

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

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**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. Dispersibility 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 drew 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<sup>4+</sup>) for lower valence ions (e.g. Al<sup>3+</sup> for Si<sup>4+</sup>). The negative charge is counterbalanced by the adsorption of hydrated cations, usually Na<sup>+</sup> and Ca<sup>2+</sup>, 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 their alkyl 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), n-dodecyltrimethylammonium 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.

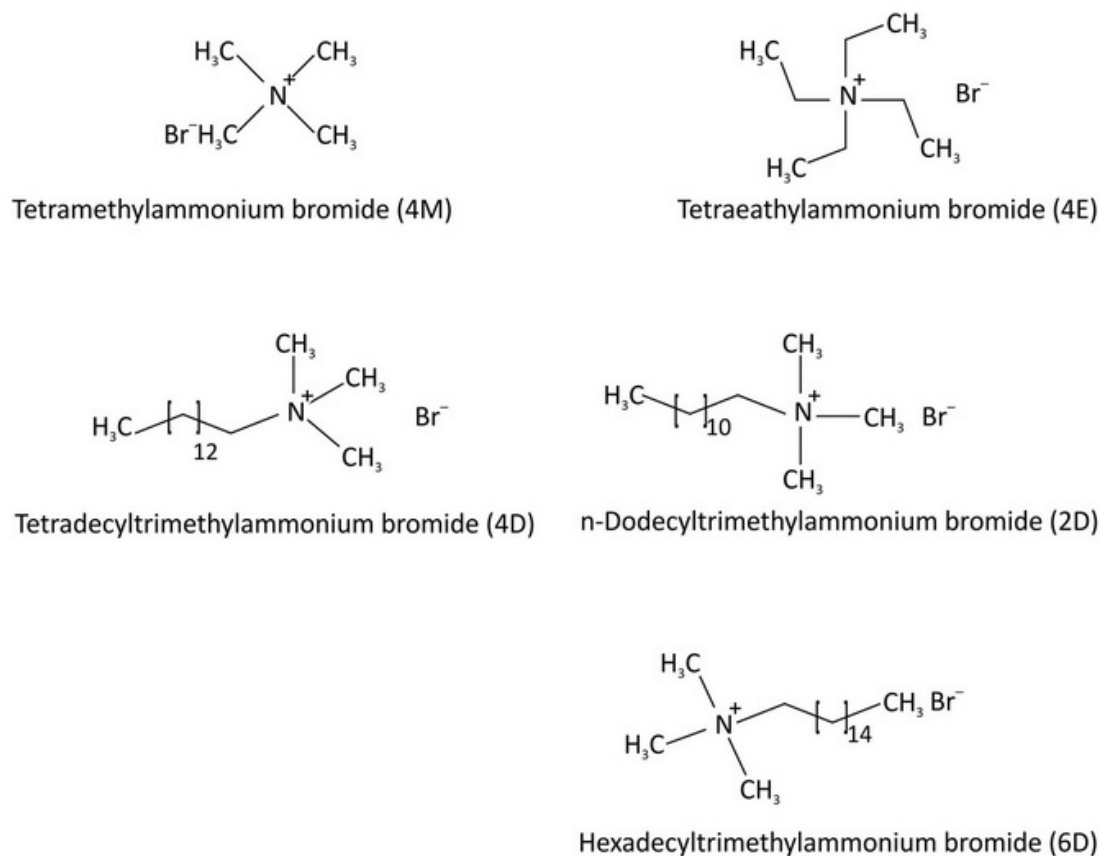


Fig. 1 The chemical structures of used cationic surfactants.

### Characterization

The d-spacing of the Cloisite Na<sup>+</sup> and organo-modified MMTs was analyzed by using XRD patterns. X-ray diffraction patterns were recorded between 2°-40° (2θ) at a step size of 0.2°/min, using Italstructures X-ray diffractometer with CuKα 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<sup>+</sup> and organo-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<sup>+</sup>, 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.

