractometer operating at 40 kV and 40 mA between 3 and 15° ( $2\theta$ ) at a step size of 0.0167°.

#### 2.3.2. Thermogravimetric analysis

Differential thermal and thermogravimetric analyses of the surfactant montmorillonite hybrids were obtained using a TA Instruments Inc. Q500 high-resolution TGA operating at ramp 10 °C/min with resolution 6.0 °C from room temperature to 1000 °C in a high-purity flowing nitrogen atmosphere (80 cm<sup>3</sup>/min). Approximately 50 mg of finely ground sample was heated in an open platinum crucible. For SWy-2-montmorillonite, the TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis (for other surfactant–montmorillonite hybrids and pure surfactant, the mass spectrometer is disconnected, because organic gases may block the capillary of the mass spectrometer). Only selected gases were analyzed.

## 3. Results and discussion

### 3.1. X-ray diffraction

With the cation exchange of the sodium ion for the cationic surfactant, expansion of the montmorillonitic clay layers occurs. This expansion is readily measure by X-ray diffraction. Fig. 1 shows the XRD patterns of SWy-2-Na-montmorillonite and surfactant montmorillonite hybrids at different surfactant concentrations (octadecyltrimethylammonium montmorillonite = OMMT). Fig. 2 clearly shows the increase in the basal spacing from 11.69 to >20 Å

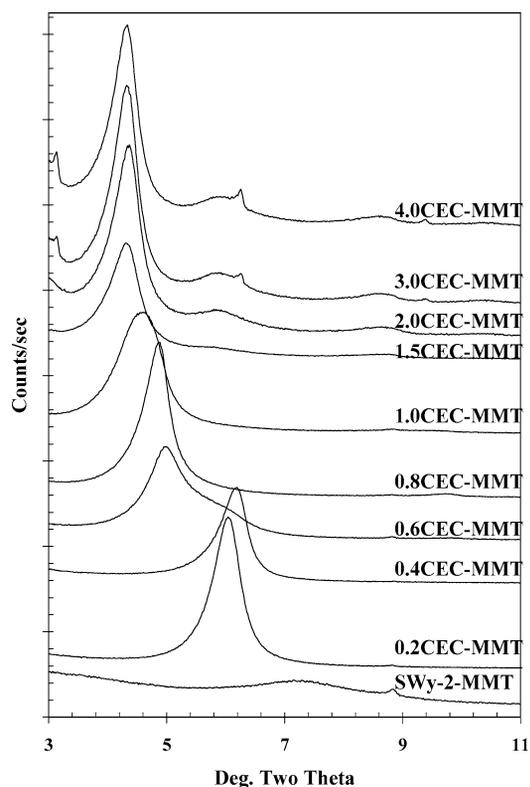


Fig. 1. X-ray diffraction pattern of SWy–montmorillonite and surfactant–montmorillonite hybrids.

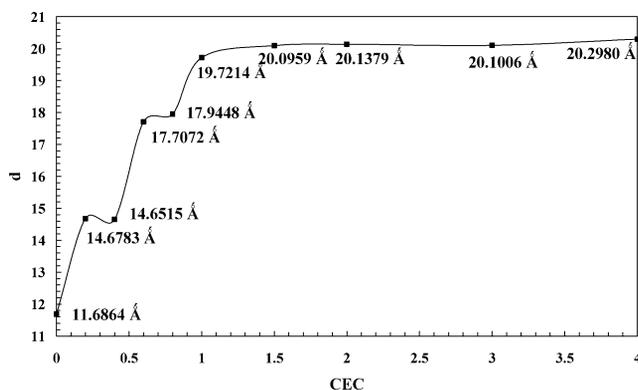


Fig. 2.  $d$  (001) basal spacings of SWy-montmorillonite and surfactant-montmorillonite hybrids.

