

Morphology, Structure, Thermal Stability, XR-Diffraction, and Infrared Study of Hexadecyltrimethylammonium Bromide–Modified Smectite

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Abstract

We characterized the interlayer structure and morphology of modified natural clays. Organoclay-based materials are increasingly used for multiple applications. We modified a purified Na-bentonite using cation exchange with hexadecyltrimethyl ammonium bromide (HDTMA) and characterized it using; UV spectroscopy, X-ray diffraction, photoacoustic FTIR spectroscopy (PA-FTIR), thermogravimetric analysis (TGA) techniques, laser scattering distribution (LSD), atomic force microscopy (AFM) and transmission electron microscopy (TEM). The adsorption of HDTMA on interlayer sites of Na-smectite fraction is nearly total until an adsorption equivalent to 1.85 times the cation exchange capacity (CEC) of the clay. The formation of the HDTMA-smectite changes the properties of the clay from hydrophilic to hydrophobic. The XRD patterns show an increase in the basal spacings. TGA characterization and analysis were shown to be useful to estimate the amount of surfactant within the organoclay. LSD analyses have shown a decrease of the effective particle diameter with increasing sonication times. AFM images showed that these Na-smectite surfaces appeared foliated with irregular aggregate structures at high HDTMA loading. The present study shows that not only the basal spacing but the morphology and the particle size of the organoclay strongly depend on the packing density of surfactant within the smectite interlayer space.

Keywords: HDTMA, adsorption, intercalation, organoclay, RDX, PA-FTIR, TG analysis, laser scattering, AFM, TEM

1. Introduction

Smectitic clays are used widely in various areas of science because of their high cation exchange and swelling capacities, high surfaces and the resulting strong adsorption and absorption capacities (Swartzen-Allen & Matijevic, 1974; Bailey et al., 1999; Murray, 2000). The adsorption of organic molecules on clay minerals has also been studied extensively (Lagaly & Weiss, 1969).

Organosmectite can be produced by inserting organic cations instead of inorganic ions (e.g. K^+ , Na^+ and Ca^{2+}) on the layer surfaces of smectite clays (Ghiaci et al., 2004). Smectite clays can easily be made organophilic as the group IA and IIA loosely-bound metal ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Ba^{2+}) occurring between the alumina and silica layers can be readily exchanged with quaternary ammonium ion such as $[R_4N^+]$ (Jordan, 1949; Jordan et al., 1950). The expulsion of the metal ions along with coordinated water molecules strongly reduces the hydrophilicity of the clay (Lee & Kim, 2002b) and it has been shown that smectite surfaces have a high selectivity for organic cations such as HDTMA cations (Jaynes & Boyd, 1991) and adsorption can proceed beyond the actual cation exchange capacity (CEC) of the clay mineral.

A number of studies have demonstrated that the d-spacings of the organoclays depend on the length of the alkyl chains and the packing density of the surfactants within the galleries of the clay minerals (Lagaly, 1981; Favre & Lagaly, 1991; Tamura & Nakazawa, 1996; Klapys et al., 2001). In intercalated phyllosilicates with

straight-chains alkylammonium, the organic cations are arranged with monolayer, bilayer, pseudobilayer or paraffin type configurations (Lee & Kim, 2002a). During the intercalation of the surfactants, the interlayer of the clay mineral is expanded, as shown by the XRD patterns (He et al., 2006).

The observed configuration will depend on the carbon chain lengths of alkylammonium cation (nc) and the layer charge of the clay mineral (Lee et al., 1989). Characteristic basal spacing, respectively of 13.6; 17.6 and 22Å distinguish the monolayer, bilayer and pseudolayer configurations; whereas basal spacing for samples with paraffin-type configurations increase linearly with nc.

When at least one of the nitrogen constituents is a long aliphatic chain, the interlayer space increases and the adsorption ion capacity is further increased (Andini et al., 2006). In addition, favorable interactions can arise with the R groups of the quaternary ammonium ions and organic molecules are more easily attracted into the expanded interlayer space of the clay. In this case, a number of Van der Waals and hydrophobic interactions can occur between alkyl chains. The combination of the hydrophobic nature of the surfactant and the layered structure of the silicate layers leads to unique physico-chemical properties (He et al., 2006a). In such applications, the behavior and properties of organoclays strongly depend on the structure and the molecular arrangement of the organic molecules within the galleries of the clay minerals. Various arrangements have been proposed for the surfactant structural arrangement of the organic molecules within the clays based mainly on XRD and IR spectroscopy.

Clays and their composites have been widely used as secondary linings for underground storage tanks and landfills. There are also many applications of clays and organoclays in agriculture for the sorption of pesticides and in the treatment of drinking and wastewater contamination. More recently, studies have used FTIR spectroscopy to characterize sorbed water and HDTMA⁺ in organoclays (Zhou et al., 2007a). It was found that sorbed water content decreases with the intercalation of HDTMA⁺. The presence of adsorbed organic cations on a clay surface changes the surface of the clay from hydrophilic to hydrophobic (Tahani et al., 1999). Changes in the surface properties may also influence the interactions between the clay particles. Thus, rheological and colloidal properties of the clay dispersions may be greatly changed; the size of the aggregates may be increased via cluster-cluster aggregation or decreased due to the deflocculating effects of the surfactants. Controlling the aggregation by means of the surfactants is very important from both technological and scientific points of view (Yilmaz & Alemdar, 2005). Different approaches have been developed using sonication as a method to reduce the size to the clay particles (Franco et al., 2004; Pacuła et al., 2006).

Atomic force microscopy (AFM) and transmission electron microscopy (TEM) are two techniques used to investigate the morphology of clay minerals and to study the nanotopography of mineral surfaces. AFM allows high resolution *in situ* imaging of clay minerals while they are exposed to an aqueous solution. AFM has been used in morphological studies and to estimate the edge-surface areas. In addition, the particle size and particle size distribution can easily be extracted from the AFM data. In the literature, TEM is widely used in the study of organoclay-based nanocomposites or used to look at adsorption of organic contaminants (Hoffman et al., 2000; Zhou et al., 2008). Very few studies used AFM for the characterization of the microstructure and morphology of pure organoclays (Lee, 2002a; Zhou et al., 2008).

In this study, we synthesized HDTMA-HP organoclays that were prepared at different surfactant concentrations using HDTMA and a natural purified bentonite (noted HP). The characterization of the prepared organoclays was done using XRD, PA-FTIR, TGA, LSD, AFM and TEM. Experimental results confirmed that HDTMA can be intercalated and adsorbed onto the clay depending on the concentration of the surfactant. This study provides new insights into the structure and properties of organoclays and it demonstrates that not only the arrangement model of surfactant but also the morphology of the organoclays strongly depends on the surfactant packing density within the smectite interlayer space.

2. Method

2.1 Materials

2.1.1 Clay Samples

A natural bentonite (noted HB) was used in this study. This clay is from Jabel Haidoudi near the town of Gabes (southeastern part of Tunisia). The sample HB contains some quartz, gypsum, and calcite as impurities. It was purified by repeatedly mixing the clay with a NaCl solution in order to obtain a homoionic Na-clay (noted HP) (El Messabeh-Ouali et al., 2008). This step was performed by shaking 4 g of clay with 120 cm³ of a 1 M NaCl solution, then centrifuging the suspensions (El Messabeh-Ouali, 2007). This process was repeated seven times. The Na-clay was then washed many times with distilled water. This cleaning is stopped when the AgNO₃ test for

chloride ions was negative. The purified clay was then dried at 60 °C. After drying, the clay was crushed and sieved through less than 80 µm. The chemical composition of HP is given in Table 1.

