Contents lists available at SciVerse ScienceDirect

# I SEVIER





www.elsevier.com/locate/jcis

# Controlling wettability and hydrophobicity of organoclays modified with quaternary ammonium surfactants

Kinjal J. Shah<sup>a,b</sup>, Manish Kumar Mishra<sup>c</sup>, Atindra D. Shukla<sup>a,\*</sup>, Toyoko Imae<sup>b,\*</sup>, Dinesh O. Shah<sup>a,\*</sup>

<sup>a</sup> Shah-Schulman Center for Surface Science and Nanotechnology, Dharmsinh Desai University, Nadiad 387 001, India

<sup>b</sup> Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

<sup>c</sup> Department of Chemical Engineering, Dharmsinh Desai University, Nadiad 387001, India

#### ARTICLE INFO

Article history: Received 16 April 2013 Accepted 21 May 2013 Available online 12 June 2013

Keywords: Quaternary ammonium salt Montmorillonite Organoclay Hydrophobicity Wettability Surface Modification

### ABSTRACT

The montmorillonite clays were modified with quaternary ammonium salts (QASs) having different alkyl chain lengths and a benzyl substitute group. The modified organoclays were characterized by different analytical techniques. The wettability and hydrophilicity/hydrophobicity of the modified clays was evaluated using water or oil penetration (adsorption) and contact angle measurements. The loading of QASs was in the range of 0.60–0.75 mmol/g per clay, irrespective of the type of QAS used for the modification of the clay. From the analytical investigations, it was elucidated that the modification of clay with QAS affected the structural, textural, and surface properties. Moreover, it should be noted that the modification with QAS having benzyl substitute group resulted in water-non-wettable and superhydrophobic surface, whereas clays modified with QAS without benzyl substitute group became more water-wettable and hydrophilic than the pristine clay. The presence of benzyl groups on the clay prevents water from penetration into the inter-clay or interlayer spacing, which yields the hydrophobic surface. These behaviors can arise from molecular arrangement of QAS on clay but not be attributable to the amount of QASs, and the surface area, size, and zeta potential of particles.

© 2013 Elsevier Inc. All rights reserved.

## 1. Introduction

Since the past two decades, organically modified clays or organoclays have been attractive candidates for various applications [1] such as their industrial use as fillers in cosmetic formulations, polymer matrices, inks, paints, lubricants, greases, and drilling operations [2]. Rigorous modification to achieve desired surface properties is becoming important to design organoclays for intending sophisticated applications. Clays modified with organic surfactants are preferably miscible with organic and polymeric materials, resulting in better dispersion and also altering their thermal, mechanical, elastic, and adhesive properties [3–5]. Lipophilicity of organoclays makes them suitable materials for incorporating drug molecules and slowing their release [6–8]. Otherwise, hydrophilicity of organoclays brings their easy water-dispersibility and layered accumulation [9,10].

Layered silicates such as montmorillonite (MMT,  $(Na,Ca)_{0.33}$ (Al,Mg)<sub>2</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·nH<sub>2</sub>O) and other smectite clays have been proven to be materials of choice for surface modification by organic molecules due to their large surface area, high cation exchange capacity, and unique structural properties such as nanometersized platelets with very small cross-sectional area [11–13]. The Si–O group on the surface of clay is hydrophilic, and this property makes them water-adsorbable but discordant to polymer matrix and other non-polar organic liquids [14]. MMT is hydrophilic like most other clays and swells due to the adsorption of water in the interlayer spacing of the clay. Presence of Na<sup>+</sup> and Ca<sup>2+</sup> in basal planes of the clay can be effectively replaced by organic cationic surfactant molecules [2,15]. This cation exchange process results in the expansion of the interlayer spacing and an increase in the basal spacing of the MMT [16]. Generally, the replacement of inorganic cations with organic cations yields modified clays with increased hydrophobicity [17]. These hydrophobic clay materials are compatible with organic materials such as polymers, drug molecules, oils, and hydrocarbons [2].

