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EFFECT OF SURFACTANT AGENT UPON THE STRUCTURE OF MONTMORILLONITE

X-ray diffraction and thermal analysis

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The modification of sodium montmorillonite (MMT) through the incorporation of amphiphilic octadecylammonium cations in various concentrations (10–200% CEC) into the clay's interlayer spaces has been studied. High resolution thermogravimetric analysis shows that the thermal decomposition of modified montmorillonite occurs in three steps. The first step of mass loss is related to dehydration of adsorbed water and water hydrating metal cations such as Na^+. The second step of mass loss is attributed to the decomposition of surfactant. The third step is due to the loss of OH units during the dehydroxylation of the montmorillonite. The conformation of the surfactant cations in the confined space of the silicate galleries is investigated by X-ray diffraction analysis. These analyses are very important for any attempt to incorporate the organomodified MMT particles into different media for various applications such as polymer nanocomposite preparation.

Keywords: *DSC, montmorillonite, octadecylammonium, organoclay, thermogravimetry, X-ray diffraction*

Introduction

Smectite are widely used in a range of applications because of their cation exchange capacity, smelling capacity, high surface area and resulting strong adsorption/absorption capacities [1–4]. The crystal structure of the unit layer consists of tetrahedral silica sheets combined with sheets of octahedral alumina or magnesia [5]. Smectite clays, such as montmorillonite (MMT), belong to the structural family of 2:1 phyllosilicates. Their unit layer includes an octahedral sheet of alumina or magnesia sandwiched between two tetrahedral silica sheets. The adjacent sheets are bonded together through the sharing of oxygen atoms between silica and alumina atoms. 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 makes natural clays ineffective sorbents for organic compounds [6–8].

Organoclays form an important type of modified clay material. Their uses are many, including some environmental applications. Organoclays are particularly useful in water purification e.g. by the removal of oil and toxic chemicals from water [9–12]. Remediation of industrial waste waters is enabled through the use of organoclays [13, 14]. These types of materials are useful for the remediation of contaminated soils [15–17]. Organoclays are particularly explored as matrix reinforcing components for their high aspect ratio, plate morphology, natural availability and low cost to synthesize nanocomposites [18–21]. Organomont- morillonites are synthesized by introducing cationic surfactants such as quaternary ammonium compounds into the interlayer space through ion exchange [22–25]. 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 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 [26]. It is generally accepted that the extent of swelling depends on the length of the alkyl chain and the cation-exchange capacity (CEC) of the clay [27].

The use of thermal analysis techniques to study montmorillonitic clays is well known [25]. A recent review has demonstrated the applicability of DTA-TGA for differentiating between adsorbed and free organic matter and also between ionic and molecular adsorption [28].

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The purpose of this paper is to report the changes in the structure of the montmorillonite which has been intercalated with long chain organic molecules. X-ray diffraction and thermogravimetric analysis are used to study the changes in the organoclay basal spacing depending on the content of the surfactant.

Experimental

Materials

Sodium montmorillonite (MMT) preparation

The original clay mineral used was Maghnia montmorillonite. It was isolated from Maghnia clay (Algeria) by successive decantations from the aqueous suspensions. The raw material was dried in the oven at 110°C for four days, ground in an agate mortar and sieved in 100 μm filter. The obtained powder was immersed in a (30%) H_2O_2 solution for 48 h in order to eliminate the organic materials. The clay suspension was then washed seven times in distilled water at 30°C using the centrifugation process. Dried at 50°C for five days, the precipitate was sieved in 100 μm filter.

170 g of the prepared clay was dispersed in 5 L of (1 M) NaCl solution and stirred for 30 min at 40°C using the centrifugation method. The procedure was repeated four times and the obtained suspension was kept for 48 h. The precipitate was collected by filtration and rinsed with distilled water at 80°C until an $AgNO_3$ test verified the absence of chloride. Dried at 80°C for 48 h, ground in a mortar and sieved with 100 μm filter, the suspension was stored in a vacuum desiccator for five days.