Table 1. Chemical composition (%w/w) of the purified smectite (HP)

LOI ^a	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	SO ₃	TO
15.87	47.58	21.52	8.35	0.14	1.99	2.27	1.53	0.499	0.015	0.12	0	99.884

^a Loss on ignition at 1000 °C.

The purified clay HP is an interstratified smectite-illite containing 75% of smectite and 20% of illite with a little fraction of kaolinite (~5%). Its smectitic fraction is a naturally sodic beidellite. Its average structural formula is:



with a molecular weight, $M_{\text{HP}} = 776.726 \text{ g mol}^{-1}$. The cation exchange capacity (CEC) was determined by the ethylene-diamine-copper method and is equal to 119.9 meq/100 g of calcined HP. Its total specific surface area is $756.4 \text{ m}^2 \text{ g}^{-1}$.

2.1.2 Ammonium Salt

The hexadecyltrimethyl ammonium bromide noted HDTMA $[\text{N}(\text{CH}_3)_3(\text{C}_{16}\text{H}_{33})]\text{Br}$ is 99% purity and was purchased from Sigma Aldrich and used as received. Figure 1 shows the chemical structures of the corresponding ammonium. Its formula weight is equal to 364.5 g mol^{-1} and its melting point is a round: 237–243 °C. The pH is: 6.0–7.5 (0.1 M in H₂O at 0 °C) (Helenius & Simons, 1975).

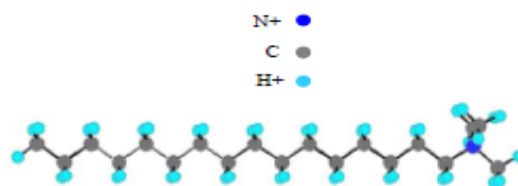


Figure 1. Atomic structure of hexadecyltrimethylammonium

2.2 Organoclays Preparation and Characterization

2.2.1 Preparation of the Organoclays

Batch equilibration isotherms were determined on 5 g of clay samples weighted into 350-mL centrifuge tubes. To these tubes, 155 mL of solution containing the quantities of HDTMA bromide equivalent to 0.5 to 2.5 times the cation exchange capacity (CEC) of the clay samples were added. These suspensions were shaken for 12 hours on a mechanical shaker at 30 °C. The mixture was centrifuged at 9000 rpm for 30 min to yield a clear supernatant. The resulting organoclay was dried at 60°C, then crushed and sieved to < 100 µm.

2.2.2 X-Ray Diffraction Characterization

The HP and organoclays were pressed in stainless steel sample holders. Measurements for samples were performed on a Bruker D8 Advance diffractometer measured in reflection mode depending on the Bragg Brentano geometry. The X-ray radiation used is from a copper anode source. The incident beam is filtered by a germanium monochromator to provide a radiation of wavelength $\lambda = 1.54 \text{ Å}$. The measurement is performed by coupled rotations of the sample holder and detector (so-called mode theta-theta 2: when the sample rotates through a theta angle, the detector will run twice this angle to maximize the measured intensities). The X-ray diffraction patterns were measured between 2 and 40 degrees with a step angle of 0.025 degrees. Measurements are performed in fixed installation by setting the source and the two-dimensional detector respectively at 10 degrees (theta) and 20 degrees (2 theta).

2.2.3 Photoacoustic (PA)-FTIR Characterization

The PA-FTIR technique can be used in the study and characterization of adsorbed and chemisorbed molecular

species and compounds on the surface of metals, semiconductors, and even insulators (Rosencwaig, 1980). PA-FTIR experiments were conducted using a FTIR spectrometer (model Digilab FTS6000) equipped with an attached PA-300 photoacoustic cell from MTEC Photoacoustics, Inc. In general, the signal to noise ratio was high enough for all the measurements, and all the samples were run in the same conditions at room temperature. Measurements used spectral resolution of 8 cm^{-1} using the rapid scan mode at the lowest mirror frequency (2.5 KHz) to maximize signal intensity and probe the deepest layers accessible within the sample.

2.2.4 Thermogravimetric Analysis

Thermogravimetric analysis of the surfactant-modified HP were obtained using High-resolution TGA (TA Instruments Inc. Q500) operating using $10\text{ }^{\circ}\text{C}/\text{min}$ ramp with resolution $20\text{ }^{\circ}\text{C}$ from room temperature to $1000\text{ }^{\circ}\text{C}$ in a high purity nitrogen atmosphere (at $80\text{ cm}^3/\text{min}$). Approximately 50 mg of finely ground sample were heated in an open platinum crucible. The TA Universal analysis software is used to obtain the diffractograms.

2.2.5 Laser Scattering Distribution

Particle size distribution measurement is used for quality control in basic research and production processing of fine ceramics, cement, drugs and other products. Estimates of particle size distributions of all samples after sonication were obtained by laser scattering of dispersed samples. The scattering experiments were carried out using an Analyser LA-950 INIFLOW model HORIBA MINIFLOW and a specifically-designed preparation unit. The preparation unit is controlled by the computer of the scattering unit. Particle size distributions from $0.01\text{ }\mu\text{m}$ to $1000\text{ }\mu\text{m}$ can be measured, without changing measurement ranges. Processing is extremely reliable and normally required only 1 min, from insertion of dispersion medium to display of results. Sample preparation is performed through the software interface. The speed level of circulation pump bath was settled at 15 r/s and the ultrasonic strength level was set at 7 arbitrary units on the scale of this particular instrument. The ultrasonic operation time was varied for each sample of clay from 0-60-90-120-150 seconds.

2.2.6 Atomic Force Microscopy

A mass of 0.2 g of each sample of organoclays was mixed with 2 mL of water. The suspension was then placed on glass plates and allowed to dry under atmospheric conditions at room temperature. This suspension of clay and water was stored at room temperature. The clay suspension was dried in an electric oven for $\sim 24\text{ h}$ at 323 K. The glass was then loaded on the AFM platform. The AFM used was a Digital Instrument Nanoscope V Extended (Dimension 3100). The AFM measurements were carried out in air at ambient conditions (298 K).

2.2.7 Transmission Electronic Microscopy

For TEM observation, small drops of dilute suspensions of 0.1 g of the clay in 5 cm^3 of 50% ethanol solution were placed on Cu mesh grids which had been coated with a thin carbon film. The grids were air-dried by briefly being placed in a $60\text{ }^{\circ}\text{C}$ oven to ensure complete drying prior to measurements. The specimens were examined in a JEM-2100F transmission electron microscope operated at an accelerating voltage of 200 KV. Although this preparation is not optimal for high resolution imaging as compared to thinned or sectioned samples, the clay crystallite layers were thin enough that imaging of the interlayer spacing could be performed where suitable orientations could be obtained.

3. Results and Discussion

3.1 X-Ray Diffraction Measurements

Following the cation exchange of the sodium ions by the HDTMA^+ cationic surfactant, expansion of the HP beidellite layers occurs. This expansion is readily measured by powder X-ray diffraction of the basal spacing.