Quaternary ammonium salts/surfactants (QASs) are commonly used for making organically modified clay because of their versatile functionalization and cost effectiveness compared to the other siloxane and phosphonium ion-based surface active agents. Moreover, the modification using QAS takes place through relatively simple and facile cation exchange process, which makes it a preferred route over the other options. The length of the alkyl chain and the functional groups on quaternary ammonium ions of the modifier can affect the final properties of the modified clay [11–13].

<sup>\*</sup> Corresponding authors. Fax: +91 268 2520501 (A.D. Shukla, D.O. Shah), +886 2 27303627 (T. Imae).

*E-mail addresses*: atindra.sscssn@ddu.ac.in (A.D. Shukla), imae@mail.ntust. edu.tw (T. Imae), dineshoshah@yahoo.com (D.O. Shah).

<sup>0021-9797/\$ -</sup> see front matter @ 2013 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jcis.2013.05.050

The maximum amount of the quaternary amine surfactant, which can be loaded, generally depends on the cation exchange capacity of each clay material. However, to achieve desired hydrophobicity on the surface of the clay, one has to choose the surfactant with appropriate chain length and the functional groups on the quaternary ammonium ion. For better oleophilicity, surfactants with chain lengths more than  $C_{12}$  are preferred [14]. The interlayer spacing, particle size, zeta potential, and thermal properties of modified clays are dependent on the substituent groups as well as the chain length of the QAS [13,14]. The QAS with long chain and ammonium ion tends to arrange randomly in the basal space of the clay and increase the basal spacing between the layers. Meanwhile, the modification of clays with QAS having one or more substituents of aromatic groups can improve properties in comparison with the clays modified with QAS having no aromatic substituent groups: The OAS with phenyl rings being planar and rigid structure tends to form accumulated planer blocks or tiles in the galleries of the modified clays, and so it would prevent water from going inside the layer of the clay.

In the present work, the modification of MMT with QAS having different chain lengths of aliphatic group and aromatic substituent group was performed. For the assessment of loading of the surfactants by comparison with the pristine clay, the QAS-modified MMT clays were analyzed by means of Fourier transform-infrared (FT-IR) absorption spectroscopy, powder-X-ray diffraction (XRD), BET (Brunauer-Emmett-Teller) surface area measurement, elemental analysis and dynamic light scattering for characterization, and particle size and zeta potential determination. Adsorption studies and contact angle measurements were carried out for determining the wettability and hydrophobicity of the modified MMT. The hypothesis on the arrangement of QAS on MMT was supported by the imaging of clay with scanning electron microscopy (SEM) and the mapping of the carbon and nitrogen with energy dispersive X-ray (EDAX) spectroscopy.

#### 2. Experimental section

#### 2.1. Materials

MMT clay lumps (Jani Clays Ltd., Ahmedabad, Gujarat, India), hexadecyldimethylbenzylammonium bromide, tetradecyldimethylbenzylammonium bromide, tetradecyltrimethylammonium bromide, dodecyltrimethylammonium bromide (Dishman Pharmaceuticals Ltd., Ahmedabad, Gujarat, India), hexadecyltrimethylammonium bromide (PrabhatChemiorganics Ltd., Surat, Gujarat, India), AgNO<sub>3</sub>, and concentrated HCl solution (S.D. Fine Chemicals, Worli Road, Mumbai, India) were commercial grade.

