Clays and Clay Minerals, Vol. 57, No. 4, 502–509, 2009.

ADSORPTION OF A $C_{10}E_3$ NON-IONIC SURFACTANT ON A Ca-SMECTITE

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Abstract—The transformation of clay minerals into organo-clays by surfactant intercalation is of great environmental and industrial importance because it causes the clay to attract hydrophobic contaminants and other non-polar organic compounds, but a better understanding is needed of the mechanisms by which different classes of surfactants are intercalated. The purpose of this study was to synthesize and characterize an organo-clay comprising triethylene glycol monodecyl ether ($C_{10}E_3$) non-ionic surfactant, which has a lamellar phase at room temperature, intercalated into Ca-montmorillonite from Wyoming (SWy-2). The $C_{10}E_3$ non-ionic surfactant differed from previous non-ionic surfactants used in the formation of a lamellar phase in that it consisted of the stacking of molecules by hydrophobic interaction. $C_{10}E_3$-clay composites were characterized by complementary techniques (adsorption isotherms, X-ray diffraction, and infrared spectroscopy) and were compared to benzyldimethyltetradecyl ammonium chloride (BDTAC) cationic surfactant-clay composites for different loadings of the surfactant. For large loadings, the amount of $C_{10}E_3$ adsorbed, which can be described by the Langmuir equation, seemed to reach a steady state close to that of the cationic surfactant. The adsorption processes of the two surfactants were different. For the cationic surfactant, the adsorption, as described in the literature, was due to ion exchange between organic cations and Ca^{2+} counterions. The adsorption of $C_{10}E_3$ did not depend on electrostatic interaction but rather was due to several interaction mechanisms (H-bonding, ion-dipole, and hydrophobic interaction). For both surfactants, the expansion was limited to two adsorbed monolayers parallel to the clay surface. The expansion of the basal spacing to 17 Å suggested a complete dissociation of the $C_{10}E_3$ lamellar phase when adsorbed on the Ca-smectite. Organo-clays made using the non-ionic surfactant were stable, changing the chemical nature of clay to hydrophobic, and allowing for other cations to be exchanged, which has importance in the manufacture of new nanocomposites or geochemical barriers.

Key Words—Ca-smectite, Infrared Spectroscopy, Organo-clay, Surfactant, X-ray Diffraction.

INTRODUCTION

Smectite clay minerals such as Wyoming montmorillonite exhibit, in the presence of water, cation exchange capacities (CEC), swelling and hydration properties, and a large surface area which lead to strong adsorption properties (Dentel *et al.*, 1995; Breen *et al.*; 1997; He *et al.*, 2001) which have been highlighted in several applications such as catalysis, nanocomposite materials, and geochemical barriers (as in the case of waste landfills) (LeBaron *et al.*, 1999; Prost and Yaron, 2001; Kim *et al.*; 2003). The structure of dioctahedral smectite is characterized by two SiO_4 tetrahedral sheets sandwiching an Al or a Mg octahedral sheet and it displays a hydrophilic surface which is inconsistent with the adsorption of organic compounds (Prost and Yaron, 2001; Kim *et al.*; 2003). The inability to adsorb organic compounds can lead to environmental problems as the majority of contaminants are non-ionic organic compounds (NOCs) which emanate from products such as household detergents and cosmetics (Portet *et al.*, 1998). One solution is to use ion exchange between the interlayer inorganic and organic cations to create organo-clays. Numerous studies have been devoted to the synthesis of organo-clays (Mortland *et al.*, 1986; Boyd *et al.*, 1988; Jaynes and Boyd, 1991; Tahani et al, 1999; Lee *et al.*, 2005; Xi *et al.*, 2005). Major features of the organo-clays provided by the intercalation of cationic surfactants, such as quaternary ammonium compounds into the interlayer space, are the adsorption of organic cations through ion exchange. The consequences for the hybrid clay are the changes in the interlayer height and the clay surface which then switches from organophobic to organophilic. Depending on the nature of the inorganic cation and the amount of cationic surfactant loaded, the basal spacing increases considerably, allowing the confinement of surfactant molecules to self-organize in one-layer, two-layer, paraffin, or micellar structures (Othmani-Assmann *et al.*, 2007). The interlayer thus becomes organophilic, which changes the properties of the hybrid material, enhancing the capacity of the resulting organo-clays to remove NOCs. The insertion of the surfactant is, however, irreversible and prevents any further cationic exchange with other cationic contaminants such as heavy metals.