Organoclays (OMMT) preparation

The preparation of surfactant clay hybrids was carried out by the following procedure: 1.5 g of MMT was first dispersed in 94 mL of bi-distilled water then stirred with a magnetic stirrer for about 3 h at 80°C. 0.5 g of octadecylamine (ODA) was dissolved in a mixture of distilled water and concentrated hydrochloric acid (35%) at 80°C within 1 h with stirring. A pre-dissolved stoichiometric octadecylammonium (ODA^+) solution was slowly added to the clay suspension at 80°C.

The concentrations of ODA used were 10% CEC (Cationic Exchange Capacity), 25, 50, 75, 100, 125, 150, 175 and 200% CEC of the MMT, respectively. The reaction mixtures were stirred vigorously for 1 h at 80°C. All organoclay products were washed free of chloride anions, dried at room temperature and ground in a mortar and stored in a vacuum desiccator for five days.

Methods

X-ray diffraction analysis was carried out on a Philips diffractometer (PW-1710) using CuK_α (λ=1.54 Å) radiation at room temperature. The basal spacing distance of silicate layers were calculated from the estimation of (001) plane peak in XRD patterns using the Bragg's law:

$$d=\gamma/2\sin\theta_{\max} \qquad (1)$$

All scanning are performed in 2θ range 2–10°.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis were performed using TA Instruments-SDT 2960 Simultaneous DSC-TG. The samples were analyzed over a wide range of temperatures which ranges from room temperature up to 700°C with 10°C min^{-1} heating rate under air condition.

Results and discussion

XRD analysis

Figure 1 shows the XRD curves for the various organophilized montmorillonites (OMMT). The interaction between the clay and the modifier agent results in shifting the $d_{(001)}$ diffraction peak of MMT toward lower angle values, implying the increase of the interlayer space. This expansion is due to the insertion of octadecylammonium chains inside the galleries of MMT. The basal distance is an indication of the interlayer proportion occupied by the amphiphilic

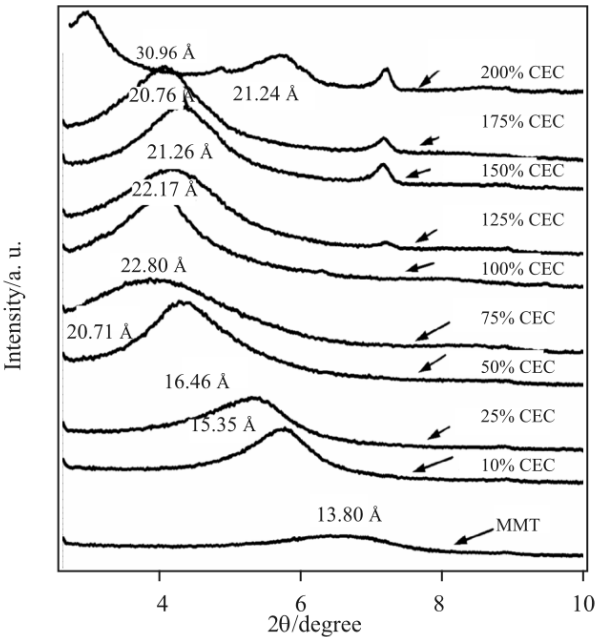

Fig. 1 XRD patterns of pristine and organomodified montmorillonite with various concentrations of octadecylamine (related to clay CEC)

