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# INTERCALATION AND SURFACE MODIFICATION OF SMECTITE BY TWO NON-IONIC SURFACTANTS

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**Abstract**—Non-ionic surfactants Brij 56 and Igepal CO 720, containing hydrophilic poly(ethylene oxide) (PEO) segments, expanded smectite from 1.5 nm to 1.7 nm at room temperature. The surfactant-smectite composites had larger layer spacings than Ca-smectite after heat treatment. The surfactant-smectite composites were solvated and expanded to 1.8–1.9 nm by polar solvents, glycerol and water, but were not affected by the non-polar or weakly polar solvents, toluene, hexane or octanol. The hydrophilic PEO segments of non-ionic surfactants would logically access the interlayer spaces of smectite whereas the hydrophobic segments extend away from the mineral. The molecular structure and solvation properties suggest that the surfactant molecules are probably concentrated in the margin area of the interlayer galleries forming an annular ring structure between two neighboring silicate sheets. Only two layers or less of the surfactants could access the interlayer galleries of smectite and layer spacings did not exceed 1.8 nm even where excess surfactant was introduced into the composites. The layer spacings of the surfactant-smectite composites were well preserved during water or electrolyte solution washings, indicating stability of most non-ionic surfactant molecules in the interlayer galleries even though ~30% of the adsorbed Igepal CO 720 was desorbed by exhaustive washing. The non-ionic surfactant treatment preserved >80% of the CEC of the smectite. The interlayer cations of the resulting surfactant-smectite were exchangeable as in the untreated smectite. Therefore, the non-ionic surfactant-smectite was much more efficient at removing heavy metal ions than activated carbon or cationic surfactant-treated smectite. The surfactant-smectite composites effectively removed aromatic chlorophenols from a pH 4.9 acetate buffer solution while untreated smectite did not adsorb these molecules. The enhanced adsorption of the aromatic compounds is attributed to the aliphatic segments of the two surfactants.

**Key Words**—Brij 56, Chlorophenol, Igepal CO 720, Intercalation, Non-ionic Surfactant, Organo-clay, Smectite, Surface Properties, Poly(ethylene oxide).

## INTRODUCTION

Synthesis and application of organo-clay composites have received considerable attention during the last two decades. Organo-clays are commonly synthesized by grafting cationic surfactants onto clay minerals. Most of the cationic surfactants are quaternary ammonium compounds with the forms $[(CH_3)_2NR_2]^+$ or $[(CH_3)_3NR]^+$, where $R$ is an alkyl or aromatic hydrocarbon group (Xu and Boyd, 1995b). The hydrophobic segments of the surfactants increase the hydrophobicity of the minerals, and the sorptive capacities of the minerals for non-ionic organic contaminants (NOCs) are greatly improved by grafting surfactants on the minerals. The high sorptive capabilities of organo-clays for NOCs suggest several environmental applications. Organo-clay can be used as earthen landfill liners to immobilize dissolved organic contaminants and to prevent hydraulic failure of the clay barrier when a high concentration of organic liquid is applied to the landfill site (Gullick *et al.*, 1996; Li *et al.*, 1996; Smith and Jaffe, 1994). Organo-clays can also be used as extenders for activated carbon in water treatment. They adsorb more oil and grease than activated carbon (Alther, 1998a,b). Organo-clays were used to adsorb airborne organic contaminants (Harper and Purnell, 1990).

There is a need for more versatile clay sorbents to retain both NOCs and toxic heavy metal cations. The grafting of the cationic surfactants on minerals occupies the cation exchange sites of the minerals. Grafted cationic surfactants cannot be easily replaced by inorganic cations (Xu and Boyd, 1994, 1995a,b). Therefore, grafting cationic surfactants onto clays reduces their ability to remove heavy metal cations.