Synthesis of organo-clays by intercalation of non-ionic surfactants has been suggested (Deng *et al.*, 2003, 2006). The mode of grafting non-ionic surfactants onto

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DOI: 10.1346/CCMN.2009.0570411

the clay surface depends on various interactions such as hydrogen-bond and ion-dipole interactions. The availability of these organo-clays to remove both NOCs and heavy metals has been demonstrated (Deng *et al.*, 2003, 2006). All of the aforementioned applications depend on the structure and properties of the organo-clays and knowledge of these properties is essential for industrial application. Numerous studies have been carried out on the adsorption of various cationic surfactants onto clays (Lee *et al.*, 2005; Othmani-Assmann *et al.*, 2007). In contrast, few studies have explored the adsorption of non-ionic surfactants on smectite (Hackett *et al.*, 2000; Deng *et al.*, 2003, 2006). In particular, no study has focused on understanding the surfactant phase in terms of adsorption onto smectite. Non-ionic surfactants such as polyethylene oxide (PEO), Brij 56, or Igepal CO 720, used in previous studies (Deng *et al.*, 2003, 2006), display common micellar phases above the critical micellar concentration (CMC) and adsorption of non-ionic surfactants is similar in behavior (Deng *et al.*, 2003, 2006). Triethylene glycol monodecyl ether ($C_{10}E_3$) is a non-ionic surfactant which, at room temperature and in the presence of water, comprises several membrane phases such as lamellar and sponge phases (Le *et al.*, 2001). The lamellar phase is characterized by a stack of surfactant molecules aggregated into a two-dimensional structure (membrane) and layers of water which display a structure at long-range order (Le *et al.*, 2001). The lamellar phase is largely stabilized by steric interactions due to the loss of entropy when molecules are stacked together by hydrophobic interaction.

The purpose of the present study was to partly overcome the paucity of information available regarding the intercalation behavior of non-ionic organic compounds in expandable clay minerals by investigating the adsorption of the $C_{10}E_3$ lamellar phase onto a Ca-montmorillonite, by characterizing the structural changes in $C_{10}E_3$-clay composites with different non-ionic surfactant loadings, and by comparing the results obtained with the adsorption of a commonly used cationic surfactant. Adsorption isotherms were used to evaluate the non-ionic surfactant loading. The degree of intercalation for different $C_{10}E_3$ loadings and the changes in the surface structure of the Ca-montmorillonite were investigated by Fourier-transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD). New insights into the structures and properties of organo-clays synthesized by the intercalation of non-ionic surfactants were gained.

MATERIALS AND METHODS

Materials

The smectite used in this study was the SWy-2-montmorillonite (Wyoming) obtained from the Source Clays Repository of The Clay Minerals Society (hosted by Purdue University, West Lafayette, Indiana). This smectite was Ca-exchanged by washing five times with a 1 M $CaCl_2$ solution. The resulting clay was washed with distilled water and centrifuged at 5000 rpm for 10 min (ROUCAIRE, Hermes Z383). The process was repeated five times. The clay obtained was dried at 100ºC for 2 days in order to remove adsorbed water and Ca^{2+} was assumed to be the only counter ion between the layers. The resulting clay was dialyzed against distilled water in order to remove excess Ca^{2+}. The cation exchange capacity (CEC) of the resulting clay, determined by the adsorption of a Cu triethylenetetramine complex (so-called Cu-trien) (Meier and Kahr, 1999), was ~82 meq/100 g.