#### 2.2. Instrumentation and techniques

The FT-IR study was carried out using a FT-IR spectrophotometer (IRPrestige-21, Shimadzu) on KBr pellets in a 1:20 weight ratio in the range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The thermal analysis was carried out by a Mettler thermal analyzer, TA4000, in the range of 50–900 °C under nitrogen flow (100 cm<sup>3</sup>/ min). The basal spacing of the clays was measured by an XRD analysis using a X-ray diffractometer (Bruker D-8 advance X-ray powder diffractometer) having Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The measurement was scanned in 2 $\Theta$  range of 2–20. Particle size and zeta potential were measured by a dynamic light scattering (Malvern Zetasizer Nano ZS) instrument. The elemental analysis was performed on a CHNS/O elemental analyzer (Perkin Elmer PE 2400 Series II) by a CHNS mode of operations. Wettability were measured as water/oil adsorption by a digital penetration meter (Model DS210) instrument, prepared by Instrumentation and

Control Department, Dharmsinh Desai University, with a specially designed cylinder of 80 mm height and 18.5 mm diameter, plotting changes in sample mass as a function of time in one second of the interval. The same measurements were performed on a force tensiometer model (Attension Sigma 700, Biolin Scientific) with a penetration rate plotted as a change in mass of the sample per second. The swelling was examined by immersing 2 g of clay in 30 cm<sup>3</sup> of water for 12 h. The contact angle measurement was performed on an optical tensiometer (Theta of Attension, Biolin Scientific). For this, the specimens were prepared under hydraulic presses, having a maximum working pressure of 260 kg/ $cm^2$ , with a sample Teflon holder of 20 mm diameter. The BET surface area was measured at five points by N<sub>2</sub> adsorption-desorption isotherm using a NOVA 1000e surface area analyzer. The surface topography was studied using a SEM (LEO 1430VP), and the EDAX analysis was carried out by an INCA software.

#### 2.3. Purification of MMT clay

The purification of commercial MMT clay was performed by the procedure according to the Stoke's law of sedimentation for isolating the higher cation exchange capacity portion of the clay lumps [15]. The major impurities like quartz, iron oxide, mica etc. were separated from this sedimentation method. The MMT clay lumps were dispersed in water (1.5 wt%), and the suspension was stirred for 30 min to homogenize and allowed to settle for 10 h at 30 °C. After the supernatant slurry was decanted in a separate vessel and centrifuged at 2000 rpm for 10 min, the sediment was collected and dried at 90–100 °C. The cation exchange capacity of the purified clay was measured by the methylene blue method as previously reported [18], and it was found to be 120 g/cm<sup>3</sup>.

#### 2.4. Preparation of organoclays

Purified MMT clay was added in an aqueous 0.01 M solution of QAS with dropwise continuous addition for 45 min at 80 °C, following the stoichiometric proportion of its cation exchange capacity (120 g/cm<sup>3</sup>). Preferable modification was achieved by adding 1:1 of HCl/Water into the clay suspension to maintain pH 3 to 4 and by stirring for additional 30 min. The organoclays were washed to remove the halide salt of unreacted surfactant with water, dried overnight at 90–110 °C in oven, and ground to pass through 200 mesh sieve. The organoclay prepared by use of QAS-n (*n* = 12, 14, 16) and QAS-Bn (*n* = 14, 16) (as shown in Fig. 1) was named as MMTQAS-n and MMTQAS-Bn, respectively.



n = 10: Dodecyltrimethylammonium bromide (QAS-12)

n = 12: Tetradecyltrimethylammonium bromide (QAS-14)

n = 14: Hexadecyltrimethylammonium bromide (QAS-16)



n = 12: Tetradecyldimethylbenzylammonium bromide (QAS-B14) n = 14: Hexadecyldimethylbenzylammonium bromide (QAS-B16)