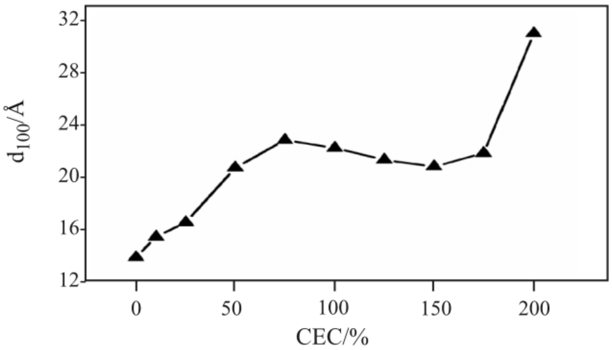

Fig. 2 The basal distance (d_{001}) of pristine (MMT) and organomodified montmorillonites (OMMT) *vs*. ODA concentration normalized to CEC%

substances. For this reason, the gallery spacing gradually increases, depending on the amount of ODA^+ intercalated within the layered silicate.

Depending on the ODA^+ packing density and the alkyl chain length, the carbon chain can be arranged in the montmorillonite interlayer spaces, forming either monolayers or bilayers parallel to the clay surface or pseudotrimolecular layers or paraffin complexes [29]. These arrangements can be detected by the clay basal spacing. The thickness of a MMT layer is 9.4–9.6 Å [30], while the height of the alkyl chain lying parallel to the clay layer ranges between 4 and 4.5 Å [31].

Figure 2 represents data relating basal distance with ODA concentrations normalized to % CEC of the unmodified clay. Comparison of these data with the alkylammonium packing modes suggested in [29] indicates that the clay basal distance changes in a stepwise fashion with the increase of the ODA loading. In addition, between steps there is a linear increase of the basal distance.

The effect of ODA loadings can be clearly seen in Fig. 2. As shown in this figure, the dependence of the basal distance on CEC follows three regions. In the first regime, the basal distance increases by increasing ODA concentration up to 75% CEC followed by, nearly, independing on the CEC% up to 175%, then jumping at 200% as shown in the third regime. However, the increase of the basal distance is more significant by the incorporation of 10% CEC since the basal distance increase from 13.8 to 15.35 Å. That due to fast substitution of Na^+ by ODA^+ cations. Beyond 10 up to 25% the basal distance increases slightly. This can be related to a relative constant basal distance and assigned to a first step where a coexistence of ODA^+ and Na^+ within the same interlayers is observed. Again the basal distance significantly increases beyond 25% CEC up 75%. This situation corresponds to a combination where both complete monolayers and incomplete bilayers of ODA^+ are present in the galleries. During this linear increase of the d-spacing, the arrangement of the ammonium cations inside the interlayer spaces undergoes a transition: The monolayer arrangement is gradually transformed into a bilayer one. This transition between the two principal conformations is also supported by the peak broadening in the diffractograph for the 75% CEC coverage (Fig. 1). This broadening may be the result of superimposing reflections that correspond to d_{001} distance of about 15.35 Å (ammonium monolayer) and 22.80 Å (ammonium bilayer). These results are in good agreement with those reported in [32].

The complete bilayer arrangement requires a higher amount of ODA than the clay CEC and up to 175% CEC coverage. Additional increase of ODA to 200% CEC gives rise to a paraffin complex arrangement of the alkylammonium cations inside the galleries. According to Lagaly [29], this kind of arrangement occurs at basal spacing greater than 22 Å. Similar profiles have been reported in [34].

However, recent studies [27] claim that the conformation of the surfactant tails is more random, which means that the step changes shown in Fig. 2 may not be as clear-cut as plotted in the figure. Moreover, a linear dependence of the basal spacing on the mass ratio of organic to clay is suggested [27, 35–39].

Thermogravimetric analysis (TG)

The preceding picture regarding the conformation of the organic molecules within the interlayer spacing is helpful to clarify the thermal behavior of the mineral.

MMT displays two thermal degradation transitions [40]. The first one starts in the range ambient to 200°C due to the volatilization of both the free water (i.e., the water sorbed on the external surfaces of crystals) and the water residing inside the interlayer space, forming hydration spheres around the exchangeable cation [41]. The second transition is ascribed to the loss of dehydroxylation of the structural OH units of the montmorillonite over the 500–1000°C temperature range. The temperature intervals of water release corresponding to these processes as well as the amount of water released is dependent upon the nature of adsorbed cations and the hydration of surface [42].