One ionic and one non-ionic surfactant were used, namely, the benzyldimethyltetradecyl ammonium chloride cation (BDTAC) and triethylene glycol monodecyl ether ($C_{10}E_3$), which were purchased from Sigma-Aldrich Chemical Company and used without further purification (Table 1). Their length and height were determined from crystallographic data in relation to the C–C, C–O, and C–N bonds as well as the C–C–C, C–O–C, and C–N–C angles (Rodier *et al.*, 1995). Above the CMC, the $C_{10}E_3$ shows, at room temperature and in the presence of water, a lamellar phase, the basal spacing of which depends on its concentration and a constant bilayer thickness of 27.6 Å (Le *et al.*, 2001). Explicit $C_{10}E_3$ concentration-temperature phase diagrams have been published elsewhere (Le *et al.*, 2001).

Synthesis of organo-clays

Aqueous solutions of BDTAC and $C_{10}E_3$ were prepared in demineralized water at room temperature at concentrations >CMC. The concentrations of the solutions used in the determination of the adsorption as well as in the physicochemical characterizations of organo-clays were calculated according to the CEC values of the clays which varied from 6.5×10^{-4} to 1.31×10^{-2} mol L^{-1} (*i.e.* 0.2 to 4 × CEC for the cationic surfactant). The average pH value of the solutions was ~6.5±0.2 and remained constant during the synthesis. Clay powder was dispersed into the surfactant solutions. The suspensions obtained were stirred for 24 h at 250 rpm. The mixtures were then centrifuged at 5000 rpm for 20 min. The organo-clays obtained were dried at 70ºC for 48 h and crushed using an agate mortar.

The CEC of both organo-clays was determined using the Cu-trien method (Meier and Kahr, 1999).

Table 1. Characteristics of the BDTAC cationic and the $C_{10}E_3$ non-ionic surfactants.

Commercial name	Molecular weight	CMC (mol L^{-1})	Length of surfactant (Å)	Height of surfactant (Å)
BDTAC	368	$2 \times 10{-}3$	23	5.5
$C_{10}E_3$	290	$6 \times 10{-}4$	23	5

Adsorption isotherms

Batch equilibration isotherms were determined using 20 mg of each of the organo-clay samples. The concentrations of N and C were measured using an element analyzer and were carried out at the Service Central d'Analyse du CNRS (Solaire, France). The amount of surfactants adsorbed was determined by the difference between the surfactant added and that remaining in the solution.

Infrared spectroscopy

Infrared spectra were collected using a NICOLET Magna IR 760 Fourier-transform infrared spectrometer with a resolution of 2 cm^{-1}. Spectra were collected over the range 400–4000 cm^{-1}. Samples consisted of pellets of anhydrous KBr mixed with 0.33% clay powder.

X-ray diffraction

The d_{001} basal spacings of the Ca-smectite and the surfactant-smectite composites were measured using an ARL X'TRA Diffractometer (Thermo Electron Corporation, Ecublens, Switzerland) operating at 40 kV and 40 mA with CuKα radiation (λ 1.54 Å). Measurements were carried out at room temperature in the step-scanning mode with a step size of 0.05°2θ. Samples were dried at 70°C, crushed using an agate mortar and pestle, and then placed directly into the sample holder.

RESULTS AND DISCUSSION

Adsorption and surface properties of the organo-clays

The BDTAC adsorption isotherm exhibited features usually encountered for cationic surfactants on clay minerals and presented two main regions of interest (Figure 1). The first region corresponded to a linear variation of the amount adsorbed as a function of its equilibrium concentration and can be explained as an exchange between the organic and the Ca-exchangeable cations (Trompette *et al.*, 1994; Xu and Boyd, 1995). The analysis performed on the resulting solution showed a Ca molar quantity of 1.6×10^{-5} mol L^{-1} which confirmed the removal of the Ca^{2+} from the interlayer spaces. The second region showed a steady state where the amount adsorbed is ~9.0×10^{-4} mol g^{-1}. The adsorption isotherm of the BDTAC on the Ca-smectite was well described by a Langmuir equation (1):

$$\theta = \alpha\theta_f C/(1 + \alpha C) \quad (1)$$

where θ is the amount adsorbed, θ_f is the maximum adsorption, α is a constant, and C is the equilibrium concentration of the surfactant. The maximum adsorption isotherm obtained, θ_f, was 8.8×10^{-4} mol g^{-1} and highlighted the good affinity of the cationic surfactant for the clay.

