

Vol. 21, No. 2, Summer 1392/2013

Pages 25 to 32



# Preparation and characterization of the Cloisite Na<sup>+</sup> modified with cationic surfactants

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(Received: 22/01/2012, in revised form: 29/04/2012)

**Abstract:** An easy method was used to modify the Cloisite Na<sup>+</sup> with different cationic surfactants. To prevent the damages in the clay crystal structure, the process was taken without acid activation. The organo-modified montmorillonite (MMT) were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal analysis (TG/DTG), field emission scanning electron microscopy (FE-SEM) and dispersibility measurements. The XRD patterns showed basal spacing increased. FTIR and TG/DTG results showed a good amount of organic compounds in all organo-modified samples. Dipersibility measurements indicated that hydrophilic Cloisite Na<sup>+</sup> turned to be organophilic and hydrophobic, in organo-modified MMTs. According to the results the modification was successful with the least harm in the Cloisite Na<sup>+</sup> crystalline structure and less environmental damages. These organo-modified MMTs are capable of removing environmental pollutants from aqueous environments.

**Keywords:** *Cloisite Na*<sup>+</sup>; *cationic surfactant; organoclay; X-ray diffraction.* 

#### Introduction

The organo-modified clays have attracted a great deal of attention because of their wide applications in science and industry such as environmental researches, Drug delivery and personal care and preparation of advanced materials (optical, electronic, nanocomposites) [1-11]. Organoclays studies drived attentions to swelling clay minerals, mostly smectites, because of their special physicochemical properties including their high cation exchange capacity, high surface area and consequential strong adsorption capacities [7, 12]. Montmorillonite is the most common smectite which has two tetrahedral silica sheets fused to an octahedral alumina sheet. Layers are negatively charged due to substitution of central ions (Al<sup>3+</sup>and  $Si^{4+}$ ) for lower valance ions (e.g.  $Al^{3+}$  for  $Si^{4+}$ ). The negative charge is counterbalance by the adsorption of hydrated cations, usually  $Na^+$  and  $Ca^{2+}$ , in the interlayer. Thus, the clay platelets are inherently hydrophilic [13,14]. These exchangeable inorganic cations could be replaced by organic ones to modify the clay mineral surface properties [15].

The most common organic cations used for organoclays preparation are cationic surfactants. They are adsorbed on the clay mineral surface and theiralkyl chains render the interlayer space organophilic. As a result, the organoclay becomes an excellent adsorbent for poorly water-soluble organic species [16].

Here is an easy method for preparation of organo-modified montmorillonite using different quaternary ammonium salts which are mostly used in detergent and cosmetic industries [17,18]. The thermal stability of ammonium salts is limited about 100°C [19] so no heating process is used in this method and the whole operation carried out in room temperature. Although acid activation is common in organoclays preparation, it is known

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that during acid activation structural ions dissolved and the structure rearranged [20]. To prevent the damages in the structure and further exfoliation in clay mineral platelets, acid activation is not used in this method. So the expansion and/or exfoliation observed in organo-modified MMTs would be the exact result of the interaction of organic cations in the clays interlayer space. In addition, no force dispersing used to study the morphology of organo-modified MMTs.

#### Materials and methods Materials

Natural sodium montmorillonite with trade name of Cloisite Na<sup>+</sup> obtained from Southern Clay Products Inc., Texas, USA. Specific gravity of Cloisite Na<sup>+</sup> is 2.86 g/cm<sup>3</sup> and its cation exchange capacity reported as 92.6 meq/100 g [21]. According to previous studies the specific surface area of exfoliated montmorillonite is about 725 m<sup>2</sup>/g [22-25]. The cationic surfactants used in this study were all quaternary ammonium bromides including: tetramethylammonium bromide (4M), tetraethylammonium bromide (4E), ndodecyltrimethylammonium bromide (2D), tetradecyltrimethylammonium bromide (4D) and hexadecyltrimethylammonium bromide (6D). Fig. 1 presents the chemical structures of used surfactants.

#### **Preparation of Organoclays**

The synthesis of organo-modified MMTs was as the following procedure. First a specific amount of each surfactant (2 times of CEC of pure Cloisite Na<sup>+</sup>) dissolved in 100 mL deionized water, then 2.0 g of the Cloisite Na<sup>+</sup> added to this aqueous solution and stirred gently for 24 h in room temperature. The mixture was centrifuged and washed over seven times with deionized water till no bromide ions were detected by AgNO<sub>3</sub> solution. The organo-modified MMTs were dried in room temperature then ground to 230 mesh size.