# 3. Results and discussion

#### 3.1. Characterization of QAS-modified organoclays

Organoclays consisting of MMT clay and QAS with different alkyl chain lengths and with/without benzyl substituent group were prepared by mixing the component materials at high temperature and acidic condition. The amount of QAS loaded in the clays by exchange of inorganic ions was estimated by CHN elemental analysis, as given in Table 1. The loading of QASs in the clay was found to be in the range of 0.60–0.75 mmol per g of clay, which was almost independent of alkyl chain length and benzyl substitution. The BET surface area ( $S_{BET}$ ) of the clay was 84 m<sup>2</sup>/g, but, after the modification by QAS, it was significantly reduced, giving a surface area of  $2-16 \text{ m}^2/\text{g}$  (see Table 1). This reduction can be attributed to the loading of the QAS on the clay surfaces. Namely, with increasing the chain length of alkyl group in QAS from 12 to 16, the  $S_{BET}$  of the modified clay successively decreased, although the presence of the benzyl group in QAS showed scarcely an effect on the  $S_{\text{BET}}$ of the organo MMT clay. This indicates the occupation of surface area by QAS. The particle size of organoclays, measured by dynamic light scattering, varied with the change in the size of the OAS, irrelevant to the existence of benzyl substituent (Table 1). The thickness of adsorbed laver increases with the increase in the alkyl chain length, and the resultant particle size increases.

The FT-IR absorption spectra of MMT and organo MMT clays are shown in Fig. 2. The spectra of the MMT clay displayed bands at 3685, 3628, and 3300 cm<sup>-1</sup> in the hydroxyl –OH stretching vibration region. Former two were attributed to Me–OH (Me = Si, Mg, or Al), and the last broad one was to hydrogen-bonded interlayer/adsorbed water. A band at 1645 cm<sup>-1</sup> is attributed to –OH bending mode, and bands at 1112 and 1037 cm<sup>-1</sup> were derived from Si–O–Si stretching vibrations [19]. A band at 908 cm<sup>-1</sup> was assigned to a vibration mode of Me–O–Me' (Me, Me' = Mg or Al or Si) and a band at 522 cm<sup>-1</sup> was for Si–O–Si bending mode [20].

In the FT-IR spectra (Fig. 2) of organo MMT clays, all the characteristic bands were maintained, independent of the exchange from inorganic to organic cation in the interlayer of the clay minerals, except the band shift from 3300 to 3400 cm<sup>-1</sup> due to the variation of the hydrogen-bonding of water. This suggests that the exchange of cation has no significant effects on the structure of the clay, but the hydrogen-bonding of interlayer/adsorbed water is influenced. Commonly in the spectra of all organo MMT clays, there were additional bands at 2924 and 2848 cm<sup>-1</sup>, which were assigned to the antisymmetric and symmetric stretching vibrations of methylene groups (-CH<sub>2</sub>-) of aliphatic chains. In addition, there was also a sharp –CH<sub>2</sub>– bending vibration band at 1470 cm<sup>-1</sup>. The FT-IR spectra of MMTQAS-B16 and MMTQAS-B14, in which QAS molecules possess the benzyl substituent group, did not show any clear bands associated with the phenyl group because of weak intensities of corresponding bands. The appearance of the IR bands of methylene groups confirms the presence of exchanged QAS in the clay. In addition, a position at 2924 cm<sup>-1</sup> of a CH<sub>2</sub> antisymmetric stretching band indicates that alkyl chains take the medium configuration between trans-zigzag-type and gauche-type [21,22].

Table I									
QAS loading,	BET	surface	area,	and	particle	size	of	clays	ί.

Clay	QAS loading (mmol/g)	$S_{\rm BET} (m^2/g)$	Particle size (nm)
MMT	-	83.7	461
MMTQAS-12	0.65	16.0	507
MMTQAS-14	0.75	7.4	898
MMTQAS-16	0.70	3.2	1050
MMTQAS-B14	0.74	5.9	902
MMTQAS-B16	0.60	2.1	1108



Fig. 2. FT-IR absorption spectra of clays. (a) MMT; (b) MMTQAS-B16; (c) MMTQAS-B14; (d) MMTQAS-16; (e) MMTQAS-14; (f) MMTQAS-12.