The $C_{10}E_3$ adsorption isotherm behaved differently and showed a gradual increase in the amount adsorbed with the equilibrium solution concentration. No Ca^{2+} was found in the resulting solution which suggested that no cation exchange occurred. Indeed, for small concentrations, the amount of $C_{10}E_3$ adsorbed did not present any linear variation with the concentration. However, for large concentrations, the adsorption of $C_{10}E_3$ seemed to reach a steady state and the final amount of $C_{10}E_3$ adsorbed was close to that of the cationic surfactant. Fitting of the isotherm with the Langmuir equation yielded a maximum adsorption, θ_f, of

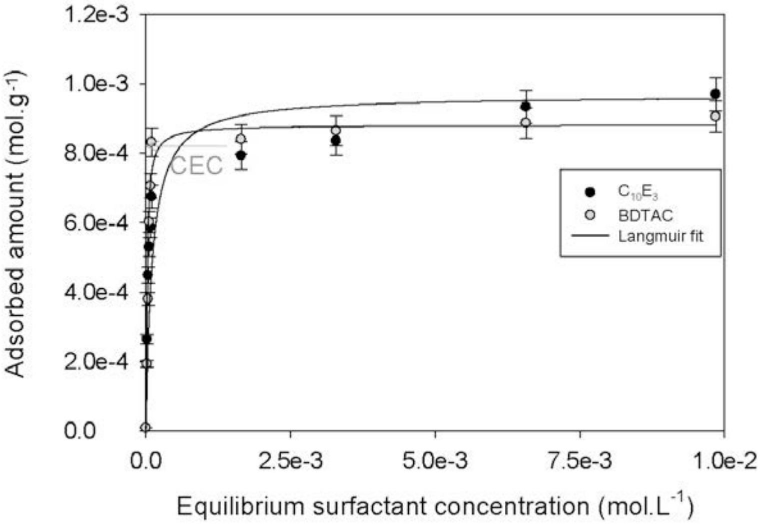

Figure 1. Adsorption of BDTAC (gray circles) and $C_{10}E_3$ (black circles) on SWy2-Ca montmorillonite *vs.* their initial concentration in solution. Langmuir fits were performed for both surfactants and are indicated by the black lines.

9.67×10^{-4} mol g^{-1}. Previous studies of the adsorption of NOC surfactants in the micellar phase onto smectite reported much less affinity for smectite (Deng *et al.*, 2003). Further work is, therefore, required on other cation-exchanged montmorillonites, especially Na-smectite. Another interesting point was the difference in the maximum adsorption isotherms between the two surfactants. The Ca-smectite showed a greater affinity for $C_{10}E_3$ than for BDTAC. The adsorption of $C_{10}E_3$ could result from several interaction processes with the surface and between the confined molecules, including the hydrophobic interactions. This interaction process involving hydrophobic molecules stacks the molecules together in a lamellar phase in solution. When molecules were adsorbed, other molecules were stacked together by hydrophobic interaction and covered the clay surface, increasing, as a result, the amount of surfactant adsorbed on clay, and explaining the greater maximum adsorption isotherm than achieved in other studies on non-ionic surfactants and BDTAC.

The CEC for the Ca-smectite was ~82 meq/100 g (Table 2). Determination of the CEC for both samples used in this study allowed identification of the anchoring bonding mode between the surfactant and the clay surface. The BDTAC-clay did not exchange any $BDTA^+$ cations with the Cu-trien complex, underlining the irreversibility of the ion exchange and the affinity of $BDTA^+$ for smectite. The $BDTA^+$ was ion-exchanged with Ca^{2+} and stabilized the negative charge surface of the clay by electrostatic interaction. The CEC results suggested that $BDTA^+$ was adsorbed irreversibly and once the surface charge was neutralized, no other cations could be exchanged but only adsorbed by other interaction processes (*e.g.* van der Waals, hydrophobic interaction, *etc.*) and may explain the amount of BDTAC adsorbed on Ca-smectite.