Tetramethylammonium bromide (4M)



Tetraeathylammonium bromide (4E)



Tetradecyltrimethylammonium bromide (4D)



n-Dodecyltrimethylammonium bromide (2D)



Hexadecyltrimethylammonium bromide (6D)

Fig. 1 The chemical structures of used cationic surfactants.

#### Characterization

The d-spacing of the Cloisite Na<sup>+</sup> and organomodified MMTs was analyzed by using XRD patterns. X-ray diffraction pattern were recorded between 2°-40° (2 ) at a step size of  $0.2^{\circ}/\text{min}$ , using Italstructures X-ray diffractometer with CuK $\alpha$  radiation, running at 40 kV and 30 mA.

FTIR spectra were recorded with PerkinElmer Spectrum 65, employing KBr pressed disc technique, monitoring changes in IR spectra in the range of 4000-400 cm<sup>-1</sup>.

Thermal analyses were taken on a TGA/DTA-SII (PerkinElmer, USA) analyzer. Samples were heated in Platinum crucible at the rate of 10°C/min, from ambient temperature to 750°C at nitrogen atmosphere.

The morphology of the Cloisite  $Na^+$  and organio-modified MMTs was studied using field emission scanning electron microscopy (FE-SEM), taken on FE-SEM Hitachi S-4160.

To observe the dispersibility of both modified and unmodified Cloisite  $Na^+$ , 0.5 g of each samples

dissolved in 100 mL of solvent (deionized water and Ethanol) at room temperature. The suspension samples stirred for 15 min and kept still for observations.

## Results and discussion X-ray diffraction

X-ray diffractometry is one of the most important ways to see if the modification was successful or not. Basal spacing of the Cloisite Na<sup>+</sup> and organomodified MMTs analyzed by using Bragg's equation ( $n\lambda = 2d\sin\theta$ ) (Table 1). As it is shown in Fig. 2, the replacement of sodium ions with organic cations caused expanding in the clay mineral interlayer and d<sub>001</sub> peak shifted to lower diffraction angles, so basal spacing increased from the Cloisite Na<sup>+</sup> to organo-modified MMTs. In addition, the alkylammonium chain length effects on the basal spacing of organo-modified MMTs straightly, meaning with the chain length increased the d-spacing increased as well.

 Table 1 Basal spacing amounts of the Cloisite Na<sup>+</sup> and organo-modified samples.

Sample	Angle $(2\theta)$	$d_{001}(A)$	
Cloisite Na <sup>+</sup>	6.8	12.98	
4M-MMT	5.9	14.96	
4E-MMT	6.0	14.71	
2D-MMT	5.2	16.97	
4D-MMT	4.2	21.01	
6D-MMT	4.0	22.06	



Fig. 2 X-ray diffraction patterns of the Cloisite Na<sup>+</sup> and organo-modified MMTs.

The orientation and arrangement of alkyl chains in the clay mineral interlayer can be proposed based on XRD results [26].The basal spacing for 4M-MMT, 4E-MMT and 2D-MMT varies from 14.71-16.97 Å which suggest the bilayer arrangement of alkylammonium chains. For 4D-MMT and 6D-MMT the d-spacing is 21.01 Å and 22.06 Å, respectively and pseudotrimolecular or paraffintype arrangement is suggested, since three layers of alkylammonium ions are energetically unstable [26].

#### **FTIR Spectroscopy**

The IR spectra of the Cloisite Na<sup>+</sup> and organomodified MMTs are shown in Fig. 3. The Cloisite Na<sup>+</sup> is characterized by stretching and bending bands of both O-H and Si-O, bending bands of Al-O and bending bands of Mg-O. All bands in 3100-3700 cm<sup>-1</sup> region are attributed to O-H stretching vibration and O-H bending vibration bands are located at 1600-1700 cm<sup>-1</sup>. Si-O stretching band is observed at 1040 cm<sup>-1</sup> as well as Si-O and Al-O bending bands at 400-600 cm<sup>-1</sup>. Mg-O bending band was observed at 470 cm<sup>-1</sup>. These bands are also observed in IR spectra of all organo-modified MMTs (Fig. 3). In addition some new bands recognized in IR spectra of organo-modified MMTs which are belong to organic part of organoclays. CH<sub>2</sub> stretching (2924 cm<sup>-1</sup>), CH<sub>2</sub> bending (1478 cm<sup>-1</sup>), CH<sub>3</sub> stretching (2870 cm<sup>-1</sup>) and CH<sub>3</sub> bending (1380 cm<sup>-1</sup>) vibrations can be observed in all organo-modified samples. It can be concluded that organo-modified MMTs show both clay mineral and alkyl characteristics in IR spectra.