To keep or enhance the clay's capacity for removing inorganic contaminants, especially heavy metal cations, Sheng *et al.* (1999) developed a dual function organo-clay sorbent. They grafted a carboxylic group-bearing surfactant, carboxydecyltriethyl-ammonium $[(HOOC)-C_{10}H_{20}N(C_2H_5)_3]^+$ cations (CDTEA), onto a montmorillonite clay, and tested the capacity of this organo-clay for removing both lead ($Pb^{2+}$) and chlorobenzene. The CDTEA increased the clay's capacity for removing both of the inorganic heavy metal cations and the NOC compound. The sorption of chlorobenzene by CDTEA-montmorillonite was comparable to a regular cationic surfactant, decyltrimethylammonium (DTMA)-grafted montmorillonite.

In this study, we propose a different bonding mode to graft non-ionic surfactants onto smectite to make the mineral surface hydrophobic, and yet preserve most of

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Table 1. Chemical formulae and properties of surfactants.

| Commercial name | Chemical name | Formula | Molecular weight | Melting point (ºC) |
|---|---|---|---|---|
| Brij 56 | polyoxyethylene (10) cetyl ether | $C_{16}H_{33}(OCH_2CH_2)_nOH$ ($n \approx 10$) | 683 | 32–34 |
| Igepal CO720 | polyoxyethylene (12) nonylphenyl ether | $4\text{-}(C_9H_{19})C_6H_4(OCH_2CH_2)_nOH$ ($n \approx 12$) | 749 | 13 |

the negative charge. Non-ionic surfactants are composed of hydrophilic polymeric segments and hydrophobic aliphatic hydrocarbon or alkylphenol groups. Poly(ethylene oxide) (PEO) is the most common hydrophilic polymer used in non-ionic surfactants. When non-ionic surfactants are bound to clay minerals, the aliphatic tails increase the hydrophobicity of the mineral surfaces (Michot and Pinnavaia, 1991). Yet the charge characteristics of the minerals are preserved since there is no charge neutralization as in the conventional organo-clay synthesis. Therefore, the non-ionic surfactant-clay composites have the dual abilities to remove both NOC contaminants and heavy metal cations, which frequently occur together in industrial process waters.

In addition to the potential environmental applications, the research on the reaction between non-ionic surfactants and clay minerals will provide insight into the fate of non-ionic surfactants in soil systems and their effect on soil surface properties. Since non-ionic polymeric surfactants have gained enormous popularity over the past 20 y in a variety of applications and fields of research (Cross, 1987), large amounts of them have been introduced into soil through agrochemical formulations, detergents and several other soil additives. Soil minerals adsorb the surfactants and certainly the adsorbed surfactants modify the surface properties of the soil components and thus influence the adsorption and transportation of other organic compounds.

The objectives of this paper are: (1) to describe the properties of smectite composites prepared by grafting non-ionic polymeric surfactants on smectite; (2) to determine the surface properties of the composites; and (3) to test their effectiveness for sorbing both aromatic chlorophenols and heavy metal cations.

## MATERIALS AND METHODS

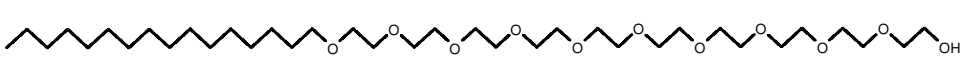
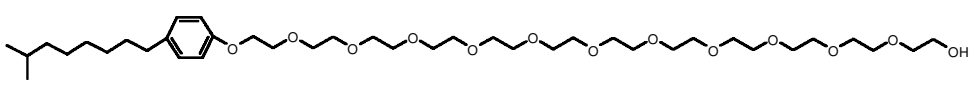
### *Clay sample and treatment*

The clay used for this study was a bentonite sample from Gonzales, Texas, supplied by Southern Clay Products. The original powder was washed three times with 1 M pH5 sodium acetate (NaOAc) solution in a Nalgene centrifuge tube. The sand particles were removed by sieving and the clay fraction (<2 μm) was separated by centrifugation. The clay fraction was saturated with $Ca^{2+}$ by washing with 0.5 M $CaCl_2$ solution. The resulting clay was dialyzed against distilled water until the electric conductivity of the balanced solution was <5 μS and then freeze dried. This $Ca^{2+}$-saturated clay sample is referred to as Ca-Sm. The cation exchange capacity (CEC) of the clay was 81.2 cmol(c)/kg by the Ca-Mg exchange method (Jackson, 1969). The surface area was 787 $m^2/g$ as determined by the ethylene glycol monoethyl ether (EGME) method (Carter *et al.*, 1986). Only smectite was detected by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) analyses.