Figure 2 presents the XDR patterns of HP-organoclays at different surfactant concentrations and the variation of the d-spacing as a function of the amount of salt in contact with the clay. Results showed that the basal spacing of the smectite fraction expanded as expected, depending on the surfactant concentrations (El Messabeh-Ouali et al., 2009). We observe an increase of the basal spacing d_{001} for untreated HP beidellite from 1.28 nm to 2.29 nm for 2.5^*CEC of HP organoclay.

The TOT layer thickness of smectite is reputed to be 0.97 nm (Harris et al., 1999; Shmidt-Rohr, 1999; Xi et al., 2007a). According to the calculation of molecular size based on the data of bond angles, when HDTMA lies stretched out, the shape of the functional group looks like a “nail” with a length of 2.5 nm consisting of the “nail-head” (0.43 nm, four methyl groups connected with a N atom) and “nail-head” 2.1 nm long alkyl chain which has 15C) (Borchardt, 1977).

In the XRD patterns of the 0.5^*CEC -HP, the main peak shifts to 2.09 nm with a shoulder at 1.48 nm,

corresponding to a monolayer arrangement. The main diffraction peak at 2.09 nm reflects a paraffin-type monomolecular arrangement. For the 1*CEC-HP and 1.5*CEC-HP modified clays, we observed two peaks corresponding to interlamellar distances of 2.19 nm and 2.24 nm. These peaks are attributed to a paraffin-type monomolecular arrangement. Peaks at 2.26 nm, 2.27 nm and 2.29 nm reflect a paraffin-type arrangement for 1.75*CEC-HP, 2*CEC-HP and for 2.5*CEC-HP, respectively. In addition, Figure 3 shows that the characteristic peak of the pure kaolin at 0.739 nm, which appears and persists in all of the diffractograms. This peak is attributed to the kaolinite fraction since (i) kaolinite does not present negative charge allowing the adsorption of cations, and (ii) it is known that interaction of the organic matter on kaolinite surfaces needs a preliminary surface treatment of the clay. The persistence of the characteristic peak of pure kaolinite at 7.39 Å on all diffractograms of the prepared organoclays reinforces the assumption of the attribution of the 10.35 Å peak to the illite portion contained in the interstratified initial clays. This can be used to identify the presence of illite in interstratified smectite-illite clays (Othmani-Assmann et al., 2007). Presumably the kaolinite and illite fractions are not concerned with the intercalation of alkyl ammoniums even if the original purified clays is an interstratified smectite-illite.

We can calculate the angle (α) between the alkyl chain and the basal surface using the length of HDTMA⁺ and the thickness of the TOT layer into account. Table 2 presents angles for all organoclays. The gradual increase in basal spacing reflects the increase of the tilt angle of surfactants in these organoclays from 26.246° for 0.5*CEC-HP to 31.492° for 1*CEC-HP. Our experimental results are similar to those reported previously (He et al., 2006; Xi et al., 2007).

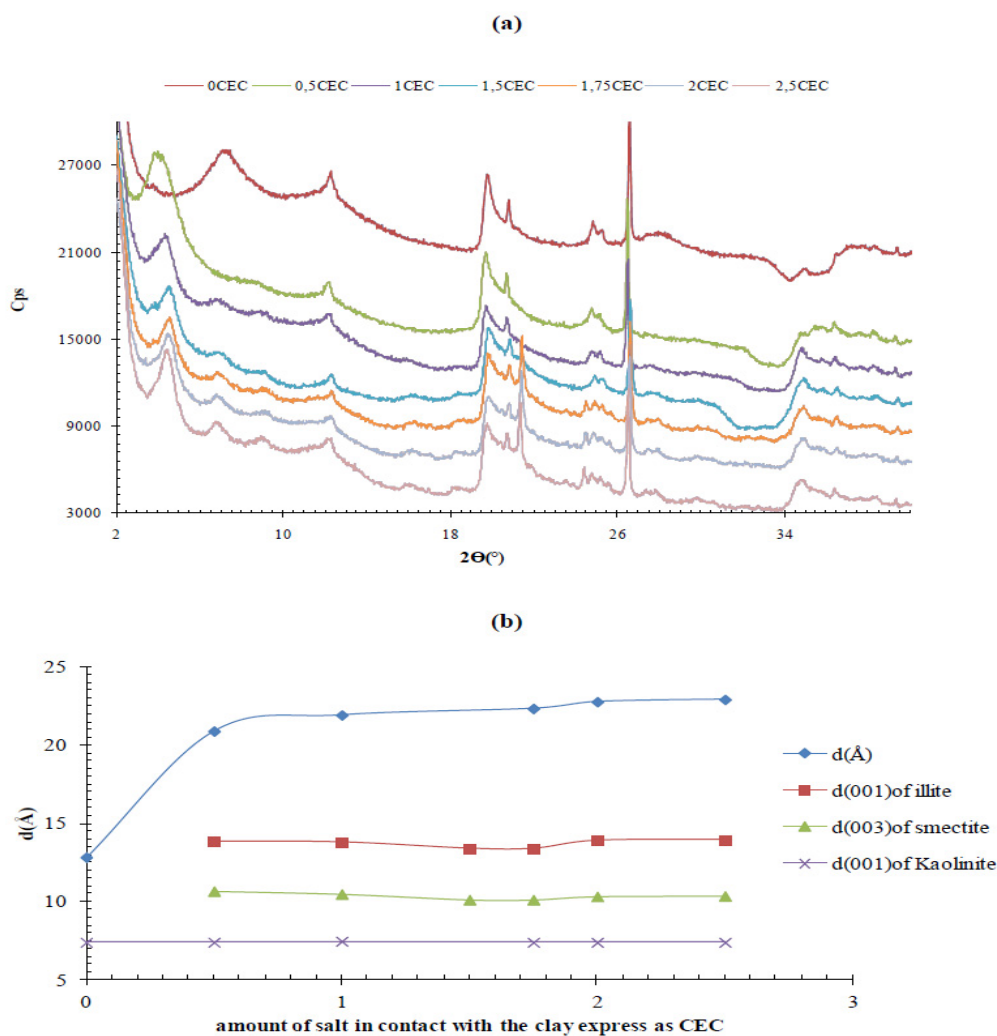


Figure 2. (a) the XDR patterns of smectite and surfactant intercalated HP-smectite clays. (b) Amount of salt in contact with the clay expressed as CEC

Table 2. Angle α between the alkyl chain and basal surface for (0.5-1-1.5-1.75-2-.5)*CEC-HP

Organophilic clay	d(001) (Å)	Interlayer spacing (Å)	Angle α (degrees)
0.5*CEC-HP	20.89	11.19	26.25
1*CEC-HP	21.92	12.22	28.88
1.5*CEC-HP	22.37	12.67	30.05
1.75*CEC-HP	22.62	12.92	30.70
2*CEC-HP	22.7	13	30.92
2.5*CEC-HP	22.918	13.218	31.49

3.2 Photoacoustic (PA)-FTIR Characterization

Figure 3 presents PA-FTIR spectra of HP and HDTMA smectite with different concentrations added (0.5-1-1.5-1.75-2-2.5)*CEC.