#### Thermal analysis

Thermal stability of the Cloisite Na<sup>+</sup> and organomodified MMTs was studied by thermogravimetric analysis. Previous studies [21, 24, 27-29] presenteddifferent decomposition steps for organomodified MMTs including water desorption and dehydration, surfactant decomposition and dehydroxylation.



Fig. 3 FTIR spectra of the Cloisite Na<sup>+</sup> and organo-modified MMTs.

The TG and DTG curves of the Cloisite Na<sup>+</sup> and organo-modified MMTs are illustrated in Fig. 4. According to Fig. 4 and Table 2, three different decomposition zones can be observed. The first decomposition zone occurred at 25-100 °C and attributed to free water volatilization. The most mass loss in this zone is pertained to the Cloisite Na<sup>+</sup> when 4E-MMT and 2D-MMT did not lose weight at this temperature (Table 2). The low amount of free water in organo-modified MMTs would be a result of their hydrophobic nature. The second decomposition zone could be observed at 100-600 °C and imputed to organic compound decomposition. This zone included two subzones (Table 2). The first subzone occurred at 100-290 °C. Two decomposition steps could be recognized for this subzone. It is proposed that physically adsorbed molecules and cations were decomposed at this temperature. The second subzone took place at 290-600 °C, represented the decomposition of interlayer adsorbed cations and had three different steps. All organo-modified samples lost weight in this subzone. The last decomposition zone ascribed to dehydroxylation, in which the Cloisite Na<sup>+</sup> showed 9.62% mass loss whenas none of organomodified MMTs lost weight (Fig. 4 and Table 2). The reason of the differences observed in TG/DTG results for organo-modified MMTs could be found in the physicochemical properties of different surfactant used for modification. As the solubility of both 4D and 6D is less than the others, a considerable amount of these surfactants remains in molecular form specially for 6D. Due to the physically adsorbed molecules, the 4D-MMT and 6D-MMT started to lose weight in lower temperature.



**Fig. 4 A.** TG and **B.** DTG curves of the Cloisite Na<sup>+</sup> and organo-modified MMTs.

Table 2 TOM results of the choisite five and organo mounted whites.											
			Cloisite Na <sup>+</sup>	4M-MMT	4E-MMT	2D-MMT	4D-MMT	6D-MMT			
Zone 1: 25 100°C	C Free Water volatilization	Temp. °C	60.00	56.21	-	-	64.50	59.16			
Zone 1. 25 - 100 C	The water volatilization	Mass loss %	5.62	4.45	-	-	1.94	2.28			
	Subzone 1: Physically adsorbed moleucles and cations	Temp. °C	-	-	-	-	193.61	-			
		Mass loss %	-	-	-	-	7.84	-			
		Temp. °C	-	-	-	-	272.01	251.60			
Zone 2: 100 -		Mass loss %	-	-	-	-	0.83	8.98			
600°C	Subzone 2: Interlayer adsorbed cations	Temp. °C	-	-	-	-	295.16	310.57			
		Mass loss %	-	-	-	-	5.13	13.90			
		Temp. °C	-	422.57	426.75	406.76	410.91	408.14			
		Mass loss %	-	7.03	18.38	25.78	9.68	10.86			
		Temp. °C	-	580.76	-	-	594.96	594.64			
		Mass loss %	-	4.29	-	-	3.26	1.38			
Zone 3: 600 -	Dehydroxylation	Temp. °C	640.00	-	-	-	-	-			
750°C		Mass loss %	9.62	-	-	-	-	-			
Total mass loss %			15.54	15.77	18.38	25.78	28.68	34.40			
Total organic mass loss %			-	11.32	18.38	25.78	26.74	32.12			
Total amounts of surfactants on samples with no Br ion (mol/g $\times$ 10 <sup>4</sup> )			-	17.24	17.30	15.21	14.23	16.63			

**Table 2** TGA results of the Cloisite Na<sup>+</sup>and organo-modified MMTs.

The total amount of surfactant on the Cloisite Na<sup>+</sup> was calculated using the following equation [21, 24, 28]:

$$X = \frac{m \times S \times 10^{-2}}{(M - y) \times m \times (100 - S) \times 10^{-2}} = \frac{S}{(M - y) \times (100 - S)}$$

where X is the amount of surfactant on the Cloisite  $Na^+$  (mol/g), m refers to the total weight of the organo-modified MMT and M is the molecular weight of surfactant where S is the total surfactant mass lose (%). y is 0 if all Br ions remain otherwise it would be 80. Table 2 presents the total amount of surfactant on the Cloisite Na<sup>+</sup> with no Br ions. As it is shown in Table 2, the highest amount of surfactant on the Cloisite Na<sup>+</sup> was

calculated for 4E-MMT and 4D-MMT showed the lowest amount.