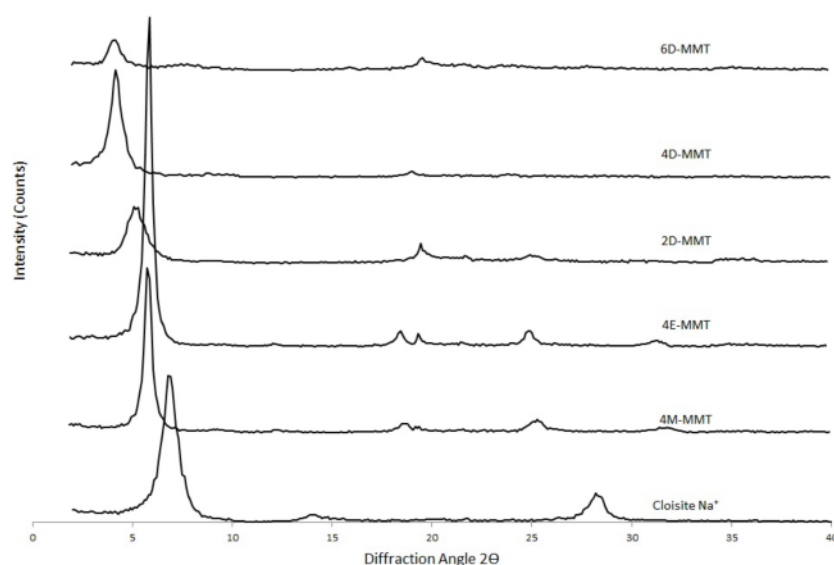
### Results and discussion

#### 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 organo-modified 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 (2θ)	d <sub>001</sub> (Å)
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 paraffin-type 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 organo-modified 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 organo-modified MMTs was studied by thermogravimetric analysis. Previous studies [21, 24, 27-29] presented different decomposition steps for organo-modified MMTs including water desorption and dehydration, surfactant decomposition and dehydroxylation.