for OMMT-1.5, OMMT-2.0, OMMT-3.0, and OMMT-4.0 as concentration of the surfactant used is increased. The graph also shows that for OMMT-0.2, the basal spacing is slightly larger than that of 0.4 CEC hybrid OMMT-0.4 (14.51 and 14.17 Å, respectively). It is possible that for OMMT-0.2, the concentration of surfactant is sufficiently low that there is still a large amount of exchangeable  $\text{Na}^+$  which can adsorb water because of its high hydration energy, making the basal spacing larger than that of OMMT-0.4. When 1.5 CEC of surfactant is used, the basal spacing reaches a plateau of 20.1 Å. From 1.5 CEC to 4.0 CEC, the basal spacings only increase slightly. The maximum value at 4.0 CEC is 20.3 Å. In addition, from the configuration structure point of view, for OMMT-0.2 (0.2 CEC) and OMMT-0.4 (0.4 CEC), the  $d$  values are 14.51 and 14.17 Å, respectively. This implies a lateral-monolayer arrangement of  $\text{ODTMA}^+$  in the interlayer space of montmorillonite. For OMMT-0.6 (0.6 CEC) and OMMT-0.8 (0.8 CEC), the  $d$  values are 17.71 and 17.94 Å, respectively, which reflect a lateral-bilayer arrangement. From OMMT-1.5 (1.5 CEC) to OMMT-4.0 (4.0 CEC), the  $d$  basal spacings reach over 20 Å which reflects a pseudotrimolecular layer arrangement. As for OMMT-1.0 (1.0 CEC), the  $d$  value is 19.72 Å; this means that the arrangement of surfactant is between lateral-bilayer and pseudotrimolecular layer structure. A model is proposed in which up to 0.4 CEC a surfactant monolayer is formed between the montmorillonitic clay layers, up to 0.8 CEC a lateral-bilayer arrangement is formed, and above 1.5 CEC a pseudotrimolecular layer is formed with excess surfactant adsorbed onto the clay surface [15]. This previous study showed that the monolayer is formed at 13.7 Å, the bilayer at 17.7 Å, the trilayer at 21.7 Å, and a complex with basal spacings greater than 22.0 Å [15]. Further research using TEM needs to be undertaken to validate this model. These authors used hexadecyltrimethylammonium bromide (HDTMA) as surfactant. In this work we are using octadecyltrimethylammonium bromide, which is a longer molecule yet for which the basal spacings are slightly smaller. It is proposed that the ODTMA molecule fits into the siloxane surface better than HDTMA. The differences in the measurements may also be

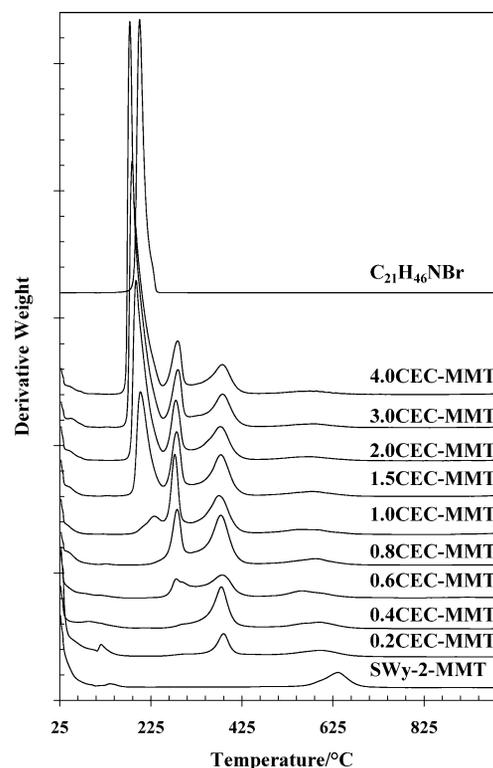


Fig. 3. High-resolution thermogravimetric analysis of SWy-montmorillonite, surfactant, and surfactant-montmorillonite hybrids.

