THERMOGRAVIMETRIC ANALYSIS OF ORGANOCLAYS INTERCALATED WITH THE SURFACTANT OCTADECYLTRIMETHYLAMMONIUM BROMIDE

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High resolution thermogravimetric analysis has been used to study the thermal decomposition of montmorillonite modified with octadecyltrimethylammonium bromide. Thermal decomposition occurs in 4 steps.The first step of mass loss is observed from ambient to 100°C temperature range and is attributed to dehydration of adsorbed water. The second step of mass loss occurs between 87.9 to 135.5°C temperature range and is also attributed to dehydration of water hydrating metal cations such as Na^+. The third mass loss occurs between 179.0 and 384.5°C; it is assigned to the loss of surfactant. The fourth step is ascribed to the loss of OH units due to dehydroxylation of the montmorillonite and takes place between 556.0 and 636.3°C temperature range. These TG steps are related to the arrangement of the surfactant molecules intercalating the montmorillonite. Changes in the basal spacing of the clay with surfactant are followed by X-ray diffraction. Thermal analysis provides an indication of the stability of the organo-clay.

Introduction

Organoclays form an important type of modified clay material. Their uses are many including some environmental applications [1–5]. Organoclays are particularly useful in water purification e.g. by the removal of oil and toxic chemicals from water [3, 6–8]. Remediation of industrial waste waters is enabled through the use of organoclays [9, 10]. These types of materials are useful for the remediation of contaminated soils [11–13] and they are also applied as clay liners in land fills. The development of some new nanocomposite materials is due to use of organoclays [14–17]. Organo-montmorillonites are synthesized by introducing cationic surfactants such as quaternary ammonium compounds into the interlayer space through ion exchange [18–20]. Long-chain alkylammonium cations can form a hydrophobic medium within the clay interlayer, and act in analogy to a bulk organic phase. The intergallery distance of d(001) plane of the clay which has not been organically modified, is relatively small, and the intergallery environment is hydrophilic. Intercalation of an organic surfactant between the clay layers can not only change the surface properties from hydrophilic to hydrophobic, but also significantly increase the basal spacing of the layers.

The use of thermal analysis techniques to study montmorillonitic clays is well known [21]. Some thermoanalytical studies of organo-modified clays have been forthcoming [22–24]. A recent review has demonstrated the applicability of DTA-TG for differentiating between adsorbed and free organic matter and also between ionic and molecular adsorption [23]. This work has shown that the location of the exothermic peaks is diagnostic and serves to show the adsorption of organic molecules on metallic cations. Many of the thermal analytical studies have been applied to nanocomposites involving organoclays [25]. However, there have been almost no studies of the thermal stability of organoclays and no studies of the structure of organoclays. Recently thermal analysis techniques have proven most useful for the study of complex mineral systems [26–28] and materials generated through the modification of surfaces [29–31]. Modification of surfaces through intercalation have also been studied using thermal analysis techniques [32, 33]. This paper reports the changes in the structure of a montmorillonitic clay intercalated with a long chain organic surfactant. X-ray diffraction and high resolution thermogravimetric analyses are used to study the changes in the organoclay basal spacing depending on the content of surfactant and this is the subject of this research.

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Experimental

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), County of Crook, State of Wyoming, USA. The cation exchange capacity (CEC) is 76.4 meq/100 g (according to the specification of its producer). The surfactant used in this study is octadecyltrimethylammonium bromide ($C_{21}H_{46}NBr$, FW: 392.52) from Sigma-Aldrich.

Preparation

The preparation of surfactant-clay hybrids were undertaken by the following procedure: 4 g of SWy-2-Na-montmorillonite was first dispersed in 400 mL of deionized water then stirred with a Heidolph magnetic stirrer at about 600 rmp for about 16 h. A pre-dissolved stoichiometric amount of octadecyltrimethylammonium (ODTMA) bromide solution was slowly added to the clay suspension at 60°C.

    The concentrations of $ODTMA^+$ used were 0.2 CEC (Cation Exchange Capacity), 0.4 CEC, 0.6 CEC, 0.8 CEC, 1.0 CEC, 1.5 CEC, 2.0 CEC, 3.0 CEC 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 organo-clay products were washed free of bromide anions, dried at room temperature and ground in an agate mortar, and stored in a vacuum desiccator for about 7 days.