#### FE-SEM

Observing the morphology of Cloisite  $Na^+$  and organo-modified MMTs, FE-SEM was used and Fig. 5 presents the morphology of all samples. It is clear that no great morphological differences can be recognized between Cloisite  $Na^+$  and organomodified samples. Sodium hydration in Cloisite  $Na^+$  caused the massive aggregated morphology, but agglomeration in organo-modified MMTs might be a result of interaction of carbon chains of organic compounds belonging to different particles.



Fig. 5 FE-SEM images of the Cloisite Na<sup>+</sup> and organo-modified MMTs.

#### **Dispersibility measurement**

Sodium is extremely hydroscopic and becomes hydrated in the atmosphere, there for the Cloisite Na<sup>+</sup> is inherently hydrophilic. The dispersibility result of the Cloisite Na<sup>+</sup> was quite the opposite of The Cloisite Na<sup>+</sup> organo-modified MMTs. dispersed well in H<sub>2</sub>O and a cloudy uniform supernatant was observed, but when added to organic solvent (Ethanol), the suspension demixed. Organo-modified MMTs showed а better dispersibility in Ethanol but the aqueous samples were clear and demixed immediately. The longer the alkyl chain the more hydrophobic the organomodified MMTs. In addition, all demixed samples swelled as well.

#### Conclusions

An easy method was used to modify the Cloisite Na<sup>+</sup> with cationic surfactants in which the whole process carried out in room temperature. Preventing the damages in clay structure, no acid activation was used. Five kinds of quaternary ammonium bromides including 4M, 4E, 2D, 4D and 6D were used to modify the Cloisite Na<sup>+</sup>. The organo-modified MMTs were characterized by XRD, FTIR spectroscopy, TG/DTG, FE-SEM and observations. dispersibility As the FTIR spectroscopy indicated the organic compounds in organo-modified samples, the XRD pattern presented increasing in d-spacing and enlarging the interlayer space in organoclays. Modification of the Cloisite Na<sup>+</sup> with 6D, has changed the interlayer spacing from 12.98 Å to 22.06 Å, but 4E-MMT showed the less change in d-spacing (14.71 Å). The total amount of surfactant on the Cloisite Na<sup>+</sup> was calculated using the thermal analysis results. The most amount of surfactant on the Cloisite Na<sup>+</sup> was 17.30 mol/g  $\times 10^4$  in 4E-MMT and the least amount was 14.23 mol/g  $\times 10^4$ in 4D-MMT. The dispersibility measurements showed that the hydrophilic/organophobic Cloisite hydrophobic/organophilic  $Na^+$ turned to organoclays. No great morphological changes had been recognized on FE-SEM images. Attending to the whole characterization results, it can be concluded that the modification was successful. No crystal harm or damages occurred during this modification method. These organoclays have the potential to remove organic pollutant from aqueous environments due to their organophilic properties.

#### Acknowledgments

This work is financially supported by Bu-Ali Sina University. The authors wish to thank Dr. Soleimani for his help in thermal analysis.

#### References

[1] Bailey S.E., Olin T.J., Bricka R.M., Adrian D.D., "*A review of potentially low-cost sorbents for heavy metals*", Water Research 33 (11) (1999) 2469–2479.

[2] Beall G.W., "*The use of organoclays in water treatment*", Applied Clay Science 24 (2003) 11–20.

[3] Du Y.J., Hayashi S., "A study on sorption properties of  $Cd^{2+}$  on Ariake clay for evaluating its potential use as a landfill barrier material", Applied Clay Science 32 (1–2) (2006) 14–24.

[4] Sen Gupta S., Bhattacharyya K.G., "*Adsorption of Ni (II) on clays*", Journal of Colloid and Interface Science 295 (1) (2006) 21–32.

[5] Davis A.M., Joanis G., Tribe L., "Molecular modeling of polymer-clay nanocomposite precursors: lysine in montmorillonite interlayers", Journal of Computational Chemistry 29 (2007) 983–987.

[6] Bergaya F.A., "*Layered clay minerals: basic research and innovative composite applications*", Microporous and Mesoporous Materials 107 (2008) 141–148.

[7] Liu R., Frost R.L., Martens W.N., Yuan Y., "Synthesis, characterization of mono, di and tri alkyl surfactant intercalated Wyoming montmorillonite for the removal of phenol from aqueous systems", Journal of Colloid and Interface Science 327 (2008) 287–294.