On the other hand, organically modified montmorillonite undergoes a four-step decomposition process [43]. The vaporization of free water takes place at temperatures below 200°C, while the surfactant's decomposition happens in the temperature range 200–500°C. Dehydroxylation of the aluminosilicates occurs between 500–800°C. The last step is the decomposition associated with the combustion reaction between organic carbon and inorganic oxygen (combustion of the charcoal) at temperatures between 800–1000°C [44].

Figures 3 and 4 display respectively the mass loss curves and their corresponding first derivatives (DTG) for pristine and organophilized montmorillonites. From the data presented in Fig. 4, it follows that there are two regions of water thermodesorption process. The peak observed at 63°C (MMT) in DTG curves is assigned to the evaporation of bulk liquids from grain spaces and capillaries [45]. The peak observed at 97.1°C is attributed to the evaporation of the interlayer water. The intensity of this peak is proportional to the amount of water comprised. Pristine MMT contains a large quantity of water (5.37%) (Table 1) due to hydrated sodium (Na^+) and hydrated calcium (Ca^{2+}) cations intercalated inside the clay layers. This quantity was progressively reduced with the increase of the surfactant added. Also, the temperature at the maximum rate of volatilization of this water was reduced too. The presence of alkylammonium within the interlayer spacing lowers the surface energy of the inorganic material and transforms the hydrophilic silicate surface to an organophylic one.

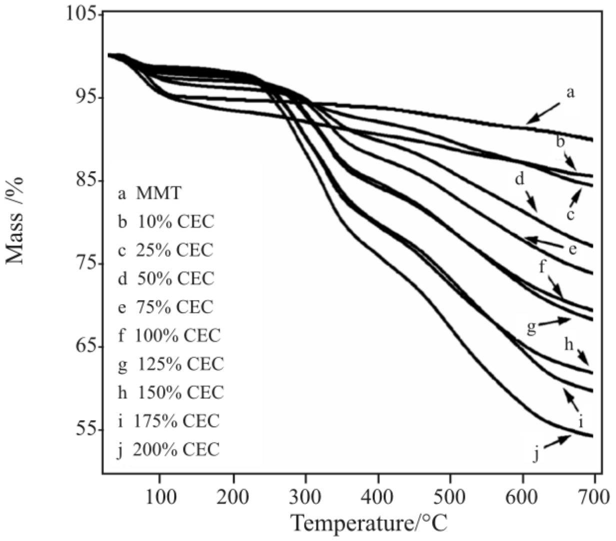

Fig. 3 Mass loss of pristine (MMT) and organomodified montmorillonite (OMMT) with various concentrations of octadecylamine (related to clay CEC)

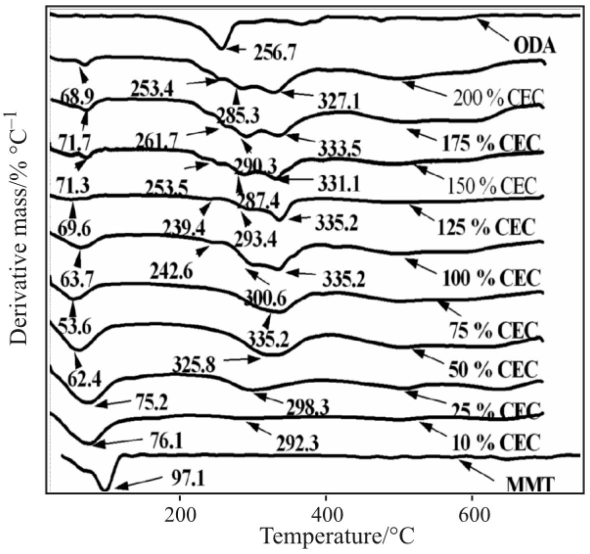

Fig. 4 Derivative mass of pristine (MMT) and organomodified montmorillonite (OMMT) with various concentrations of octadecylamine (related to clay CEC)