In the case of the $C_{10}E_3$, Ca^{2+} cations in the interlayer were exchanged with the Cu-trien complex and the $C_{10}E_3$-smectite composite preserved almost all of its initial CEC (Table 2). Ca^{2+} was removed from the interlayer space by the exchange reaction. The difference in CEC values of the two organo-clays can, therefore, be explained by their different adsorption mechanisms. Ion exchange did not occur between $C_{10}E_3$ and the exchanged Ca^{2+} in the smectite so this non-ionic surfactant must have been absorbed by another mechanism (Deng *et al.*, 2003, 2006). In previous models, the non-ionic surfactant formed H-bonds with water in the hydration shells of exchangeable cations, or bound directly to the inorganic cations through ion–dipole interactions. Another possible scenario is that direct H-bonding of the surfactant to the surface occurred. Further analysis, such as by nuclear magnetic resonance (NMR), needs to be performed in order to clarify this particular point.

Table 2. CEC values of Ca-smectite and the two organo-clays.

Sample	CEC (meq/100 g)	Percentage relative to Ca-smectite
Ca-smectite	82	100
BDTAC-clay	5	6
$C_{10}E_3$-clay	76	92

FTIR study

The FTIR spectra of Ca-smectite and of both organo-clays at the greatest concentration of 1.31×10^{-2} mol L^{-1}, unwashed, washed once, and washed twice (with distilled water, for 12 h) were normalized with respect to the band at ~3620 cm^{-1} (Figures 2, 3). This band, arising from the OH group of the smectite, is expected to be unaltered (according to Deng *et al.*, 2003) by the surfactant adsorption and can, therefore, be used as a reference band.

The spectra for both the Ca-smectite and organo-clays showed a broad band in the range 3000–3600 cm^{-1} which corresponds to the OH-stretching of adsorbed H_2O and OH groups of the $C_{10}E_3$. The presence of this broad band relative to the OH-stretching emphasized that for organo-clay samples, even after heat treatment at 70ºC for 48 h, water molecules remained adsorbed, indicating that the adsorption mechanism of both surfactants must involve H-bonding, ion-dipole, and hydrophobic interaction. The adsorption bands at ~2850 and 2920 cm^{-1} are related to the symmetric and antisymmetric CH_2 stretching modes. The intensities of these stretching adsorption bands are related to the density of the alkyl chains within the interlayer space (Peker *et al.*, 1995). In order to estimate the strength of the surfactant–clay interaction, the organo-clays were washed once and then a second time. The integrated intensity of the CH_2 stretching mode, linked to the density of the confined surfactants (Peker *et al.*, 1995), remained constant, demonstrating the strong interactions and affinity for Ca-smectite, even for different adsorption mechanisms for the two surfactants. Some small differences did occur, however. For BDTAC, after one or two washings the integrated intensity of the CH_2 stretching mode remained the same, confirming the irreversibility of the ion exchange between Ca^{2+} and the organic cations and the strong electrostatic interaction with the surface (Tahani *et al.*, 1999; Othmani-Assmann *et al.*, 2007). In the case of $C_{10}E_3$, the CH_2 integrated intensity decreased with washing (~5% each time), without calling into question the strong interaction between the non-ionic surfactant and the clay surface. The adsorption isotherms showed the good affinity of the $C_{10}E_3$ for Ca-smectite leading to a maximum adsorption isotherm which was greater than for BDTAC. This difference was explained by the hydrophobic interaction which confined more molecules, though this interaction is rather weak when exposed to a washing procedure.