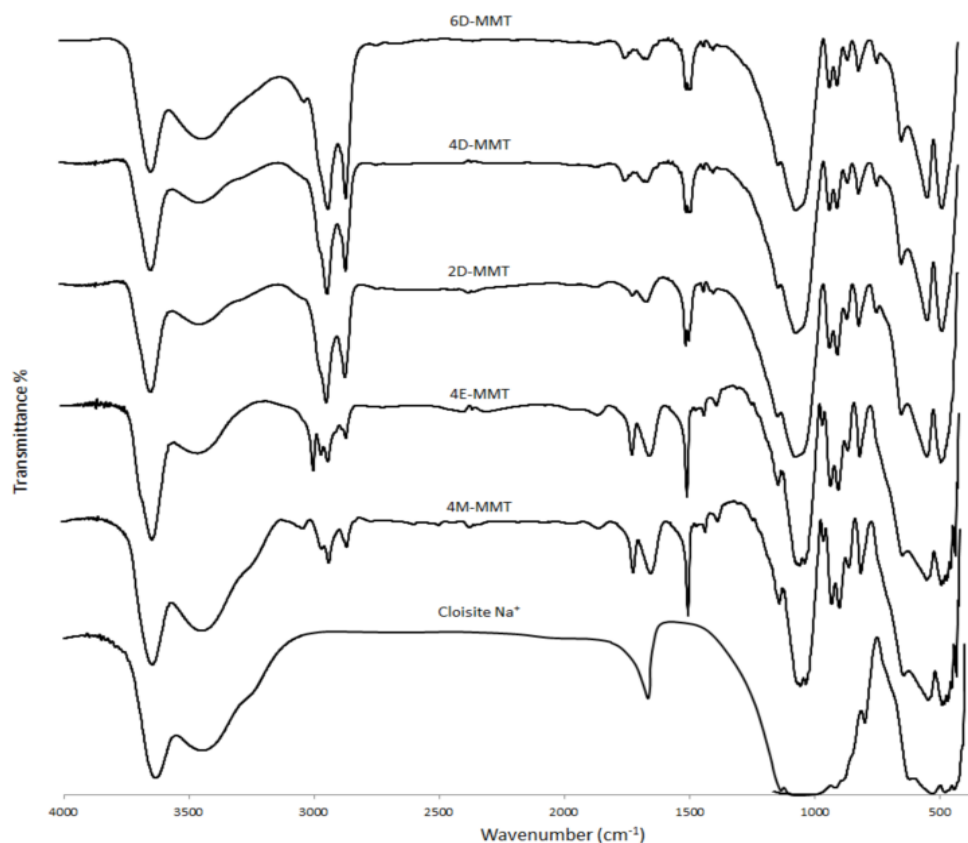
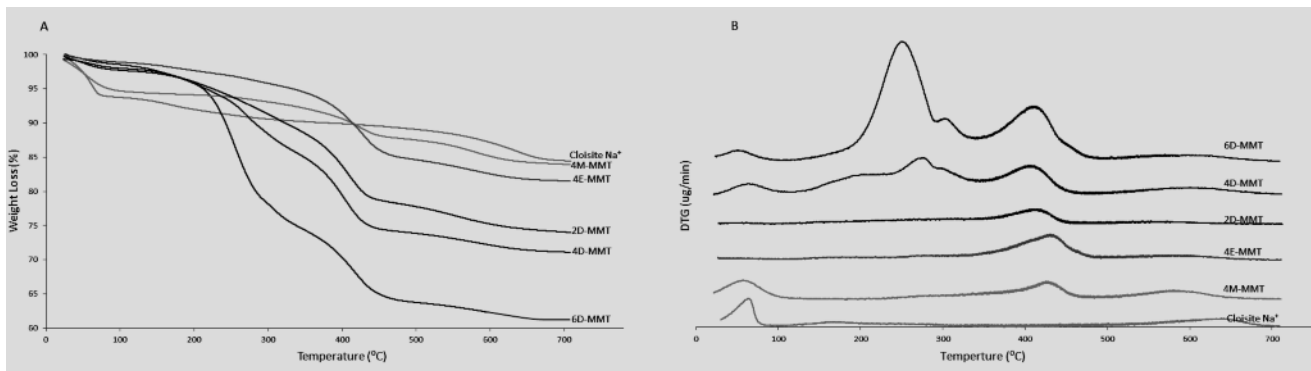


Fig. 3 FTIR spectra of the Cloisite Na<sup>+</sup> and organo-modified MMTs.

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 whereas none of organo-modified 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** TGA results of the Cloisite Na<sup>+</sup> and organo-modified MMTs.

			Cloisite Na <sup>+</sup>	4M-MMT	4E-MMT	2D-MMT	4D-MMT	6D-MMT
Zone 1: 25 - 100°C	Free Water volatilization	Temp. °C	60.00	56.21	-	-	64.50	59.16
		Mass loss %	5.62	4.45	-	-	1.94	2.28
Zone 2: 100 - 600°C	Subzone 1: Physically adsorbed molecules and cations	Temp. °C	-	-	-	-	193.61	-
		Mass loss %	-	-	-	-	7.84	-
		Temp. °C	-	-	-	-	272.01	251.60
		Mass loss %	-	-	-	-	0.83	8.98
	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
Zone 3: 600 - 750°C	Dehydroxylation	Temp. °C	-	580.76	-	-	594.96	594.64
		Mass loss %	-	4.29	-	-	3.26	1.38
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 × 10 <sup>4</sup> )			-	17.24	17.30	15.21	14.23	16.63