### *Non-ionic polymeric surfactants*

Two non-ionic polymeric surfactants, Brij 56 and Igepal CO720, were obtained from Aldrich Chemical Company and used without further purification. The molecules of the two surfactants contain similar numbers of repeating ethylene oxide (EO) units (Tables 1 and 2). The surfactant Igepal CO 720 is a colorless liquid at room temperature, whereas Brij 56 is a wax-like white solid material. The critical micelle concentration (CMC) for Brij 56 is 0.002 mM as reported by Aldrich Chemical Company. The CMC value for Igepal CO 720 is not

Table 2. Ideal structure of surfactants.

| Surfactant | Structure |
|---|---|
| Brij 56 |  |
| Igepal CO 720 |  |

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available from that company. A very similar non-ionic surfactant TX100 has a CMC of 0.2 mM (Breen *et al.*, 1999), the CMC of Igepal CO 720 is believed to be close to this value. The $^{13}C$ NMR spectra of the two surfactants showed that Brij 56 molecules have more homogeneous structures than Igepal CO 720 molecules (our unpublished data).

*Surfactant adsorption isotherms*

The sample Ca-Sm was dispersed in distilled water to make a 2.00% (w/v) clay suspension. 5 mL of the 2.00% Ca-Sm suspension and 25.00 mL of different concentrations of surfactant solutions (containing 0.005 M $CaCl_2$ electrolyte) were introduced into 50 mL Pyrex heavy-duty glass centrifuge tubes. The tubes were shaken for 24 h at room temperature (23±1°C) and then centrifuged for 10 min at 2000 rev/min. The supernatant liquids were collected for surfactant concentration determination. The amount of adsorbed surfactant was calculated from the concentration difference of the surfactants before and after adsorption. Surfactant Igepal CO 720 was analyzed with a Beckman DU 640B UV-Visible spectrophotometer at 276 nm. Surfactant Brij 56 was quantified with a total organic carbon analyzer (Model 1010 Wet Oxidation TOC Analyzer). Only ~76% recovery was achieved for a pure 0.4 mM Brij 56 solution with the TOC analyzer, and thus data for Brij 56 from the TOC analyzer were considered less accurate than the data for Igepal CO 720 from the UV method. The clay deposited at the bottom of each centrifuge tube was washed once with distilled water and mounted on a glass slide and air dried for XRD analyses.

*Surfactant-clay composite synthesis and characterization*

For each composite, 5 g of Ca-Sm were dispersed in 50 mL of distilled water in a 250 mL Nalgene centrifuge tube. An aliquot of 150 mL of 27 mM surfactant solution was added to the tube. The suspension was shaken overnight. The resulting clay was centrifuged down and the supernatant was decanted. The surfactant treatment was repeated three times. During the third treatment, clay remained in suspension even after centrifugation, 10 mL of 0.5 M $CaCl_2$ solution was added to flocculate the suspended clay. After the surfactant treatment, each resulting composite was washed three times with distilled water (150, 100 and 50 mL subsequently) to remove excess surfactant. In the second washing, 10 mL of 0.5 M $CaCl_2$ solution were added to reduce dispersion. The composites were freeze dried and characterized by XRD and FTIR analyses.

*Stability of surfactants on smectite*

*Layer spacing $d_{001}$ resistance to water washing.* 100 mg samples of surfactant-smectite composite were dispersed in 10 mL of distilled water in a 40 mL Nalgene centrifuge tube. After sonication, ~1 mL of the composite suspension was mounted on a glass slide and air dried as an oriented clay film. The remaining suspension was brought to 25 mL by adding distilled water, shaken for 2 h and centrifuged for 5 min at 2000 rev/min. After decanting the supernatant liquid, the remaining clay was dispersed in 10 mL of distilled water again and 1 mL of the suspension was mounted on a glass slide. The washing and mounting procedure was repeated five times. An oriented film was prepared for XRD analysis after each washing.