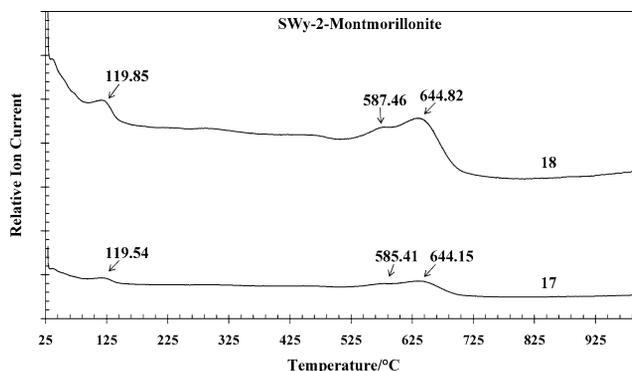


Fig. 4. Mass spectrometric curves for SWy-montmorillonite.

as a result of the way in which the XRD data is obtained and in the control of the humidity.

### 3.2. High-resolution thermogravimetric analysis (HRTG)

The high-resolution thermogravimetric analysis (HRTG) for the SWy-montmorillonite, surfactant, and organoclays is shown in Fig. 3 (derivative wt% versus temperature). The temperatures of the evolved gas mass gain of SWy-2-MMT are shown in Fig. 4. The results of the analyses of the mass loss and temperature of the mass loss are reported in Table 1. Several mass-loss steps are observed. A mass-loss step is observed from room temperature and is attributed to mass loss due to dehydration/dehydroxylation (adsorption water). A second mass-loss step is observed over the temperature

Table 1  
Results of the HRTG of SWy-MMT, surfactant, and surfactant–MMT hybrids

Samples	Dehydration/hydroxylation (adsorption water)		Dehydration/hydroxylation (water adsorbed by metal cations)		Desurfactant		Dehydroxylation (the structural OH units)	
	% mass-loss	Temp.	% mass-loss	Temp.	% mass-loss	Temp.	% mass-loss	Temp.
	(step 1)	(°C)	(step 2)	(°C)	(step 3)	(°C)	(step 4)	(°C)
Swy-2-MMT	4.369		1.065	135.53			4.917	636.35
0.2 CEC–MMT	6.664		1.525	116.37	5.146	384.51	3.543	598.16
0.4 CEC–MMT	2.069		2.204	87.91	9.099	380	3.686	598.2
0.6 CEC–MMT	3.114		0.5015	113.61	10.16	281.17/381.16	4.539	556.01
0.8 CEC–MMT	2.475		0.2189	126.99	17.78	283.03/378.83	3.417	589.13
1.0 CEC–MMT	1.953				20.31	233.05/277.74/374.75	3.593	562.04
1.5 CEC–MMT	2.131				29.70	202.26/281.87/379	2.899	579.36
2.0 CEC–MMT	2.201				36.31	192.49/279.97/377.78	2.547	573.25
3.0 CEC–MMT	1.958				44.25	183.99/284.68/382.58	2.224	582.98
4.0 CEC–MMT	1.787				47.47	178.97/283.96/381.83	2.130	589.33
C <sub>21</sub> H <sub>46</sub> NBr					100	200.44		