3.2.1 Structural Groups of HP-Montmorillonite

Figure 3 illustrates that for the HP-smectite, the 400–3700 cm^{-1} region of the spectrum shows characteristic bands for O-H, Si-O as well as Al-O, Al-OH, Al-Fe-OH, Al-Mg-OH vibrations. The 3626 cm^{-1} and 914 cm^{-1} bands are typical of dioctahedral smectites. The bands corresponding to Al-Al-OH, Al-Fe-OH bending vibrations are observed at 914 and 883 cm^{-1} . The bands at 3680 cm^{-1} and 841 cm^{-1} (Al-OH-Mg bonds) and the deep 796 cm^{-1} band (Fe³⁺-OH-Mg bonds) indicated that the HP-montmorillonite was Mg and Fe³⁺ rich. The bands at 628 cm^{-1} and 690 cm^{-1} are attributed to Si-O-Al and Si-O-Mg bonds. This indicated that most of the layer charge resulted from trivalent (Al³⁺, Fe³⁺) to divalent (Mg²⁺) ion substitution in the octahedral sheet. The 3433 cm^{-1} and 1639 cm^{-1} bands corresponded to OH deformation frequencies of the entrapped water molecules. The band around 2357 cm^{-1} is attributed to ambient CO₂. The Si-O out-of-plane stretching band occurs in HP-smectite at 1091 cm^{-1} .

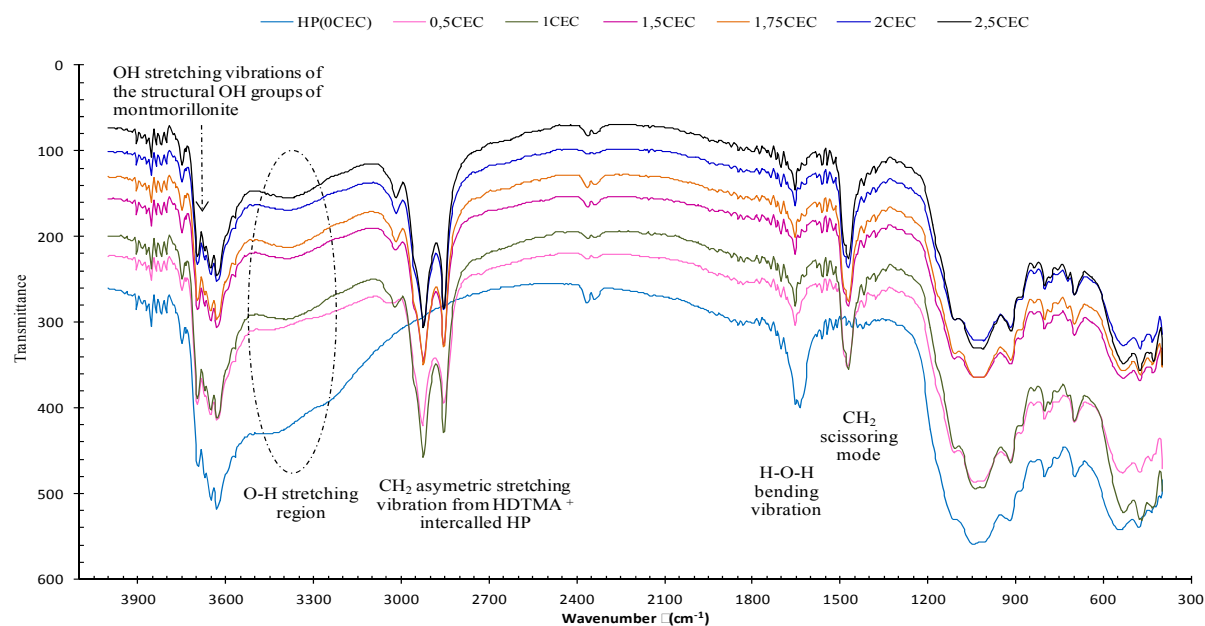


Figure 3. The Photoacoustic FTIR spectra of six studied clay (0.5-1-1.5-1.75-2-2.5)*CEC-HP in the energy range of 4000-400 cm^{-1} at scan speed of 0.15 cm^{-1}

3.2.2 Sorbed Water in HDTMA-HP Samples

Figure 3 illustrates the intensity and quantity of water adsorption for all the studied sample clays. Sorbed water contributes to the H–O–H bending region ($1600\text{--}1700\text{ cm}^{-1}$) and to the O–H stretching region ($3234\text{--}3486\text{ cm}^{-1}$). The position of this band is gradually shifted with an increase of surfactant concentration from 1631 cm^{-1} and 1635 cm^{-1} (for sample HP-smectite and 0.5*CEC-HP , respectively) and to 1639 cm^{-1} (for sample 2.5*CEC-HP). Simultaneously, the intensity of this absorption decreases significantly. We observe a decrease of the band intensity which reflects the higher amount of hydrogen-bonded H_2O molecules present in the organophilic clays (El Messabeb-Ouali et al., 2009). The higher amounts of hydrogen-bonded water are dependent on the concentration of surfactant used. This could be explained by the lower H_2O content resulting from the replacement of the hydrated cations by HDTMA^+ ions (Xu, 2000). With the intercalation of the surfactant, the surface properties of the smectites are modified, i.e. the hydrophilic surface of the smectite fraction has become hydrophobic (Farmer, 1964).

Our results are similar to those reported earlier showing that H_2O molecules clustered around exchangeable cations are polarized by the close proximity to the exchangeable cation with the oxygen of the H_2O directed toward the metal cation (Xu et al., 2000). The intercalation of HDTMA^+ is expected to increase such polarization. Therefore, a decrease in hydrogen bonding is consistent with isolated hydrated clusters of the residual metal cations within the smectite galleries.

3.2.3 HDTMA^+ Intercalation in HP-Smectite Interlayer

The PA FTIR spectra of the $\text{HDTMA}^+/\text{HP-smectite}$ composites are in the range of $2800\text{--}3000\text{ cm}^{-1}$. The intensities of two intense adsorption bands at 2920 and 2850 cm^{-1} correspond to the antisymmetric and symmetric CH_2 stretching modes of amine, respectively, and both increase gradually with increasing packing density of ammonium chains within the smectite galleries. At the same time, the symmetric and antisymmetric C–H stretching of the terminal $-\text{CH}_3$ groups appears at 2866 and 2951 cm^{-1} , respectively, as a function of the packing density of amine chains. This means that the intensity of the absorption bands strongly depends on the packing density of amine chains within the smectite galleries. The wavenumber variation of the antisymmetric CH_2 stretching absorption band is only a slight shift of 4 cm^{-1} from 2920 cm^{-1} for 0.5*CEC-HP to 2916 cm^{-1} for 2.5*CEC-HP . The frequencies of the CH_2 stretching absorption bands of amine chains are extremely sensitive to conformational changes when the chains are highly ordered (all-trans conformation) (Venkataraman & Vasudevan, 2001; Li & Ishida, 2003). This is illustrated by the narrow absorption bands that appear around 2916 ($\nu_{\text{as}}(\text{CH}_2)$) and 2848 cm^{-1} ($\nu_{\text{as}}(\text{CH}_2)$) in the infrared spectrum. Following the HDTMA intercalation in HP-smectite, new infrared adsorption bands appear between 1475 and 1420 cm^{-1} . Those bands are associated with the methylene scissoring modes and are quite similar to the $735\text{--}715\text{ cm}^{-1}$ methylene rocking modes in the disposition and shape of the bands.