**Fig. 3.** (A) TGA and DTG of MMT and organo MMT clays. (A) TGA of (a) MMT; (b) MMTQAS-B16; (c) MMTQAS-B14; (d) MMTQAS-16; (e) MMTQAS-14; (f) MMTQAS-12. (B) DTG of (a) MMT; (b) MMTQAS-B16; (c) MMTQAS-16.

The thermal analyses of MMT and organo MMT clays were carried out to study their thermal properties. The Thermo gravimetric analysis (TGA) and differential thermo gram (DTG) profiles of MMT clay, as seen in Fig. 3A and B, showed three step weight losses on the thermal treatment in the range of 50–800 °C. The first step mass loss up to ~130 °C was attributed to the desorption of absorbed water on the clay, and the second step weight loss at



Fig. 4. XRD patterns of MMT and organic MMT clays.



Clay	d- spacing (Å)	Zeta potential (mV)	Length of surfactant (Å)	Width of surfactant (Å)
MMT	12.8	-39.0	NA	NA
MMTQAS-12	14.6	-22.6	15.9	3.65
MMTQAS-14	17.4	-8.4	19.03	3.65
MMTQAS-16	18.9	+0.1	21.12	3.65
MMTQAS-B14	23.1	+14.4	23.11	3.65/8.29
MMTQAS-B16	23.6	+22.7	25.67	3.65/8.29

 $\sim$ 160 °C was because of dehydration of the interlayer hydrated water. The third step mass loss at high temperature ( $\sim$ 360 to 550 °C) was due to the dehydroxylation of the clay.

The TGA–DTG curves of the organo MMT clays (see Fig. 3A and B) involving four steps of weight loss indicated that the first step mass loss to be desorption of water from organoclays took place at a slightly lower temperature (up to ~90 °C) than MMT clay. The second step weight loss in the temperature range of 180–350 °C was attributed to thermal decomposition of loaded surfactants in the clays <sup>2,15</sup>. It is evident from the thermal analysis that all the surfactants decomposed almost in the same temperature range, indicating the similar thermal stabilities of all the organo MMT clays. The third and fourth step mass losses in the ranges of 360–520 °C and of 530–730 °C in the organoclays were due to the dehydroxylation of hydroxyl groups in different structures [15].

The XRD analysis was used to determine the variation in the interlayer spacing (d-spacing) between clay sheets. The XRD pattern of MMT clay showed the characteristic profile of MMT (PCPDF No. 03-0015 from database PDF-2, supplied with Bruker Advance D8). As it can be seen in Fig. 4, the chain length of QAS affects the value of a Bragg peak and thus the interlayer spacing d in all organoclays. It is expected that inorganic ions inside the interlayer space are replaced by guaternary ammonium cations, and the aliphatic chain attached to the guaternary ammonium ion is penetrated therein. In fact, the presence of aliphatic chains in the interlayer spacing contributed to the increase in *d* value (Table 2). Moreover, the organo MMT clays having benzyl substituent group showed the wider interlayer spacing. That is, the spacing distances of MMTQAS-B16 and MMTQAS-B14 were higher than those of MMTQAS-16 and MMTQAS-14. Moreover, distinctive sharpness in XRD pattern was observed for MMTQAS-B16 and



**Fig. 5.** A diagram of an apparatus for measuring liquid (water or oil) penetration into the clay.



Fig. 6. Wettability of MMT and organo MMT clays. (A) Water; (B) Oil (*n*-octane) penetration.



**Fig. 7.** Contact angel pictures of MMT and organo MMT clays and purified clay. (A) MMTQAS-B16; (B) MMTQAS-B14; (C) MMTQAS-16; (D) MMTQAS-14; and (E) MMTQAS-12.

MMTQAS-B14. This could be attributed to the increased crystallinity of these organic clays.

#### 3.2. Wettability and hydrophobicity of MMT and organoclays

When the swelling of MMT and organo MMT clay was examined by immersing clay in water, MMTQAS-B16 and MMTQAS-B14 did not immerse in water and floated on water surface. However, MMTQAS-12, MMTQAS-14 and MMTQAS-16 swelled up at some level but lesser than MMT clay, which swelled three times of its original size. These findings forced us to investigate additionally wettability and hydrophobic nature of organo MMT clays.