At surfactant concentration ranging from 10 to 75% CEC, the temperature at the maximum rate of decomposition of the intercalated octadecylammonium varies from 292.3 to 335.2°C and includes one step. As the surfactant addition exceeds 75% CEC, initialization of a second and a third DTG peak were observed at lower temperatures. The temperature of the second peak decreases from 300.6°C (100% CEC) to 285.3°C (200% CEC). This peak was associated with the surfactant adsorbed to the external surfaces of the clay. In the same samples, the third peak temperature approaches 256°C, temperature of the pure surfactant, was probably due to the thermal decomposition of the free surfactant molecules that were not adsorbed. Xi *et al.* [46] distinguished three different molecular environments for surfactants in montmorillonite-ammonium organoclays: (1) surfactant cations intercalated into the interlayer spaces 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 particles and (3) surfactant molecules located within the interlayer spaces. The authors found that the organoclays prepared at low surfactant concentrations exhibited better thermal stability than those prepared at high surfactant concentrations. Consequently, the thermal stability of organoclays was influenced significantly by the surfactant adsorbed on the external surfaces. Our results are in agreement with these observations.

Xi *et al.* [47] indicated that the molecules of surfactant exceeding the CEC adhere to the clay mineral surface by van der Waals forces and their properties are very similar to those of pure surfactant. The surfactant, physically adsorbed on the external surface, can be removed after washing, resulting in an increase in thermal stability and a decrease in surface energy of the resulting organoclay [48].

Another peak was observed at a temperature around 500°C. This peak was associated to the oxidized residual carbon compounds.

The mass loss at temperature higher than 550°C was attributed to the water molecules formed from hydroxyl groups and the corresponding temperature (T_{max}) at which the dehydroxylation takes place, are given in % CEC 1. As long as the concentration of

Table 1 Decomposition steps of pristine and organomodified montmorillonites

	Step 1 Ambient–200 °C		Step 2 200–400 °C		Step 3 540–700 °C	
	WL/%	T_{max}/°C	*WL*/%	T_{max}/°C	*WL*/%	T_{max}/°C
MMT	5.37	97.1			4.91	645.5
10% CEC	6.73	76.1	2.85	292.3	2.46	632.4
25% CEC	4.02	15.2	3.98	298.3	3.94	638.5
50% CEC	3.01	62.4	7.17	325.8	6.64	603.2
75% CEC	2.63	53.6	9.68	335.2	6.65	618.4
100% CEC	2.69	63.7	15.01	242.7 300.6 335.2	7.51	631.2
125% CEC	2.42	69.6	13.62	239.4 293.4 335.2	6.40	622.8
150% CEC	2.22	71.3	18.46	253.5 287.4 331.1	7.34	633.3
175% CEC	2.04	71.7	18.29	261.7 290.3 333.5	8.79	656.2
200% CEC	2.22	68.9	21.85	253.4 285.3 327.1	7.92	643.6
Description	Dehydration of: – adsorbed water – water adsorbed by metal cations		De-surfactant		Dehydroxylation of OH units	

WL: Percent of mass loss; T_{max}: Temperature at a maximum rate of decomposition (peak temperature)

surfactant is low, this temperature does not significantly change. Surfactant addition higher than 25% CEC results in a considerable change of dehydroxylation temperature. Furthermore, as the surfactant concentration rises, the intensity of the respective DTG peak decreases, owing to the smaller part of inorganic material in the organoclay. Figure 5 shows the values of the mass loss as a function of its content added.