3.3 Thermogravimetric Analysis (TG)

Thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) of HP-smectite and all HDTMA-HP studies samples are shown in Figure 4. Temperature analyses of the mass loss are reported in Table 3. Several mass-loss steps are observed. HP decomposition evolved in two steps.

The first step is observed before $200\text{ }^\circ\text{C}$, at exactly $50.78\text{ }^\circ\text{C}$ for HP-smectite at $23.0\text{ }^\circ\text{C}$ for 2.5CEC-HP with a mass loss varying from 6.22 to 1.42% , respectively. It is attributed to mass loss due to dehydration of physically adsorbed water and water molecules around metal cations such as Na^+ and Ca^{2+} on exchangeable sites in smectite. Only minimal dehydration is observed for $(0.5\text{--}1.5\text{--}1.75\text{--}2\text{--}2.5)\text{*CEC-HP}$ and it decreases with increasing organophilicity (Farmer, 1964; Borchardt, 1977; Xu et al., 2000). This probably corresponds to interlayer water trapped by the HDTMA ammonium salt. The mass loss of water adsorption varies from 1.608% (0.5*CEC-HP) to 1.417% (2.5*CEC-HP), suggesting that the 0.5*CEC-HP contains more water than the 2.5*CEC-HP (Xi et al., 2004).

The second step occurs between $200\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$. This second mass loss is attributed the decomposition of the HDTMA surfactant by the departure of alkyl groups with long chains (Vaia et al., 1994). This concurs with previous results comparing the DTG results of these organoclays (El Messabeb-Ouali et al., 2009), and suggests that the phenomenon is specific to alkyl cation groups binding on easily accessible external surfaces and extremities. Indeed, it has been shown that the implication of two peaks in the DTG analysis is indicative of two different structures within the organoclays (Xi et al., 2007b). Figure 6 for 0.5*CEC-HP also shows two peaks, one at $260\text{ }^\circ\text{C}$ and the other at $395\text{ }^\circ\text{C}$. Such observations are also observed in the TG patterns of the higher surfactant-loaded organoclays. When surfactant concentration reached 2.5*CEC-HP , three peaks can be observed, at $228\text{ }^\circ\text{C}$, $350\text{ }^\circ\text{C}$ and $397\text{ }^\circ\text{C}$. According to previous studies when the concentration of the surfactant was

relatively low, the organic cations exchanged with the Na^+ ions and adhered to surface sites predominantly via electrostatic interactions (Mendelsohn et al., 1995; Barman et al., 2003; Li & Ishida, 2003; Xi et al., 2004). With increasing surfactant concentrations, some surfactant molecules are attached to the surface of the smectite. This resulted in the appearance of the second peak. If the concentration increased even more, the concentration of the surfactant exceeded the CEC of clay. Surfactant molecules then adhered to the surface-adsorbed surfactant cations by Van der Waals forces. The properties of these organic cations were very similar to that of a pure surfactant. The HDTMA is presumed to decompose or burn at 202 °C (Zhou et al., 2007), so the third peak which appeared was very close to this critical temperature. In addition, with increasing surfactant concentration, the temperature of the third peak decreased gradually (getting closer and closer to that of the pure surfactant).

The third step occurring with the mass loss over 400 °C was attributed to the loss of dehydroxylation of the structural OH units of the clay. This is shown in Figure 7 at 461.3 °C for HP-smectite and varied from 409 to 486 °C for 0.5*CEC-HP and 2.5*CEC-HP, respectively. These peaks are, as before, assigned to the dehydroxylation of the smectite. It is noted that there is a significant shift to lower temperatures of the dehydroxylation of the organoclays. This shift is attributed to the penetration of the methyl groups of the surfactant into the siloxane layer. This may provide a mechanism for the removal of the OH units as water vapor.

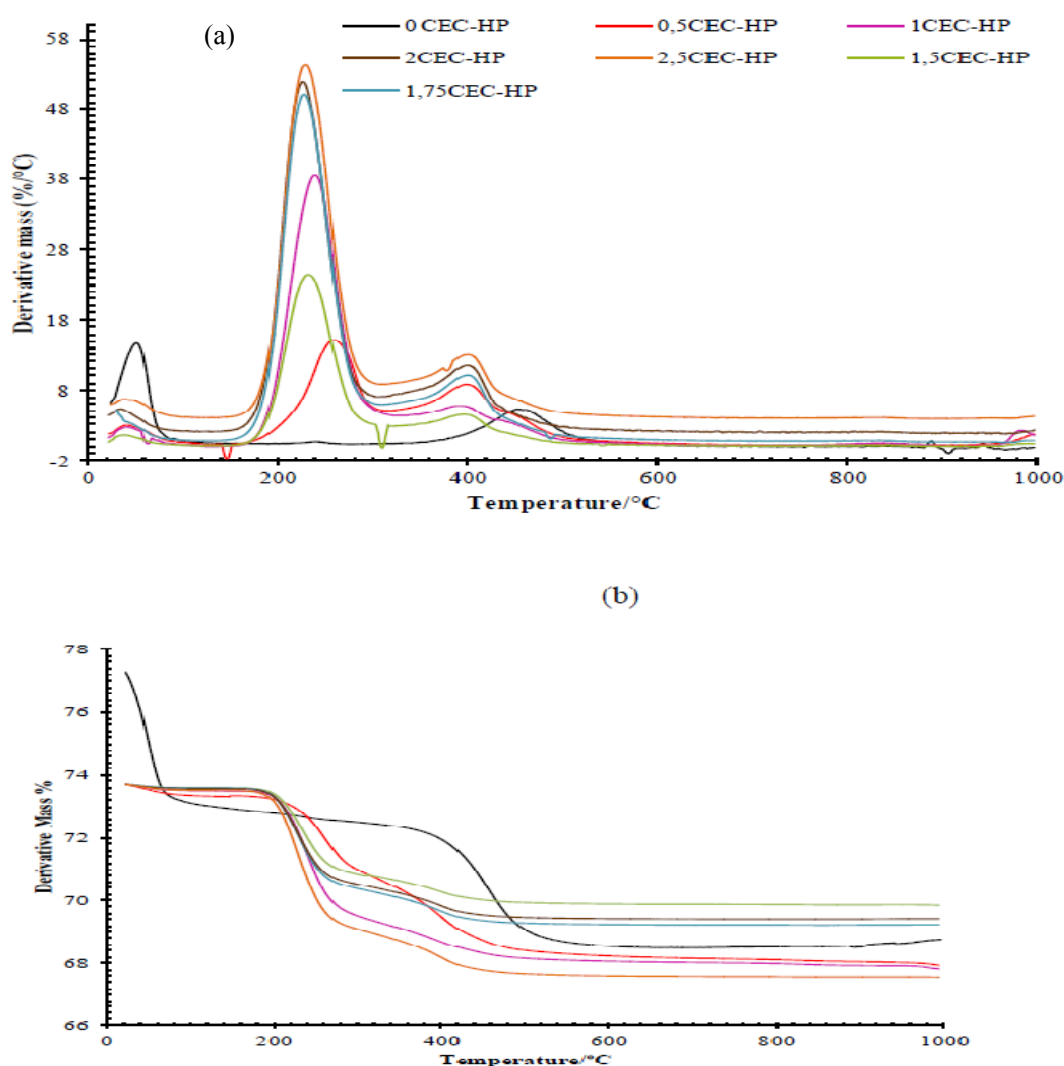


Figure 4. (a) DTG and (b) TG results of HP-smectite and organoclays HDTMA-HP

As shown by XRD patterns, PAFTIR and TG curved, the HDTMA surfactants have been successfully intercalated into clay interlayers or on the surface of HP-smectite. The loaded surfactant amount could be determined by thermogravimetry (TG) According to previous results of differences between the amounts of surfactant added and load may be detected (Xi et al., 2004; Zhou et al., 2007; Zhou et al., 2008).