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_α radiation (λ=1.5418 Å) on a Philips PANalytical X' Pert PRO diffractometer operating at 40 kV and 40 mA between 3 and 15° (2θ) at a step of 0.0167°.

Thermogravimetry

DTG and TG analyses of the surfactant montmorillonite hybrids were obtained using a TA® instruments Inc. Q500 high resolution TG operating at a heating rate 10°C min^{-1} and resolution 6.0 from room temperature to 1000°C in a flow of high purity flowing nitrogen atmosphere (80 cm^3 min^{-1}). Approximately 50 mg of sample was heated in an open platinum crucible. No preparation was required other than grinding the sample up finely. For SWy-2-montmorillonite, the TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. For other surfactant montmorillonite hybrids and pure surfactant, the mass spectrometer was disconnected, because organic breakdown products may block the capillary of the mass spectrometer. Only selected gases such as water and carbon dioxide were analyzed.

Results and discussion

X-ray diffraction

Montmorillonite consists of tetrahedral silica layers and octahedral alumina layers, carrying negative charges which must be counterbalanced by exchangeable cations in the interlayers. Such an arrangement results in a basal spacing of around 11.7 Å in an air dry state. This basal spacing is dependent upon the size of the cation be it Na, Ca or Mg and also on the degree of hydration of the cation. This degree of hydration is very dependent on the vapour pressure of water and the temperature. Upon ion exchange of the inorganic cation by an organic one, the properties of the clay material changes dramatically from a hydrophilic medium to a hydrophobic medium. Hence such materials have application both in organic media and in water. This ion exchange is dependent upon the cation exchange capacity of the montmorillonite being used. The degree of ion exchange of the sodium ion by octadecyltrimethylammonium bromide will affect the basal spacing of the organoclays. This expansion is illustrated in Fig. 1.
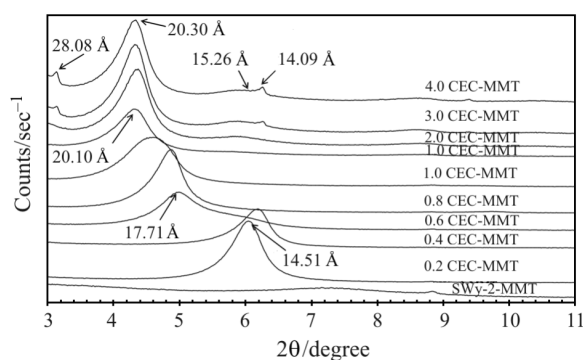

Fig. 1 X-ray diffraction patters of the d(001) spacing for octadecyltrimethylammonium bromide surfactant intercalated montmorillonite

    Upon exchange of the Na^+ ion by octadecyltrimethylammonium bromide at a 0.2 CEC, the basal spacing increases from 11.7 to 14.51 Å. At the 0.4 CEC level, the resultant expansion is 14.17 Å which

Table 1 Table of d(001) spacings for surfactant modified organoclays

	Main peak		Other peaks					
	2θ°	d/Å	2θ°	d/Å	2θ°	d/Å	2θ°	d/Å
SWy-2	7.56	11.69						
0.2 CEC	6.09	14.51						
0.4 CEC	6.24	14.17						
0.6 CEC	4.99	17.71						
0.8 CEC	4.92	17.94						
1.0 CEC	4.48	19.72						
1.5 CEC	4.40	20.10						
2.0 CEC	4.39	20.14			5.83	15.15	6.00	14.74
3.0 CEC	4.40	20.10	3.15	28.05	5.76	15.35	6.27	14.09
4.0 CEC	4.35	20.30	3.15	28.08	5.79	15.26	6.27	14.09

is slightly less than the previous value. It is thought that insufficient octadecytrimethylammonium bromide has been added to displace all of the water from the interlayer space. The increase in d(001) spacing is approximately 4.8 Å. This value is about the thickness of the surfactant molecule. On exchange of the Na^+ by the surfactant at the 0.6 and 0.8 CEC level, expansions of 17.71 and 17.94 Å result. Again there is an increase in d(001) spacing of around 3.5 Å. This suggests that there are two overlapping molecules in the interlayer space. The 8.2 Å represents the overlapping of the long chain alkyl groups. At the 1.0 CEC concentration the expansion is 19.72 Å and at the 1.5 CEC level the expansion is 20.10 Å. Thus the increase is by 2 Å. This indicates a rearrangement of the surfactant molecules between the clay layers. Perhaps instead of laying flat between the clay layers the molecules are perpendicular to or at some angle to the clay surface. On further increasing the CEC value little change in the d(001) spacing is observed.