[8] Xi Y., Mallavarapu M., Naidu R., "Preparation, characterization of surfactants modified clay minerals and nitrate adsorption", Applied Clay Science 48 (2010) 92-96.

[9] Ghaemi N., Madaeni S.S., Alizadeh A., Rajabi H., Daraei P., "Preparation, characterization and performance of polyethersulfone organically modified montmorillonitenanocomposite membranes in removal of pesticides", Journal of Membrane Science 382 (2011) 135-147.

[10] Iliescu R., Andronescu E., Voicu G., Ficai A., Covaliu C.I., "Hybrid materials based on montmorillonite and citostatic drugs Preparation and characterization", Applied Clay Science 52 (2011) 62-68. [11] Lv G., Li Z., Jiang W.T., Chang P.H., Jean J.S., Lin K.H., "*Mechanism of acridine orange removal from water by low-charge swelling clays*", Chemical Engineering Journal, 174 (2011) 603–611.

[12] He H., Ma Y., Zhu J., Yuan P., Qing Y., "Organoclays prepared from montmorillonites with different cation exchange capacity and surfactant configuration", Applied Clay Science 48 (2010) 67-72.

[13] Kozaka M., Domka L., "*Adsorption of the quaternary ammonium salts on montmorillonite*", Journal of Physics and Chemistry of Solids 65 (2004) 441–445.

[14] Lee S.Y., Cho W.J., Hahn P.S., Lee M., Lee Y.B., Kim K.J., "*Microstructural changes of reference montmorillonites by cationic surfactants*", Applied Clay Science 30 (2005) 174–180.

[15] Grim R.E., "*Clay mineralogy*", McGraw-Hill Book, New York (1968) 596 p.

[16] Kooli F., Liu Y., Alshahateet S.F., Messali M., Bergaya F., *"Reaction of acid activated montmorillonites with hexadecyltrimethylammonium bromide solution"*, Applied Clay Science 43 (2009) 357-363.

[17] Beall G.W., Goss M., "*Self-assembly of organic molecules on montmorillonite*", Applied Clay Science 27(2004) 79–186.

[18] Avalos F., Ortiz J.C., Zitzumbo R., López-Manchado M.A., Verdejo R., Arroyo M., *"Phosphonium salt intercalated montmorillonites"*, Applied Clay Science 43(2009) 27–32.

[19] Sarier N., Onder E., Erosy S., "*The modification of Na-montmorillonite by salts of fatty acids An easy intercalation process*", Colloids and Surface A: Physicochemical and Engineering Aspects 371(2010) 40-49.

[20] Komadel P., Madejová J., "Acid activated clays. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science", Developments in Clay Sciences 1 (2006) 263-287.

[21] Mallakpour Sh., Dinari M., "*Preparation and characterization of new organoclays using natural amino acids and Cloisite Na*<sup>+</sup>", Applied Clay Science 51 (2011) 353-359.

[22] Ho D.L., Briber R.M., Glinka C.J., "Characterization of organically modified clays using scattering and microscopy techniques", Chemistry of Materials 13 (2001) 1923–1931.

[23] Lee S.Y., Hanna M.A., "Preparation and characterization of tapioca starch-poly (lactic acid)-CloisiteNa<sup>+</sup>nanocomposite foams", Journal of Applied Polymer Science 110 (2008) 2337–2344.

[24] Zhou L., Chena H., Jiang X., Lu F., Zhou Y., Yin W., Ji X., "*Modification of montmorillonite surfaces using a novel class of cationic gemini surfactants*", Journal of Colloid and Interface Science 332 (2009) 16–21.

[25] Schmidt D.F., Giannelis E.P., "Dispersion and mechanical reinforcement in polysiloxane/layered silicate nanocomposites", Chemistry of Materials 22 (2010) 167–174.

[26] de Pavia L.B., Morales A.R., Valenzuela Díaz F.R., "*Organoclays: Properties, preparation and applications*", Applied Clay Science 42 (2008) 8-24.

[27] Xi Y., Frost R.L., He H., Kloprogge T., Bostrom T., "Modification of Wyoming montmorillonite surfaces using a cationic surfactant", Langmuir 21 (2005) 8675–8680.

[28] Xi Y., Frost R.L., He H., "Modification of the surfaces of Wyoming montmorillonite by the cationic surfactants alkyl trimethyl, dialkyl dimethyl and trialkylmethylammonium bromides", Journal of Colloid Interface Science 305 (2007) 150–158.

[29] Marras S.I., Tsimpliaraki A., Zuburtikudis I., Panayiotou C., "*Thermal and colloidal behavior of amine-treated clays: the role of amphiphilic organic cation concentration*", Journal of Colloid Interface Science 315 (2007) 520–527.