Table 3. Results of the TG of HP-smectite and HDTMA-HP

Samples	Dehydration/ hydroxylation (Adsorption water) and water adsorbed by metal cations		Desurfactant (HDTMA Decomposition)		Dehydroxylation (Structural OH units)	
	% mass- loss	Temp (°C)	% mass-loss	Temp (°C)	% mass-loss	Temp (°C)
	(Step 1)		(Step 2)		(Step 3)	
HP	6.22	50.78	-	-	5.10	461.30
0.5 CEC-HP	1.61	41.95	16.32	259.68/395.84	8.87	408.90
1 CEC-HP	0.67	41.51	21.50	240.04/370.19	3.82	430.12
1.5 CEC-HP	1.131	39.28	37.41	233.25/397.36	1.67	447.91
1.75 CEC-HP	1.079	32.94	39.49	226.03/399.03	1.63	470.39
2 CEC-HP	1.444	22.53	39.75	226.721/397.52	1.60	471.80
2.5 CEC-HP	1.417	23.20	40.98	228.58/349.81/396.15	1.55	485.85

The loaded surfactants could be calculated according to Equation (1) (Xi et al., 2007b), and the results are summarized in Table 3 where X is the loaded surfactant amount; m is the total weight of organoclay; M is the molecular weight of surfactant; S % is the weight loss percentage of surfactant within the organoclay; y is 0 (if all the Br ions remain) or 80 (no Br ion, the molecular weight of Br is 80), extreme y values of 0 or 80 are not possible but it this helps to work out the range of X by calculating theoretical maximum and minimum values. As shown in Table 3, there are differences between the amount of surfactant added and the amount of surfactant loaded. These results agree with those given through the HDTMA adsorption isotherm of the HP clay. The data is well correlated to the theoretical values for both 0.5 and 1.75*CEC-HP. It was concluded that for 1*CEC-HP and 1.5*CEC-HP, only about (0.5–0.8) CEC and (0.8–1.3) CEC was loaded on this clay, independently of the initial concentration of added surfactant. This conclusion also explained the lower surface areas of HDTMA-modified bentonites where a larger quantity of surfactant was loaded on the clay surface and thus blocked some surface area. These results agree with those given through the HDTMA adsorption isotherm clay by HP.

$$X = \frac{m \times S \times 10^{-2} \times 100}{(M - y) \times m \times (100 - S) \times 10^{-2} \times \text{CEC} \times 10^{-3}} = \frac{S \times 10^5}{\text{CEC} \times (M - y) \times (100 - S)} \quad (1)$$

3.4 Laser Scattering Distribution

Figure 5 gives the particle size of (0-0.5-1.5-2.5) CEC-HP as determined by laser scattering distribution (LSD). It clearly shows that with increasing sonication time, the average cluster size of HP shows a slight decrease and remains almost constant from 0.211 to 0.179 µm from 0 to 150 seconds. With higher sonication periods, effective diameter particle of the 0.5*CEC-HP clays shows a remarkable increase between 93.213 to 441.801 µm. For 1.5 times of CEC for the two types of clay, these particle sizes showed a decrease with increasing sonication time. On the other hand, particles diameters of 2.5*CEC-HP showed an increase with increasing sonication time. The plateau of its curve is nearly at 120 µm. The average particle size (measured LSD) of the final product in the presence of HDTMA was larger and had a broader particle size distribution in comparison to that in the absence of HDTMA, i.e, for sodic clay. The LSD technique shows the size of the organoclay aggregates and measures it at the same time, i.e, it has the potential to act as both a flocculant and a deflocculant depending on the concentration of the organoclay.

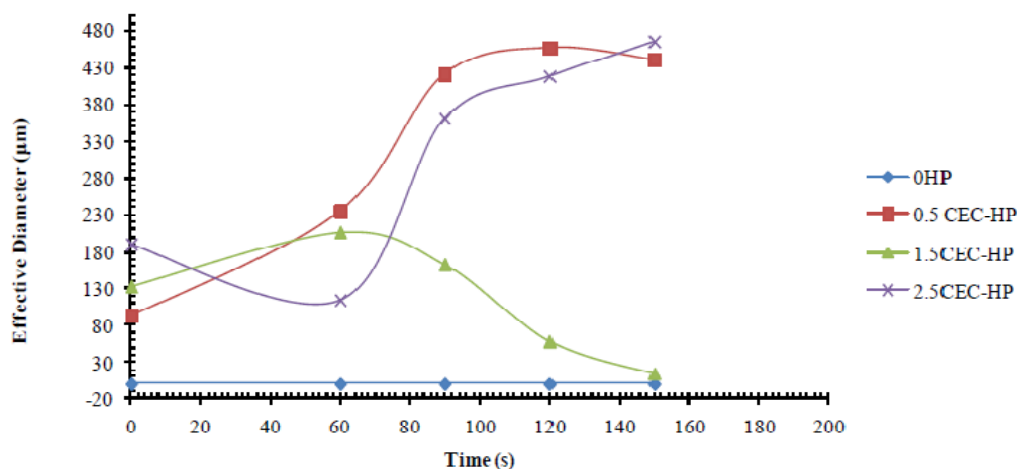


Figure 5. Effective diameters (DLS measurement) for HP and HDTMA-HP as a function of sonication time

Sonication has been used to reduce the size of clay particles in a study of the influence of ultrasound on the thermal behavior of clays minerals (Poli et al., 2008) and it was also observed that sonication produces a significant increase in the specific surface areas due to decreased particle size (Pérez-Rodríguez et al., 2006). The presence of adsorbed organic cations on a clay surface changes the surfaces of the clay from hydrophilic to hydrophobic and has a significant impact on the surface properties that influence the interactions among clay particles. Thus the size of aggregates may be increased via cluster-cluster aggregation, or decreased due to the defloculant effect of surfactants. The three dimensional network of the clay particles (a gel) can even be observed when the organoclay is dispersed in an appropriate medium (Tahani et al., 1999). However, there has been some reluctance to rely on laser scattering techniques because of perceived concerns with; 1) absolute calibration of these instruments and 2) documented examples of poor results for clay size distributions when compared with conventional sedimentation techniques (McCave et al., 1986; Mackinnon et al., 1993).

3.5 Atomic Force Microscopy

AFM was found to be a powerful tool to investigate the nanoclay surface on a micrometer scale and in some cases even on a nanometer scale. In the literature, there are few studies that used AFM to characterize organoclay morphology. Previous works have pointed out that different approaches such as AFM may give a different picture of the morphology (Becker et al., 2002; Zbic & Forst, 2010). To enable swelling or intercalation and exfoliation of the layered smectite, the inorganic interlayer cations have to be exchanged by hydrophobic organic cations, which are usually of the alkylammonium group (Becker et al., 2002).