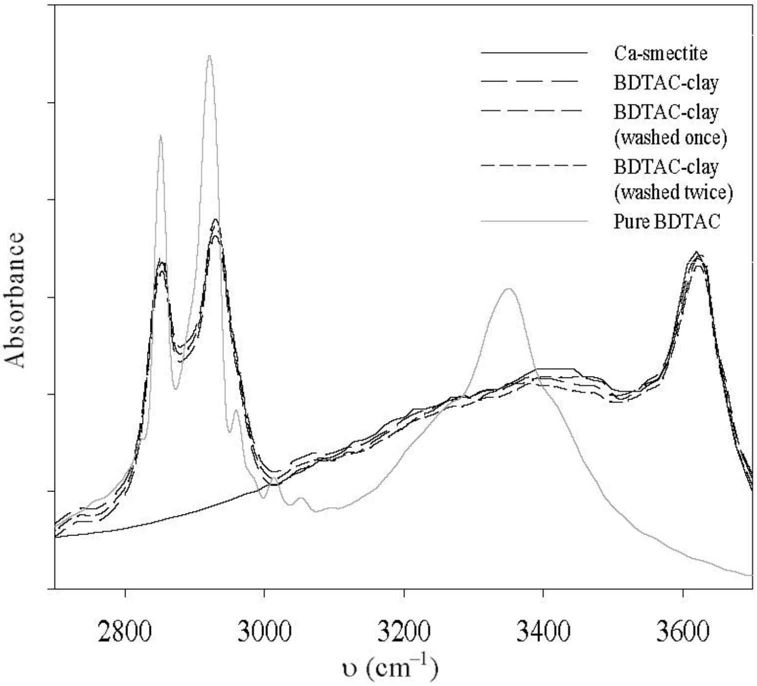

Figure 2. FTIR spectra of pure BDTAC, BDTAC-clay, BDTAC-clay (washed once), and BDTAC-clay (washed twice) at the concentration of 1.31×10^{-2} mol L^{-1} (*i.e.* 4 × CEC) and Ca-smectite, over the wavenumber range 2700–3700 cm^{-1}.

The washing treatments should remove $C_{10}E_3$ molecules adsorbed by hydrophobic interaction.

Limited expansion of the basal spacing at two adsorbed surfactant layers

The XRD patterns revealed that the d_{001} reflections of the BDTAC-clay were well defined compared to that of the Ca-smectite (Figure 4). The evolution of the basal spacing depends on the initial amount of surfactant and conformed with results from previous studies (Peker *et al.*, 1995; Tahani *et al.*, 1999; Othmani-Assmann, 2007). For small concentrations, the basal spacing increased due to the adsorption of a BDTAC monolayer (insert in Figure 4). At a concentration of 1.96×10^{-3} mol L^{-1},

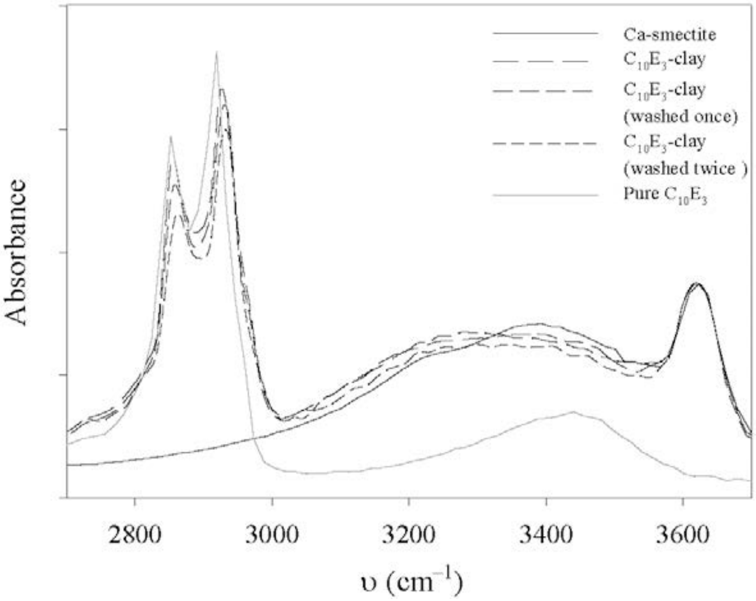

Figure 3. FTIR spectra of pure $C_{10}E_3$, $C_{10}E_3$-clay, $C_{10}E_3$-clay (washed once), $C_{10}E_3$-clay (washed twice) at the concentration of 1.31×10^{-2} mol L^{-1}, and Ca-smectite, over the wavenumber range 2700–3700 cm^{-1}.

XRD patterns exhibited two (001) reflections, corresponding to two interlayer distances of 14.2 and 16 Å, suggesting a regularly interstratified BDTAC-smectite. For large concentrations, the basal spacing reached ~18 Å, corresponding to the insertion of two $BDTA^+$ layers (Deng *et al.*, 2006).