A study of these results suggests that the expansion occurs in steps which results in a given arrangement of the surfactant molecules between the clay unit layers. At low concentrations the clay is not fully expanded as the surfactant concentration is simply too low. At the surfactant content 0.4 CEC the montmorillonite is expanded completely with one single layer of surfactant molecules. At 0.6 CEC the second interlayer starts to form and it is completed at 0.8 CEC, whereas the third layer is completed at 1.5 CEC. At higher CEC values the surfactant does not cause any further clay expansion and the surfactant is simply adsorbed on the surface of clay particles.

Thermogravimetric analysis

Often thermoanalytical studies can lead to new insights into the structure of intercalated clays

[27–29, 33]. Often the way in which the mass loss steps occur provides information on the structure of the inserting molecules. The thermogravimetric analyses of the octadecyltrimethylammonium bromide organoclays are shown in Figs 2 to 7. Mass spectrometry was not undertaken as the combustion of the
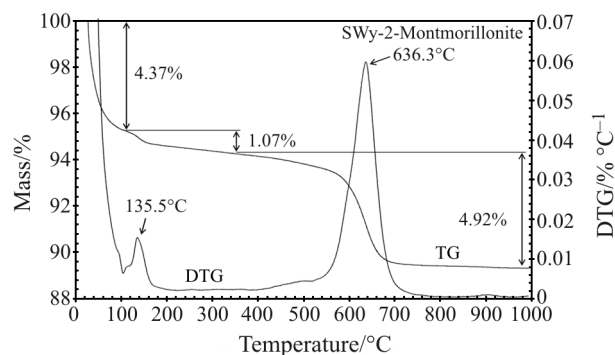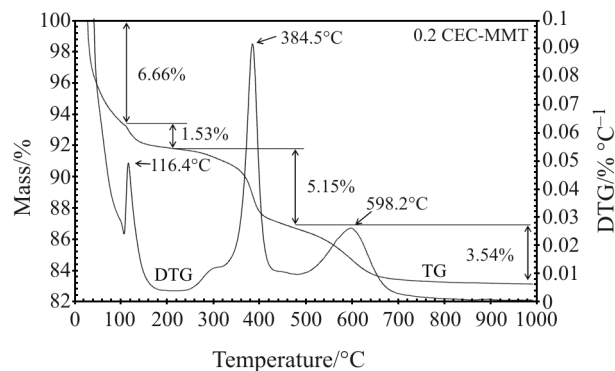