Figure 6 presents the typical height and the 3-dimensional AFM images for the (0-0.5-1.5-2.5)*CEC-HP samples in which the scale represents surface profile of a glass cover slip on which particles have been deposited (lighter areas are higher). It is also important to notice that the distribution of particles is not uniform over the glass surface.

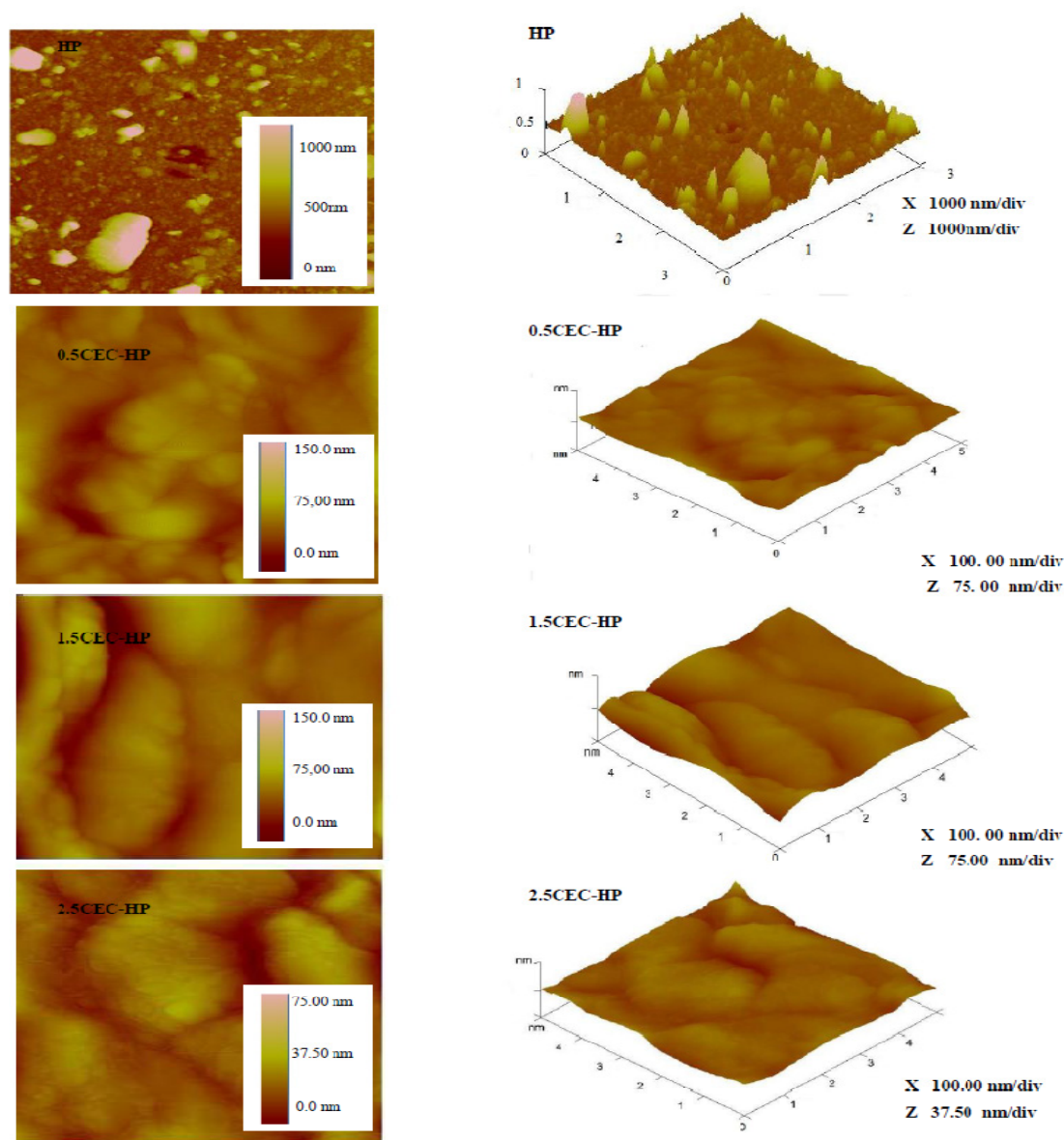


Figure 6. Topography AFM representing the height image (left) and the 3D image (right) of (0-0.5-1.5-2.5)*CEC-HP

The AFM images were typically taken at random locations near the center of the drop, where the particles are well dispersed and detached. Indeed, the receding liquid front during evaporation at the glass surface has a tendency to concentrate particles at its boundary, making those areas too crowded for easy particle identification. The AFM results suggest a higher particle thickness which may be due to the tip broadening effect. The spongy structure of smectite built from the assemblage of flexible platelets in clay films may hinder the AFM probe by interacting with similar structures on the surface of the substrate. This artefact from platelets interactions would be unavoidable. If this mechanism is responsible for our force measurement results, it reflects the squeezing of the cellular monolayer of the HP-smectite structure, which has dimensions that are consistent with microscopy observations. In the typical images of HP-smectite, the small dark spots scattered over the image are indicative of empty spaces, i.e., the bare substrate. The white spots indicate vertical aggregation of HP-smectite particles, which have irregular morphologies, somewhat like corn flakes. Their direction cannot be attributed to any particular crystallographic direction. Thin isolated sodic clay particles are identified both in the *in situ* experiment and in the dry experiment. Some particles present several lateral domains with different heights. These height differences can be attributed either to precipitates or to platelet stacking. In the dry experiments, many high circular peaks are observed. One of the possible explanations is the heterogeneity of particle sizes,

where the surfactant is rarely taken into considerations for smectite modifications of platelets during adsorption of water and cations (Hetzel et al., 1994; Michot & Villieras, 2002). The HDTMA-HP particles were packed more densely than HP-smectite. Individual 0.5*CEC-HP particles are difficult or impossible to distinguish clearly, given the irregularity and the rugosity of the HDTMA-HP surface morphology. The increase in surface coverage of the monolayer with increased organophilicity is an indication of the HDTMA intercalation in the interlayer of HP-montmorillonite. The morphology of the samples changed after the intercalation of HDTMA in the interlayers of the clay, as indicated by the rugosity of the clay surfaces. With the increase of organophilicity, AFM images show that at least part of the HDTMA content remains in tactoids or stackings of layers rather than forming a homogenous morphology throughout the whole material. The location of isomorphous substitution in the lateral sheet of smectite is expected to result in an increased lateral extension of overlapping layers (Lantenois et al., 2007). Increased number of layers in particles was found with increasing surface charge density. Accordingly, the geometric organization of the particles is critical to the understanding of the ability of Na^+ clay to hold HDTMA surfactant against an applied suction.

3.6 Transmission Electronic Microscopy

The results of the X-ray diffraction can be complemented by the TEM images which showed basal spacings similar to that of X-ray diffraction. Figure 7 gives the HP morphologies. Generally, HP-smectite composed of regular layers with regular layer-to-layer distances remained about 1.28 nm. Many curved layers were founded with regular basal distances. Figure 8 shows the morphologies of 0.5*CEC-HP.

