Adsorption of a C10E3 non-ionic surfactant on a Ca-smectite

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To cite this version:


HAL Id: insu-00421309
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Submitted on 21 May 2012

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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 benzylidimethyltetradecyl 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 (Porter 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 organophilic to organophobic.

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
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; Orhmani-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 monododecyl ether (C10E3) 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 (Lee 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 (Lee 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 C10E3 lamellar phase onto a Ca-montmorillonite, by characterizing the structural changes in C10E3-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 C10E3 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 CaCl2 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 100°C for 2 days in order to remove absorbed water and Ca2+ was assumed to be the only counter ion between the layers. The resulting clay was diazylized against distilled water in order to remove excess Ca2+. 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 benzyltrimethylyldecyl ammonium chloride cation (BDTAC) and triethylene glycol monododecyl ether (C10E3), 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 C10E3 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 (Lee et al., 2001). Explicit C10E3 concentration-temperature phase diagrams have been published elsewhere (Lee et al., 2001).

Synthesis of organo-clays

Aqueous solutions of BDTAC and C10E3 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 x 10−4 to 1.31 x 10−3 mol L−1 (i.e. 0.2 to 4 x 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 70°C 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 C10E3 non-ionic surfactants.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Molecular weight (g/mol)</th>
<th>CMC (mol L−1)</th>
<th>Length of surfactant (Å)</th>
<th>Height of surfactant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDTAC</td>
<td>368</td>
<td>2 x 10−3</td>
<td>23</td>
<td>5.5</td>
</tr>
<tr>
<td>C10E3</td>
<td>290</td>
<td>6 x 10−4</td>
<td>23</td>
<td>5</td>
</tr>
</tbody>
</table>
**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 CuKa radiation (\(\lambda = 1.54\) Å). Measurements were carried out at room temperature in the step-scanning mode with a step size of 0.05\(^°\)2\(\theta\). 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 \(\times\) 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 \(\sim 9.0 \times 10^{-4}\) mol g\(^{-1}\). The adsorption isotherm of the BDTAC on the Ca-smectite was well described by a Langmuir equation (1):

\[
\theta = \frac{\theta_f}{1 + \alpha C} \tag{1}
\]

where \(\theta\) is the amount adsorbed, \(\theta_f\) is the maximum adsorption, \(\alpha\) is a constant, and \(C\) is the equilibrium concentration of the surfactant. The maximum adsorption isotherm obtained, \(\theta_f\), was 8.8 \(\times\) 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, \(\theta_f\), 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.](image-url)
of CEC values of the two organo-clays.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CEC (meq/100 g)</th>
<th>Percentage relative to Ca-smectite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-smectite</td>
<td>82</td>
<td>100</td>
</tr>
<tr>
<td>BDTAC-clay</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>C8E3-clay</td>
<td>76</td>
<td>92</td>
</tr>
</tbody>
</table>

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.

**FTIR study**

The FTIR spectra of Ca-smectite and of both organo-clays at the greatest concentration of $1.31 \times 10^{-2}$ mol L$^{-1}$, unwashed, washed once, and washed twice (with distilled water, for 12 h) were normalized with respect to the band at $\sim 3620$ 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$_2$O and OH groups of the C8E3. The presence of this broad band relative to the OH-stretching emphasized that for organo-clay samples, even after heat treatment at 70°C 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 $\sim 2850$ 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 C8E3, the CH$_2$ integrated intensity decreased with washing ($\sim 5\%$ 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 C8E3 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.
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 d001 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 \times 10^{-3} \text{ mol L}^{-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 C₁₀E₃ 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 x 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 C₁₀E₃-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 C₁₀E₃ 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 C₁₀E₃ 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-montmorillonite 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 Ca²⁺ 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 C₁₀E₃ 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 C₁₀E₃ non-ionic surfactant on a Ca-smectite was studied,
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.

REFERENCES


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