In a parallel washing experiment, three samples from the Igepal CO 720 adsorption isotherm experiment were mixed and centrifuged five times in 25 mL of 0.005 M $CaCl_2$ solution each time. The surfactant concentration in the supernatant liquids from each washing was determined with the UV spectrophotometer. Desorption of the surfactant was calculated according to the surfactant concentration in the washing solution.

*Resistance to electrolyte solution washing.* Each surfactant-smectite complex was washed three times with several electrolyte solutions containing 1 M $Cl^-$, these electrolyte solutions included NaCl, KCl, $MgCl_2$, $CuCl_2$ and $CrCl_3$. After washing with the electrolyte solutions, the composites were washed three times with distilled water to remove the excess salts, mounted on Vycor slides, and air dried as oriented films for XRD analysis.

*Solvation*

To investigate whether the central areas of the interlayer galleries of smectite were occupied by surfactants, the $d_{001}$ spacing of the clay and the composites was measured by XRD after treating with five solvents having different polarity as described below. The five solvents were non-polar cyclohexane and toluene, weakly polar octanol, and strongly polar glycerol and water. For the volatile solvents cyclohexane and toluene, 0.1 g of clay or composites and 10 mL of solvents were mixed in capped centrifuge tubes and shaken for 24 h. A few drops of the mixture were transferred to glass slides and were immediately scanned by XRD before the solvents evaporated. Free cyclohexane or toluene was maintained in the XRD sample chamber during the XRD analysis to reduce solvent evaporation from the samples. The solvation tests by water, glycerol and octanol were carried out slightly differently. The clay or composite suspensions were deposited on glass slides and air dried to obtain oriented films. A few drops of water or octanol were added to the films and the slides kept in sealed containers for 1 week. The containers were saturated with the vapors of the corresponding solvents. For the glycerol solvation test, 10% glycerol aqueous solution was sprayed on air-dried films and the glycerol-treated slides were left for 5 days in ambient conditions before XRD analysis.

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*Surface properties of surfactant-smectite composites*

In this experiment, a cationic surfactant, benzyl-dimethyl-tetradecyl-ammonium- (BDTA, obtained from Fluka Chemical Company) treated smectite and activated carbon were used as references to compare the surface properties of the non-ionic surfactant-smectite composites. The BDTA-smectite was synthesized by adding an amount of BDTDA in solution equal to the CEC of smectite to the mineral and shaking and washing as described by Boyd *et al.* (1988). A batch equilibration method was used to determine the sorption capacity of the surfactant-smectite composites for 4-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol in pH 4.9 Na acetate buffer solution as in Environmental Protection Agency (EPA) method 1311. At room temperature, the solubilities of the chlorophenols in water are 24.0, 4.50 and 0.80 g/L, respectively. The decrease in solubility of the three chlorophenols reflects their increasing hydrophobicity in some sense (Mortland *et al.*, 1986). The quantity of adsorption on particles reflects the hydrophobicity of the surfaces of the particles. The chlorophenols concentration was determined with the Beckman DU 640B UV-Visible spectrophotometer.

The cation exchange capacities of the surfactant-smectite composites were determined with the Ca-Mg exchange method (Jackson, 1969). The charge properties of the surfactant-smectite complexes were further tested for their sorptive capacities in removing $Cu^{2+}$ and $Cr^{3+}$ ions from aqueous solution. A batch equilibrium method was used to determine the adsorption of the heavy metal ions from solution. The final pH of the equilibrated $Cu^{2+}$ and $Cr^{3+}$ solutions were 5.3 and 3.9, respectively. The concentration of the heavy metal ions in solution was determined by atomic absorption spectrometry (AAS). The chlorophenol and heavy metal cation adsorption analyses were duplicated. Typically, the differences between two duplicates were 1% or less.

*X-ray diffraction*

The $d_{001}$ basal spacings of the smectite and the surfactant-smectite composites were measured using a Philips diffractometer operating at 30 kV and 18 mA with CuKα radiation (λ = 0.15418 nm). Measurements were carried out in the step-scanning mode with a step size of 0.05º2θ counted for 5 s. Samples were prepared by air drying the suspensions of clay or clay-surfactant composites onto glass or Vycor slides forming oriented films. For the heating experiment, the oriented samples on the Vycor slides were heated at specified temperatures for 1 h and then immediately scanned by XRD while the slides were still hot, to minimize moisture adsorption during analysis.