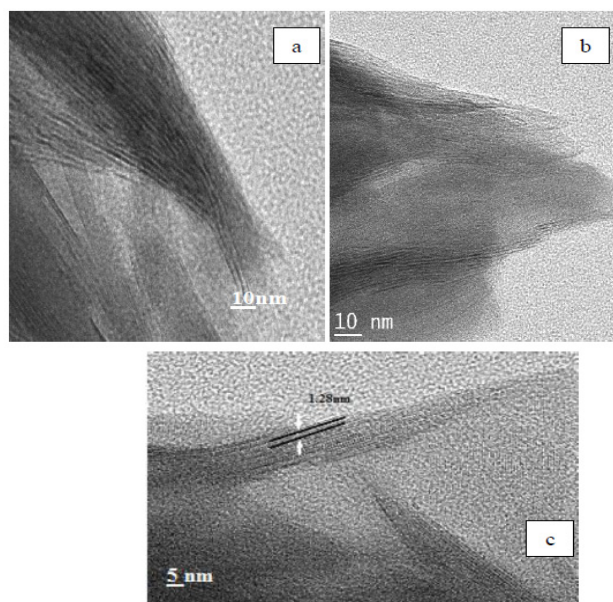


Figure 7. TEM micrographs of HP with regular staking intercalated layers (a) and (c), and curved with a regular basal distance (b)

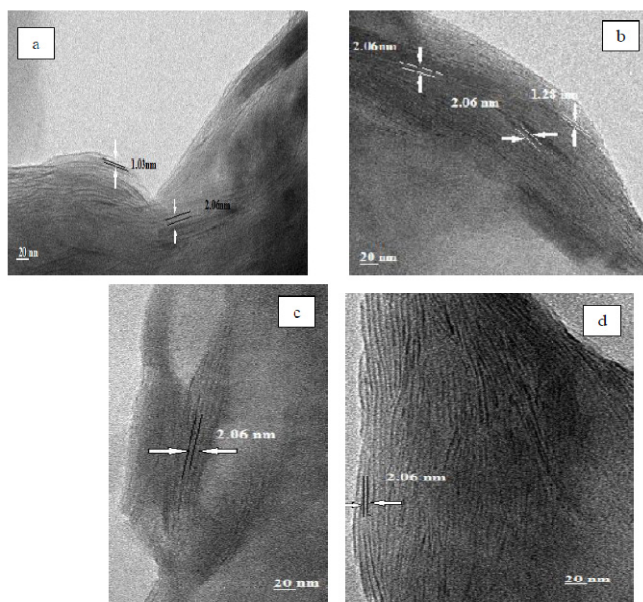


Figure 8. TEM micrographs of 0.5*CEC-HP intercalation with regular layers occurring in a small region (a) and (c) and for irregular intercalated layers (b) and (d)

However, some regularly intercalated layers only occur in a small area. In the majority of the surface, the interlayer distance was about of 2.06 nm, indicative of the intercalation of HDTMA in the interlayer spaces. In some areas, d-spacing remains about 1.28 nm, similar to that of HP-smectite. This indicates that not all interlayers are intercalated by surfactants, resulting from lower surfactant concentration and/or irregular intercalation

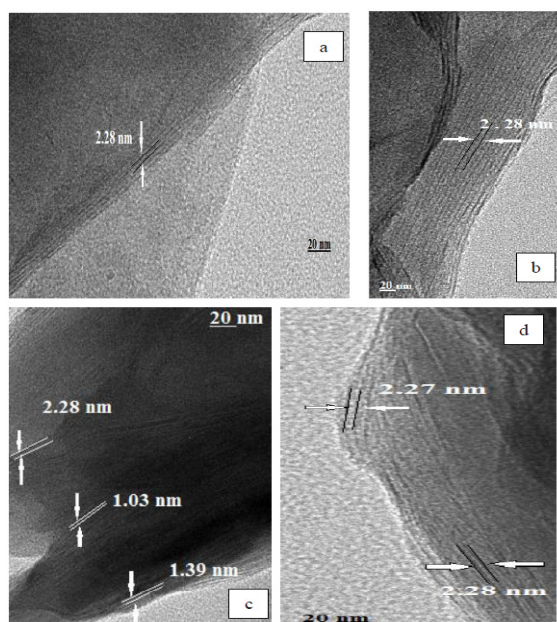


Figure 9. TEM micrographs of 2.5*CEC-HP with regularly intercalated layers with a slight difference of layer height from layer to layer (three versions: (a), (b) and (c) and coexistence of d(003) intercalated layers (d))

The morphologies of 2.5*CEC-HP are presented in Figure 9, and were mainly composed of regularly intercalated layers. In spite of a slight differences between 2.27 and 2.28 nm, the layer height for the regularly intercalated layers can still be observed for 2.5*CEC-HP in Figure 9(d). A different basal distance of 1.39 nm

was observed. It can be attributed to the $d(003)$ corresponding to the basal distance of smectite beyond 40 Å (4nm) for (001) reflection. Compared with 2.5*CEC-HP sample, the morphologies of 0.5*CEC-HP show that there are much more variation for layer height relative to the organoclay. In addition there are more curved layers found in the 0.5*CEC-HP, similarly to the results reported for a natural HP-smectite (Bauluz et al., 2002). This has been attributed to the lower packing density of surfactants within the galleries based on the variable basal spacing and the board profiles of X-ray patterns leading to the HDTMA⁺/organoclays representing multi-phase systems consisting of both regularly and randomly intercalated layers (He et al., 2006).

The Na-smectite layer may be retained since there is not enough surfactant provided to exchange the sodium cations in the smectite interlayer. This is similar to what we observed in the TEM micrographs in the present study (Figures 7, 8 and 9) and indicates that with increasing surfactant packing density in the interlayer, the curved plates in HP-smectite will transform to flat layers. Hence the results of TEM images are in harmony with the results from XRD. Our data show that not only the basal spacing but also the morphology of the organoclay strongly depends on the packing density of the surfactant within the interlayer space and galleries, as reported earlier by others (He et al., 2006).

4. Conclusion

In this work, sodium clay was used as the base clay for the synthesis of organoclays with an alkyl chain surfactant (hexadecyltrimethyl ammonium bromide–HDTMA Br) and using a range of surfactants concentration based on the CEC of the clay. These new materials were characterized using the XRD; PAFIR; TG-ATD; LSD; AFM, and TEM techniques.

The d_{001} spacings measured by XRD are a function of the CEC value. The interlayer spacings of organoclays increase with increasing CEC. The gradually larger basal spacing reflects the increase of the tilt angle of surfactants in these organoclays. The thermal analysis provides information on the dehydroxylation which decreases with increasing CEC, with the conformation of the surfactant HDTMA⁺ molecules in the clays layers, the thermal decomposition of the interlayer and the amount of loaded surfactant.

Moreover, the PAFTIR was used to investigate the change in the structure and surface characteristics of water and surfactant molecules in smectite and organoclays prepared with the HDTMA⁺ surfactant with different surfactant loading. The AFM images allowed the study of the morphology of the surface with the increase of surfactant intercalated in the clays. With increased sonication time, the particles size of the clays has suffered from deflocculation, as measured using the laser scattering distribution–LDS. TEM micrographs demonstrate that the organoclays with lower surfactant packing density are mainly composed of irregular layer stackings with a number of curved organoclay layers. Organoclays with higher surfactant packing density are mainly composed of regular layers stackings with fewer curved organoclay layers. Our present study demonstrates the surfactant packing density within the montmorillonite interlayer space will have an impact on the basal spacing, the arrangement of the intercalated surfactant in the clay, but also on the morphology of the organoclays.

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