range 87.9 to 135.5 °C and is also attributed to dehydration of water adsorbed by metal cations such as Na<sup>+</sup> and Ca<sup>2+</sup>. For 0.2 CEC and 0.4 CEC–MMT, the total weight losses of adsorption water are 8.189 and 4.273%, respectively. This shows that 0.2 CEC–MMT contains more water than 0.4 CEC–MMT and serves to explain why the basal spacing of 0.2 CEC–MMT is larger than that of 0.4 CEC–MMT. The third mass loss occurs from 178.9 to 384.5 °C. For OMMT-0.6, -0.8, -1.0, -1.5, -2.0, -3.0, and -4.0, there is more than one peak. By comparing the TG patterns of pure surfactant with that of SWy-2-MMT, it is concluded that the loss of surfactant occurs at 225 °C for pure C<sub>21</sub>H<sub>46</sub>NBr. The fourth mass-loss step is ascribed to the loss of dehydroxylation of the structural OH units of the montmorillonite over the 556.0–636.3 °C temperature range. Generally speaking, the second dehydration/dehydroxylation step is observed for montmorillonite and some of the low-concentration-of-surfactant-modified clays (SWy-2-MMT, 0.2–0.8 CEC surfactant-modified clays). The first % mass loss for dehydration of adsorption water varies from 1.787 up to 6.664%. The experimental % mass loss during the second dehydration/dehydroxylation of adsorption water varies from 0.2189 up to 2.204%. The experimental % mass loss during the desurfactant procedure varied from 5.146% (0.2 CEC–MMT) to 47.47% (4.0 CEC–MMT) to 100% (pure surfactant). In addition, the peak maxima of the DTG desurfactant procedure of organoclays are different. For 0.2 CEC and 0.4 CEC–MMT, there is only one peak. The centres of the peaks are 384.5 and 380 °C, respectively. For 0.6 CEC and 0.8 CEC–MMT, there are two peaks for each sample (281.2/381.2 °C for 0.6 CEC–MMT and 283.0/378.8 °C for 0.8 CEC–MMT). From 1.0 CEC–MMT to 4.0 CEC–MMT, there are three peaks for every sample. As a conclusion, when the concentration of the organoclay is relatively low (for example, 0.2 and 0.4 CEC), there is only one peak (the peak position is around 380 °C); with the increase of the concentration of surfactant, a new peak appears (centre position is about 280 °C) and the intensity of this peak increases with the increase of surfactant used; if the concentration of sur-

factant increases further, the third peak will appear (it varies from 178.9 to 233.0 °C) and the intensity of this peak also increases with the increase of the surfactant used.

When the concentration of the surfactant is relatively low, the organic cations exchange with the Na<sup>+</sup> ions and mainly adhere to surface sites via electrostatic interactions. With the increase of the concentration of surfactant, some of surfactant molecules attach to the surface of montmorillonite. This results in the appearance of the second peak. If the concentration increases further, the concentration of the surfactant exceeds the CEC of clay. Surfactant molecules then adhere to the surface-adsorbed surfactant cations by van der Waals forces.

The properties of these organic cations are very similar to that of pure surfactant. So the third peak appears at about 178.9–233.0 °C, which is close to 200.4 °C—the temperature of the pure surfactant. In addition, with the increase of the concentration of the surfactant, the temperature of the third peak decreases gradually (becomes closer to that of the pure surfactant). In addition, there was a considerable difference between the temperature of pure surfactants and surfactants in the organoclays. This may be due to some surfactants attached strongly to the montmorillonite, which causes an increase in the decomposition temperature.

#### 4. Conclusions

A model is proposed based upon the changes in the *d* (001) spacings as a function of surfactant concentration. The basal spacing obtained from X-ray diffraction give details of arrangement of surfactant in the organoclays. For OMMT-0.2 and OMMT-0.4, there is a lateral-monolayer arrangement of ODTMA<sup>+</sup> in the interlayer space of montmorillonite. For OMMT-0.6 and OMMT-0.8, the surfactant takes a lateral-bilayer arrangement. From OMMT-1.5 to OMMT-4.0, the *d* basal spacings reach >20 Å, which reflects a pseudotrimolecular layer arrangement. As for OMMT-1.0 (1.0 CEC), the arrangement of surfactant is in between a

lateral-bilayer and pseudotrimolecular layer structure. The utilization of HRTGA allows one to distinguish between different concentrations of surfactant-modified clays and to provide more information on their configuration and structural changes in the organoclays. This shows that there are about four mass-loss steps, ascribed to (a) water desorption, (b) dehydration, (c) desurfactant process, and (d) dehydroxylation of clay OH units. In addition, three different environments of the surfactant in organoclays have been described.

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