Wettability of a liquid on any surface, that is, water/oil adsorption measurement depends on mutual interactions between the particles. The basis of the division between hydrophobicity and hydrophilicity is a competition between the interfacial free energy of cohesion of the solid and the free energy of cohesion of the liquid (water or oil), in which the solid is immersed [23]. Fig. 5 shows the schematic representation of the wettability measurement. When the sample holder touches the surface of the liquid (water and *n*-octane) kept in a petri dish, the change in the weight due to the liquid absorption is measured by the detector. In this experiment, a set of polar and non-polar liquids such as water and *n*-octane was used. In a typical penetration experiment, exactly the opposite trend of liquid penetration was observed with



Fig. 9. A plot of zeta potential of clays.

respect to water and *n*-octane. To our knowledge, this is the first report on quantification of the wettability by means of the liquid penetration test.

As seen in Fig. 6A and B, liquid adsorption, namely, liquid penetration sharply increased initially and approached to saturation. In Fig. 6A, MMTQAS-B16 showed the least saturated water penetration, followed by MMTQAS-B14, compared to the other organic clays. However, their saturated penetration of *n*-octane was higher than the other clays. This implies that the presence of the benzyl substituent in a surfactant plays a decisive role in determining the wettability or the hydrophobicity of the clays. With the variation from MMTQAS-16 to MMTQAS-12, the water penetration increases (Fig. 6A). In an alternative wettability experiment with non-polar liquid (n-octane), as shown in Fig. 6B, exactly the reverse trend of liquid penetration was found. However, as shown in Table 2, the interlayer spacing is reduced with this variation. This proves that the water penetration or the water wettability of the clays is not dependent on the interlayer spacing of the clay but *n*-octane penetration depends on it. These indicate that the surface of the clay plays a crucial role on the liquid wettability.

Similar results were also obtained from the water contact angle measurement (Fig. 7). MMTQAS-B16 and MMTQAS-B14 showed contact angles of 118° and 98°, respectively, while the contact angle of MMT was 76°. Moreover, the contact angle further decreased in an order of MMTQAS-16, MMTQAS-14, and MMTQAS-12 (72°,



Fig. 8. Plots of water adsorption (-■-), *n*-octane adsorption (-●-) and water contact angle (-■-) clays.



Fig. 10. SEM images with EDAX data of (A) MMTQAS-B16 and (B) MMTQAS-16. Green and red dots represent the presence of "carbon" and "nitrogen" elements, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Schematic illustration of the arrangement of surfactant in interlayer and on surface of clay.

 $69^{\circ}$ , and  $62^{\circ}$ , respectively). Apart from an obvious effect of chain length on contact angles, a drastic increase in contact angles is decisive for organo MMT clays with benzyl substituent, as seen in Fig. 8. These results are in agreement with the results obtained from wettability of the clays. That is, *n*-octane penetration increased in the same order of clays as water contact angle but water penetration decreased simultaneously (Fig. 8). Thus, results from the liquid adsorption and contact angle are in agreement with and confirm the superhydrophobic nature of MMTQAS-B16.

# 3.3. Arrangement of QASs on clays

The effect of surface modification by QASs on wettability of clay is evident from the results described above. However, in order to prove the structural modification on surface of clay by the adsorption of QAS, additional analytical techniques were employed: Zeta potential measurement and scanning electron micrographical observation were carried out on clays to determine the surface charges and surface morphologies of the clay particles.