Fig. 2 TG and DTG of montmorillonite

Fig. 3 TG and DTG of 0.2 octadecyltrimethylammonium bromide montmorillonite

Table 2 Results of the HRTG of SWy-MMT, surfactant and surfactant MMT hybrids

|	SWy-2-MMT	0.2CEC-MMT	0.4CEC-MMT	0.6CEC-MMT	0.8CEC-MMT	1.0CEC-MMT	1.5CEC-MMT	2CEC-MMT	3CEC-MMT	4CEC-MMT	$C_{21}H_{46}NBr$	Desciption
Step 1												
Mass loss/%	4.37	6.66	2.07	3.11	2.48	1.95	2.13	2.20	1.96	1.79		Dehydration/(adsorption water
Temp/°C												
Step 2												
Mass loss/%	1.07	1.53	2.20	0.50	0.22							Dehydration(water adsorbed by metal cations)
Temp/°C	135.5	116.4	87.9	113.6	127.0							
Step 3												
Mass loss/%		5.15	9.10	10.16	17.78	20.31	29.70	36.31	44.25	47.47	100	De-surfactant
Temp/°C		384.5	380	281.2 381.2	283.0 378.8	233.0 277.7 374.7	202.3 281.9 379.0	192.5 280.0 377.8	184.0 284.7 382.6	179.0 284.0 381.8	200.4	
Step 4												
Mass loss/%	4.92	3.54	3.69	4.54	3.42	3.59	2.90	2.55	2.22	2.13		Dehydroxylation (the structural OH units)
Temp/°C	636.3	598.2	598.2	556.0	589.1	562.0	579.4	573.2	583.0	589.3		
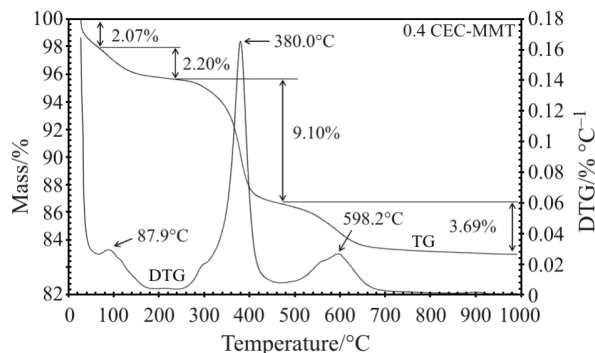
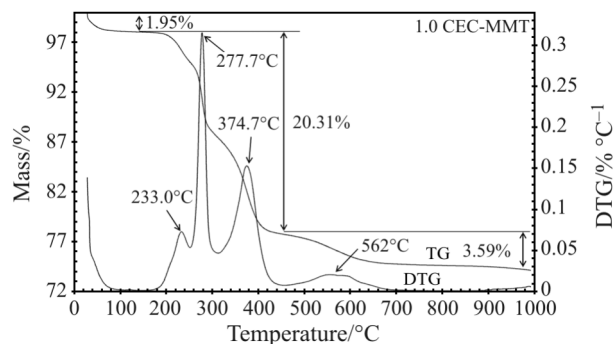**Fig. 4** TG and DTG of 0.4 octadecyltrimethylammonium bromide montmorillonite

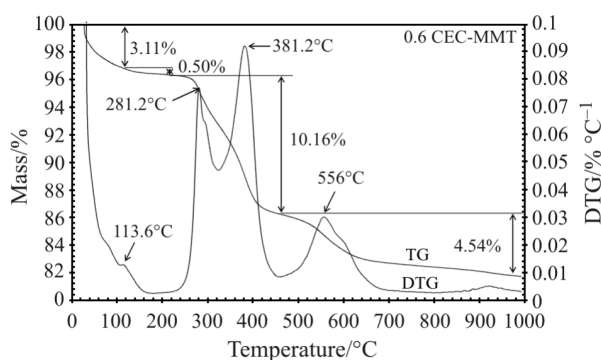**Fig. 7** TG and DTG of 1.0 octadecyltrimethylammonium bromide montmorillonite

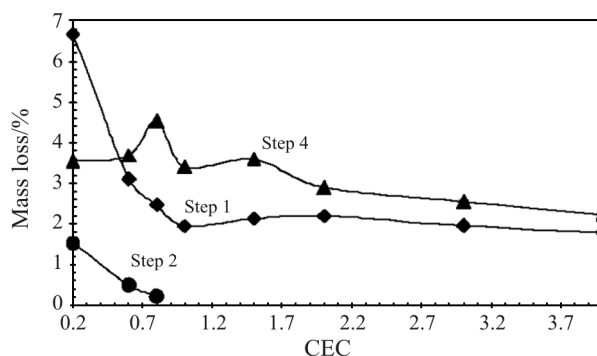**Fig. 5** TG and DTG of 0.6 octadecyltrimethylammonium bromide montmorillonite

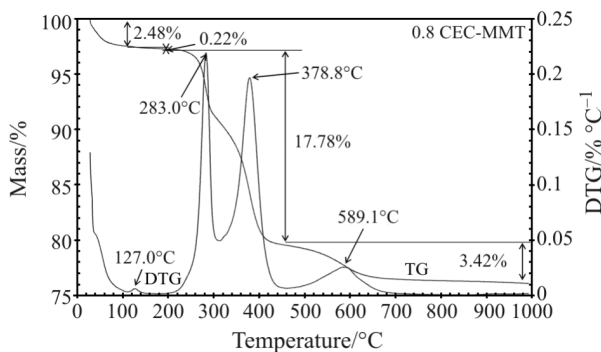**Fig. 8** Variation in mass loss with CEC for steps 1, 2 and 4