Evolutions of $C_{10}E_3$ diffraction patterns and basal spacing were similar to those of the cationic surfactant (Figure 5 and insert). For small concentrations, the basal spacing grew from 11.7 to 14 Å, corresponding to the adsorption of a surfactant monolayer (Figure 5 insert). At 1.96×10^{-3} mol L^{-1}, two (001) reflections described the XRD patterns, corresponding to basal spacings of 14 and 16.5 Å, respectively, proving a regularly interstratified $C_{10}E_3$-smectite with one lateral and two adsorbed layers in the interlayer space. Thus, for large concentration, the *d* spacing increased to ~17.2 Å and then remained constant. The limited expansion of the interlayer space was interesting, considering the constant 27.6 Å bilayer thickness of the $C_{10}E_3$ lamellar phase. Preparation of the organo-clay disrupted the arrangement of the lamellar phase, leading to the adsorption of a monolayer parallel to the surface. The adsorption isotherm showed the affinity of the $C_{10}E_3$ for the clay mineral surface. Ca-smectite disturbed the lamellar phase completely, and attracted isolated molecules which are stabilized with the clay surface.

However, no ion exchange was achieved, proving that adsorption did not take place by a surface-binding mechanism. The adsorption should result from an aggregation process. When molecules were adsorbed, other molecules could be stacked on each other by hydrophobic interaction and cover the clay surface, thereby increasing the amount of surfactant adsorbed. However, bilayers cannot be formed for either surfactant. Previous studies of the adsorption of cationic surfactants on Na-montmotillonite showed an increase in the basal spacing, allowing the confined surfactant molecules to self-organize into one-layer, two-layer, paraffin, or micellar structures. The nature of the counterion in the interlayer space is of great importance for the swelling of the clay mineral. Synthesis of organo-clays was undertaken in clay suspension, where the Ca-smectite was very swollen, so the hydration process for Ca^{2+} in the smectite allowed the adsorption of two or three layers of water, leading to a maximum interlayer space of ~18 Å. The swelling of the clay then allowed the intercalation of surfactant into the structure either by ion exchange or by H-bonding with the clay surface. Experiments and numerical simulations demonstrated the large increase in the interlayer space for Li^+ and Na^+ compared to other interlayer cations, allowing the organization of cationic surfactants in paraffin or micelle structures (Othmani-Assmann *et al.*, 2007). Studies of the adsorption of non-ionic surfactant on Na-smectite showed the confinement of one or two organic layers parallel to the clay surface (Tahani *et al.*, 1999; Othmani-Assmann *et al.*, 2007). Investigation of the adsorption of the $C_{10}E_3$ lamellar phase on a Na-smectite would help to understand further the mechanisms of adsorption of non-ionic surfactant on clay.

CONCLUSIONS

The adsorption of a lamellar phase made from $C_{10}E_3$ non-ionic surfactant on a Ca-smectite was studied,

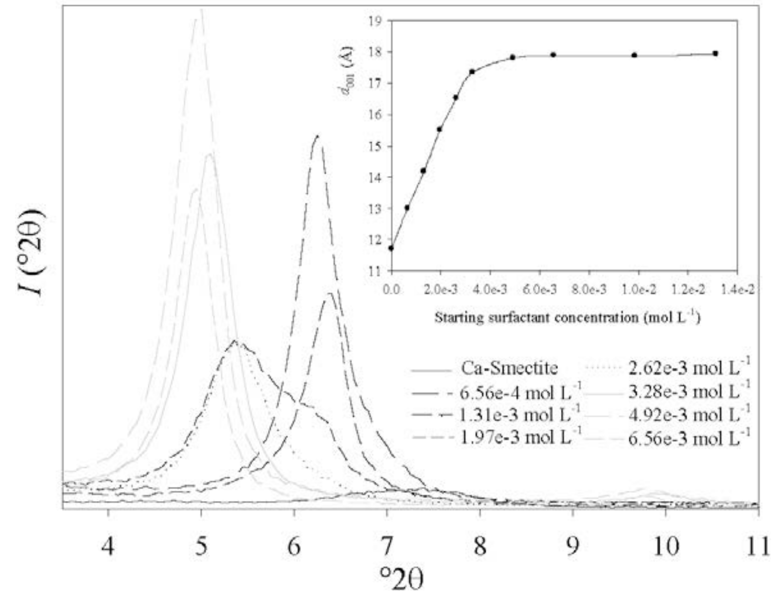

Figure 4. XRD patterns of BDTAC for several initial concentrations. The insert represents the change in basal spacing, d_{001}, for BDTAC as a function of the initial concentration (CuKα radiation).