The zeta potential value of MMT clay was found to be -39.0 mV (Fig. 9), indicating that its surface is negatively charged. The surface modification of clay particles with QAS-n increased the zeta potential of the particles in positive direction and the zeta potential of the clay particles increased with increasing the alkyl chain length of QAS-n, as seen in Fig. 9 and in Table 2. However, the zeta potential of MMTQAS-B14 and MMTQAS-B16 (+14.4 and +22.7 mV, respectively) was higher than the zeta potential of the MMTQAS-n clay particles, that is, the surface of MMTQAS-Bn was more positively charged than that of MMTQAS-n with the equivalent alkyl chain length.

SEM images of two clays, MMTQAS-B16 and MMTQAS-16, are given in Fig. 10A and B, respectively, along with the mapping of

elements, carbon and nitrogen, measured by EDAX. EDAX analysis proved the adsorption of QAS on MMT outer surface in consistency with the variation of zeta potential. Additionally, on the distribution of two elements on the surface of MMTQAS-B16, carbon seemed to exist more plenty than nitrogen, suggesting the much content of carbon on its surface, although MMTQAS-16 showed apparently the less unbalance of the contents of carbon and nitrogen on its surface. This result is originated from the difference of the number ratio of elements in QAS, that is, carbon/nitrogen = 25: 1 and 19: 1 for MMTQAS-B16 and MMTQAS-16, respectively.

Observed *d*-spacings and zeta potentials of clays, and dimensions of surfactants are listed in Table 2. Based on these parameters, the arrangement of surfactants on and in clay platelets was estimated and schematically illustrated in Scheme 1. In case of surfactants having benzyl substituent, the adsorption of these surfactants is governed by steric hindrance and stacking interaction of aromatic rings. The larger width of head group (8.29 Å) in this kind of surfactants is larger than the width of alkyl chain (3.65 Å). Then, this type of surfactants creates an array consisting of  $\pi$ - $\pi$  stacking in the clay, which resists the penetration of water molecules into adsorbed surfactant monolayer. However, non-polar organic liquids are suitable to this surfactant array because of the affinity of long hydrocarbon chains and aromatic rings toward such liquids like *n*-octane.

The total concentration of surfactants being loaded onto clay is almost same for all surfactant molecules, as found from elemental analysis. Then, surfactants which possess hydrophobic aromatic group in hydrophilic head might exist less in the interlayer spacing but significant amount could be present on clay surface. In such case, more positive charges are loaded outside of the clay, as observed in zeta potential measurement. Meanwhile, in case of linear surfactant molecules, since they have a small width without steric hindrance of head group, a large amount of surfactants are exchangeable in clay layers but a small amount of molecules stay on the surface. Thus, such clays show their zeta potential values slightly less negative than that of MMT clay.

#### 4. Conclusions

This work throws light on the choice of quaternary ammonium salts with substituents as a surface modifier. To our knowledge, this is the first report which uses wettability measurements to quantify the hydrophobicity/hydrophilicity character of organoclay materials. All organoclays show ~70 mmol/g. loading of surfactants, and clays modified with aliphatic ammonium salts having one of the substituents as benzyl group showed less water wettability than clays modified with simple quaternary ammonium salts and a clay without modification. Thus, it can be concluded that the adsorption of a cationic surfactant to the clay does not necessarily guarantee the greater hydrophobicity, but the presence of benzyl substituent group is an important prerequisite for providing hydrophobicity to the clay surface. The finding of wettability was supported by contact angle measurements, where the order of

water contact angle was MMTQAS-B16 > MMTQAS-B14 > MMT > MMTQAS-16 > MMTQAS-14 > MMTQAS-12, same as *n*-octane wettability but contrary to water contact angle. FT-IR of the samples gives us a verification of a modification with organic cations. Thermal analysis shows the degradation profiles of organic surfactants intercalated in clay layers in a range of 300-350 °C, while the loss of structural hydroxyl was prolonged from 360 to 730 °C in all organoclays. Despite of structural similarities, the quaternary ammonium cations having benzyl substituent group behave differently, in terms of surface properties, from the quaternary ammonium cations without the benzyl group. It can be finally noted that to control hydrophobicity of the clay surfaces, the role of substituent on quaternary ammonium cations is more important than that of the chain length of alkyl group.