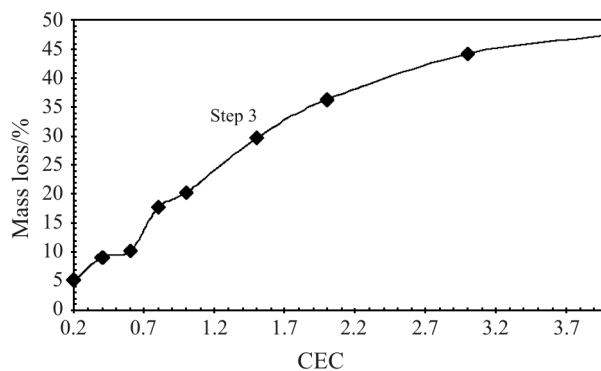**Fig. 6** TG and DTG of 0.8 octadecyltrimethylammonium bromide montmorillonite

Fig. 9 Variation in mass loss with CEC for step 3

surfactant causes the capillary outlet from the furnace to the mass spectrometer to be clogged. The results of the thermogravimetric analyses are reported in Table 2. Figure 2 displays the TG and DTG results for the montmorillonite without intercalation with the surfactant. Figures 3 to 7 show the TG and DTG for 0.2, 0.4, 0.6, 0.8 and 1.0 CEC surfactant modified montmorillonite. It is noted that the TG of the unmodified montmorillonite has three mass loss steps at between ambient and 100°C, secondly at 135.5 and at

636.3°C (Fig. 2). These mass loss steps are attributed to desorption of water from the clay, dehydration of the hydrated cation in the interlayer and the dehydroxylation of the montmorillonite respectively. Four steps of the mass loss steps are observed for the organoclays. The first step form the ambient to 100°C temperature range and is attributed to the desorption of water. The second step occurs from 87.9 to 127.0°C temperature range and is assigned to the loss of hydration water from the Na^+ ion. It is noted that this step does not occur at surfactant con-

tent higher than 0.8 CEC. The third mass loss step is attributed to the removal of the surfactant. It is noted that the temperature of the de-surfacting is higher than the boiling point of the surfactant. The DTG curve of the surfactant shows a peak at 200°C whereas the escape of surfactant at its content 0.2 and 0.4 CEC organoclays is around 380°C, thus a value by 180°C higher. Figures 8 and 9 show the values of the mass loss as a function of its content added.

This is no doubt an indication of the stability of the organoclays. In the 0.6 and 0.8 CEC range two mass loss steps are observed for the escape of surfactant. These occur at temperatures around 380 and 280°C and indicate two types of bonding of surfactant molecules in the organoclays. One type of bonding is to the silica surface and the second to other surfactant molecules. In this way the use of TG techniques enable a better understanding of the organoclays. It is considered that the arrangement of molecules in the interlayer space consists of more than one molecular layer (see above). In the 1.0 to 4.0 CEC concentration range three mass loss steps are observed for the loss of surfactant. The temperatures are around 380, 280 and 180°C. The latter temperature simply represents the desorption of the surfactant molecules from the surface of the clay particles. The fourth mass loss step in the TG curves is assigned to the loss of structural hydroxyl groups from within the clay. It is noted that the dehydroxylation temperature of the unreacted montmorillonite is 636.3°C whereas the 0.2 CEC organoclays is 598.2°C, which is a difference of 38°C.

Conclusions

Marked changes occur in the surface properties of montmorillonitic clay (MMT) when the cation Na^+ is replaced with an organocation, in this case octadecyltrimethylammonium (ODTMA+) ion added as bromide. The clay changes from being hydrophilic to hydrophobic. Significant changes occur in the basal spacing as increasing amounts of surfactant are intercalated into the surfactant, related to CEC. For MMT-0.2 CEC and MMT-0.4 CEC, there is a lateral-monolayer arrangement of $ODTMA^+$ in the interlayer space of montmorillonite. For MMT-0.6 CEC and MMT-0.8 CEC, the surfactant forms a bilayer arrangement. From MMT-1.5 CEC to MMT-4.0 CEC, the d(001) basal spacing is higher than 20 Å, which reflects a pseudotrimolecular layer arrangement. As for MMT-1.0 CEC, the arrangement of surfactant molecules is between lateral-bilayer and pseudotrimolecular layer structure. The utilization of TG allows one to distinguish between different concentrations of surfactant modifying clay proper-

ties and to provide more information of their configuration and structural changes in the organo-clays. It shows that there are mainly four mass loss steps ascribed to (a) water-desorption (b) dehydration (c) surfactant escape (d) dehydroxylation of clay OH units. In addition, TG enables three different structural arrangements of surfactant molecules intercalating the montmorillonite to be proposed.

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