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

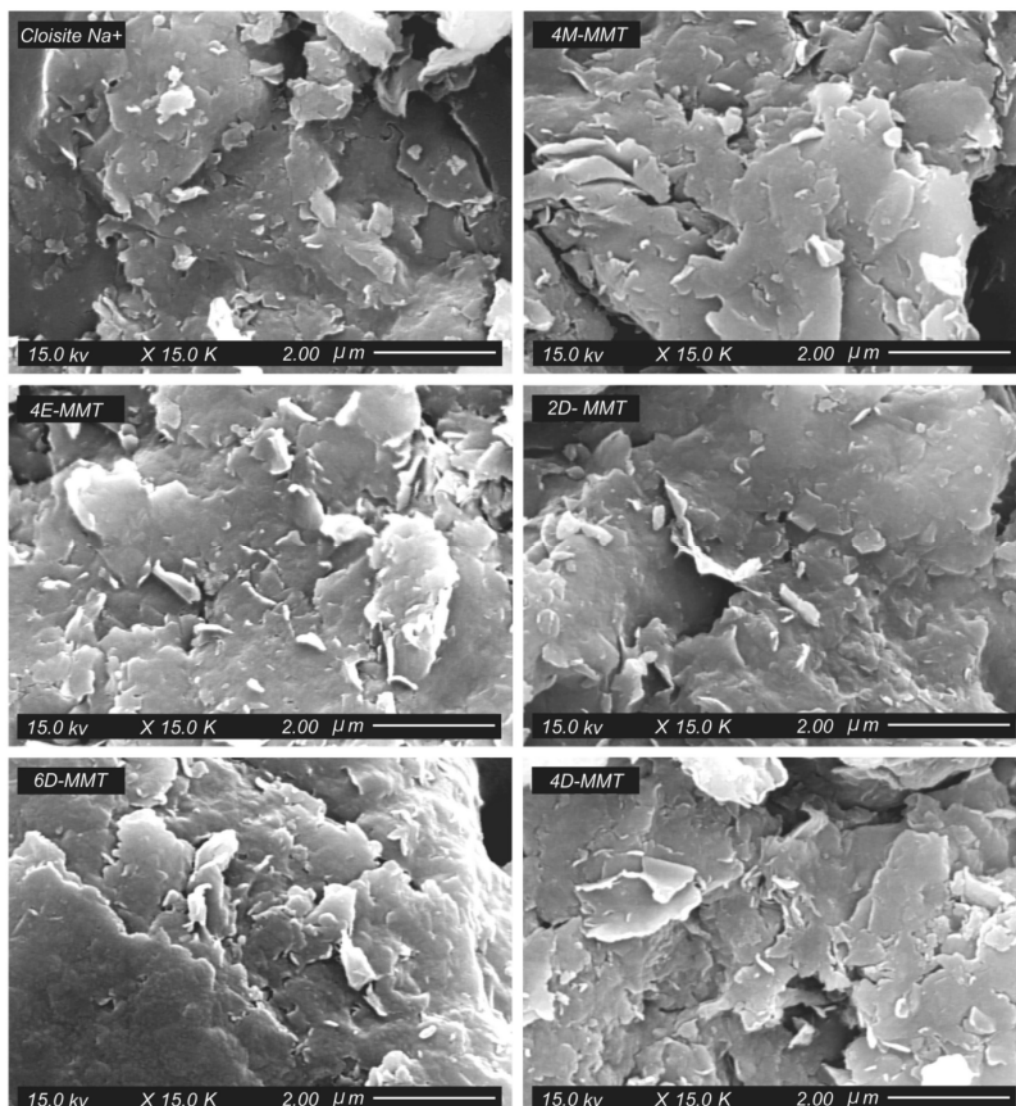
$$X = \frac{m \times S \times 10^{-2}}{(M - y) \times m \times (100 - S) \times 10^{-2}} = \frac{S}{(M - y) \times (100 - S)}$$

where X is the amount of surfactant on the Cloisite Na<sup>+</sup> (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<sup>+</sup> 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<sup>+</sup> and organo-modified samples. Sodium hydration in Cloisite Na<sup>+</sup> 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 hygroscopic and becomes hydrated in the atmosphere, therefore the Cloisite Na<sup>+</sup> is inherently hydrophilic. The dispersibility result of the Cloisite Na<sup>+</sup> was quite the opposite of organo-modified MMTs. The Cloisite Na<sup>+</sup> 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 a better dispersibility in Ethanol but the aqueous samples were clear and demixed immediately. The longer the alkyl chain the more hydrophobic the organo-modified 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 dispersibility observations. 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 Na<sup>+</sup> turned to hydrophobic/organophilic 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.

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