#### Acknowledgments

We thank Dr. Chintan Jani, Director, Jani Clays, for the valuable discussions on Indian bentonites. Kinjal Shah would like to thank Jani Clays for sponsoring this research and his scholarship. The authors also thank Mr. Manish Thakker for providing us a water penetration measurement instrument. We also thank Dr. Sanjeev Kumar for discussions and suggestions for the XRD experiment. Authors want to extend sincere thanks to Dr. Sunil Shah for his help in getting the chemicals and especially quaternary ammonium salts.

#### References

- [1] A. Okada, A. Usuki, Macromol. Mater. Eng. 291 (2006) 1449-1476.
- [2] H.A. Patel, R.S. Somani, H.C. Bajaj, R.V. Jasra, Ind. Acad. Sci. 29 (2006) 133-145.
- [3] G. Srinath, R. Gnanamoorthy, J. Mater. Sci. 40 (2005) 2897-2901.
- [4] Z.A. Kushmono Mohdlshak, W.S. Chow, T. Takeichi, Polym. Compos. (2009) 1– 12.
- [5] P.K. Maji, P.K. Guchhait, A.K. Bhowmick, J. Mater. Sci. 44 (2009) 5861–5871.
- [6] C.B. Dornelas, A.M. Da silva, C.B. Dants, C.R. Rodrigues, S.S. Continho, P.C. Sathler, H.C. Castro, L.R. Souse Dias, V.P. De souse, L.M. Cabral, J. Pharm. Pharmaceutsci. 14 (2011) 17–35.
- [7] H.A. Patel, S. Shah, D.O. Shah, P.A. Joshi, Appl. Clay Sci. 51 (2011) 126–130.
- [8] R. Suresh, S.N. Borkar, V.A. Sawant, V.S. Shende, S.K. Dimple, Int. J. Pharm. Sci. Nanotechnol. 3 (2010) 901–905.
- [9] A.S. Costa, T. Imae, Langmuir 20 (2004) 8865-8869.
- [10] A.S. Costa, T. Imae, K. Takagi, K. Kikuta, Prog. Colloid Polym. Sci. 128 (2004) 113–119.
- [11] S. Manocha, N. Patel, L. Manocha, Defence Sci. J. 58 (2008) 517–524.
- [12] W. Kim, D. Chang, J.K. Kim, J. Appl. Polym. Sci. 110 (2008) 3209-3216.
- [13] H. Jin, J.J. Wie, S.C. Kim, J. Appl. Polym. Sci. 117 (2010) 2090-2100.
- [14] G.I. Nakas, C. Kaynak, Polym. Compos. (2009) 257-263.
- [15] J.C. Dai, J.T. Huang, Appl. Clay Sci. 15 (1999) 51-65.
- [16] A. Baltusnikas, I. Lukosiute, K. Baltakys, Mater. Sci. 15 (2009) 325-328.
- [17] C. Bertagnolli, A.L. Pereira de Araujo, S. Kleinubing, M.G. Carlos da Silva, Chem. Eng. Trans. 24 (2011) 1537–1542.
- [18] P.T. Hang, G.W. Brindley, Clays Clay Miner. 18 (1970) 203-212.
- [19] D. Onoshima, T. Imae, Soft Matter 2 (2006) 141-148.
- [20] K.C. Cole, Macromolecules 41 (2008) 834-843.
- [21] D.A. Myrzakozha, T. Hasegawa, J. Nishijo, T. Imae, Y. Ozaki, Langmuir 15 (1999) 3601-3607.
- [22] D.A. Myrzakozha, T. Hasegawa, J. Nishijo, T. Imae, Y. Ozaki, Langmuir 15 (1999) 6890-6896.
- [23] C.J. Van Oss, R.F. Giese, Clays Clay Miner. 43 (4) (1995) 474-477.