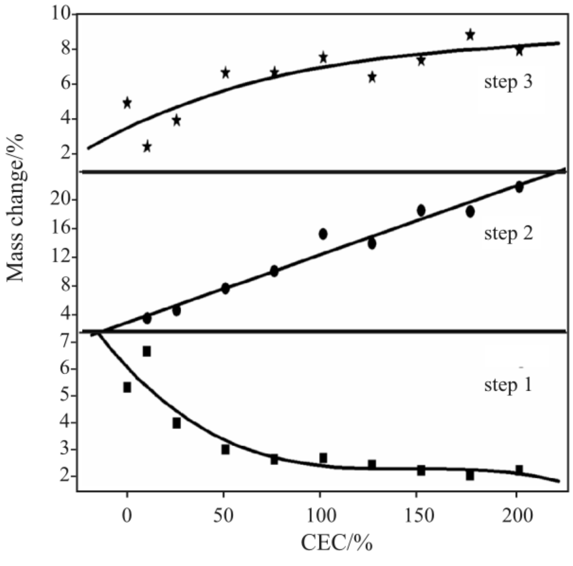

Fig. 5 Variation in mass loss with CEC for steps 1, 2 and 3

Differential Scanning Calorimetric Analysis (DSC)

DSC curves of organoclays are displayed in Fig. 6. At concentration of octadecylamine ranging from 10 to 75% CEC, one significant exothermic change is observed at maximum temperatures between 346.2 and 363.2°C. This change is due to the successive decompositions of adsorbed and intercalated organic cation associated with maximum rate of thermooxidative destruction of the various organic compounds and the deposition of various condensation products formed as the results of a complex series of reactions. The endothermic reactions associated with ODA desorption and breakdown are not observed since the oxidation of the amine and its decomposition products are themselves highly exothermic processes. As the concentration of octadecylamine exceeds 75% CEC, a second exothermic change with lower temperature (243.9 to 253.8°C) and intensity is observed. This change is attributed to the decomposition and oxidation of free octadecylamine molecules. Another change is detected between 450 and 650°C, (488.3°C in the case of 200% CEC). This may be ascribed to the oxidation of residual carbon,

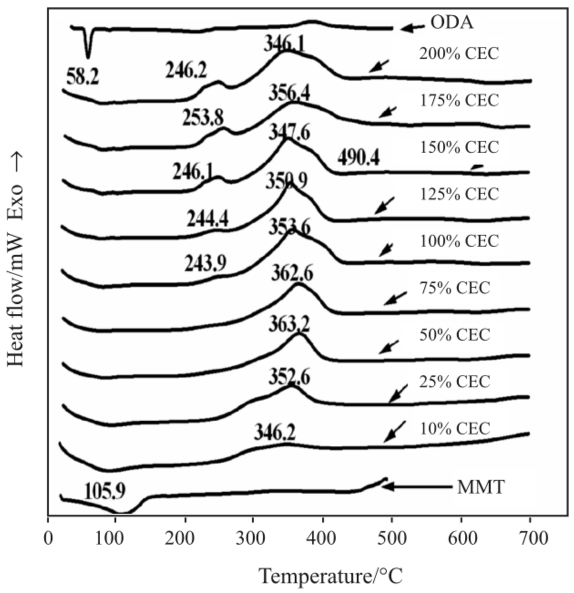

Fig. 6 DSC curves of organomodified montmorillonite with various concentrations of octadecylamine (related to clay CEC)

part of which is oxidized at higher temperature, along with the dehydroxylation of the clay [49].

Conclusions

Modified montmorillonite by various surfactant concentrations was studied using a combination of two techniques, thermogravimetric and X-ray diffraction analysis. TG studies showed that an increase in the surfactant packing density inside the interlayer space decreases the clay's thermal stability. XRD analysis indicates that the conformation of the octadecylammonium cation within the gallery spacing of the layered silicate strongly depends on the quantity of surfactant loaded.

The preceding results accentuate the importance of alkylammonium concentration in the modification process of natural montmorillonite and have important implications for any attempts to incorporate the organomontmorillonite particles in the preparation of polymer nanocomposites.

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