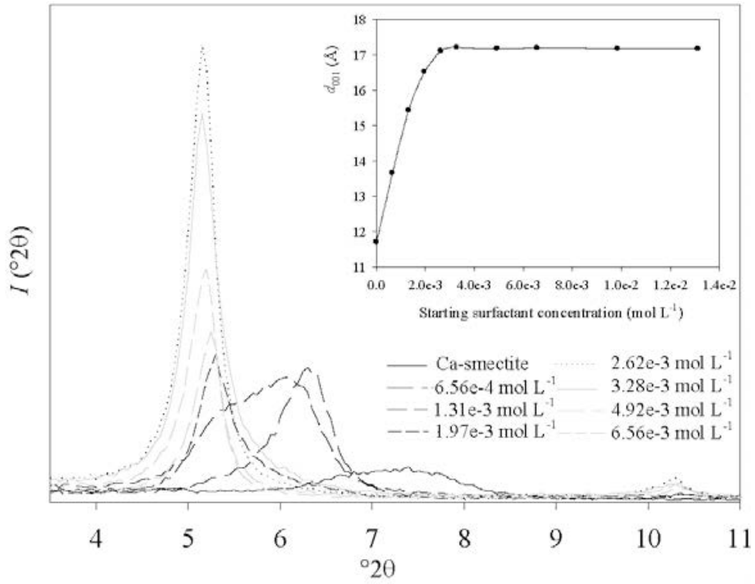

Figure 5. XRD patterns of $C_{10}E_3$ for several initial concentrations. The insert represents the change in basal spacing, d_{001}, for $C_{10}E_3$ as a function of the initial concentration (CuKα radiation).

resulting in the formation of organo-clays, which were characterized by several complementary techniques (adsorption isotherms, XRD, and IR spectroscopy) and compared with organo-clays synthesized using BDTAC cationic surfactant. The adsorption mechanisms differed for the two surfactants. The BDTAC was ion exchanged in stoichiometric proportions with the Ca^{2+} counter ions present in the interlayer space. For $C_{10}E_3$, the adsorption process did not result in ion exchange. The interaction between the adsorbed $C_{10}E_3$ and Ca-smectite depended on several possible mechanisms (ion-dipole, H-bonding, van der Waals forces, and hydrophobic interactions). The adsorption isotherm demonstrated good affinity of the $C_{10}E_3$ for the clay-mineral surface, and the narrow opening of the basal spacing led to the complete reorganization of the lamellar phase into isolated molecules which were adsorbed parallel to the surface. The hydrophobic interaction allowed $C_{10}E_3$ molecules to be retained, increased the amount of surfactant adsorbed in the clay, and explained the greater maximum adsorption isotherm than for the cationic version. The hydrophobic interaction was, however, rather weak as indicated by the relative ease with which molecules adsorbed by this mechanism were removed by washing treatments. This explains the 5% decrease in the integrated intensity of the CH_2 stretching bands in the infrared. For both surfactants, the expansion was limited to two adsorbed layers parallel to the surface and was mainly due to the nature of the counterion of the montmorillonite. Synthesis of the organo-clay was undertaken in clay suspension, where the Ca-smectite was very swollen. The hydration process for Ca^{2+} cations in smectite allowed the adsorption of two or three layers of water, leading to a maximum opening for the interlayer space of ~18 Å and which permitted the retention of two monolayers of either surfactant. The synthesis of organo-clays using $C_{10}E_3$ non-ionic surfactant to produce stable composites changed the chemical nature of clay to hydrophobic and allowed other cations to be exchanged, which could lead to the realization of new nanocomposites or geochemical barriers in waste landfills.

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(*Received 25 November 2008; revised 30 July 2009; Ms. 0238; A.E. D.C. Bain*)