*Fourier transform infrared analysis*

Self-supporting films of the clay and the composites were prepared according to White and Roth (1986): ~1.5 mL of 2% (w/w) smectite or surfactant-smectite composite suspension was pipetted onto a Mylar plastic film (Spex CertiPrep Inc.) and left to air dry. The clay film was separated carefully from the supporting film by pulling the plastic film over a sharp edge at an angle greater than 90º. The IR spectra were recorded with a resolution of 1 $cm^{-1}$ using a Perkin Elmer System 2000 FTIR, a mid-IR range deuterated triglycine sulfate (TGS) detector was selected in the study. Continuous data collection was achieved with 64 co-added scans for each sample. The optic bench of the instrument and sample chamber were purged with dry and low-$CO_2$ air from a Balston 75-52 FTIR purge gas generator. The spectra were processed with an IR data management software SPECTRUM V3.01 (Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire, England).

## RESULTS

*Adsorption isotherms*

Surfactants Brij 56 and Igepal CO 720 showed similar adsorption properties on smectite (Figure 1): they exhibited a steep initial increase over a narrow concentration range and have L-type adsorption isotherms. The isotherms can be fitted to Langmuir equation:

$$q = bkC/(1 + kC)$$

where $q$ is the adsorbed amount, $b$ represents the maximum adsorption and $k$ determines the magnitude of the initial slope of the isotherm and $C$ is the surfactant concentration in solution at equilibrium. The maximum adsorption $b$, initial slope $k$ and the regression coefficients of the two isotherms are given in Table 3. The fact that the regression coefficients were >0.98 suggested that the isotherms fitted the Langmuir equation very well. The initial slope of the Brij 56 isotherm was slightly steeper than that of Igepal CO 720 and might imply that the Brij56 had a greater affinity for smectite. The isotherm maximum adsorption for Brij 56 and Igepal CO 720 were 352 and 293 µmol/g, which are equivalent to 0.240 and 0.220 g of surfactants per gram of clay, respectively.

*Expansion of smectite by non-ionic surfactants*

The $d_{001}$ spacing of the smectite samples used in the surfactant adsorption isotherms were monitored by XRD. Surfactant adsorption expanded the $d_{001}$ spacing

Table 3. Langmuir equation parameters for the isotherms of surfactant adsorption on smectite.

| Surfactant | Maximum adsorption $b$ (µmol/g) | Initial slope $k$ (g/µmol) | Regression coefficient |
|---|---|---|---|
| Brij 56 | 351.9 | 49.98 | 0.985 |
| Igepal CO 720 | 293.0 | 48.65 | 0.990 |

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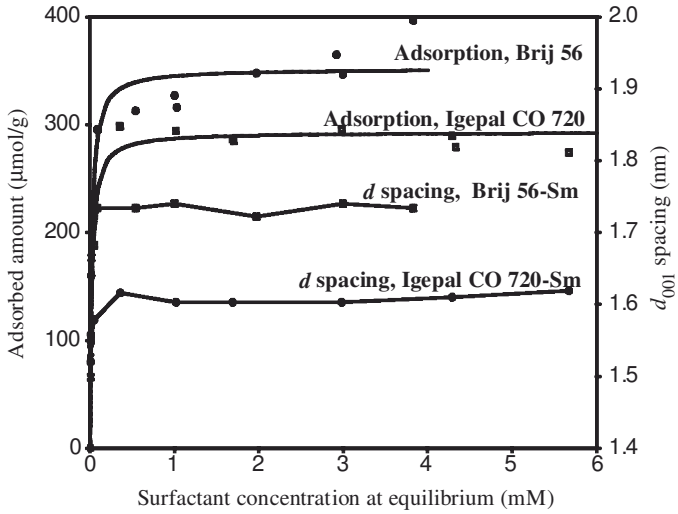



Figure 1. Adsorption isotherms of surfactants Brij 56 and Igepal CO 720 on Ca-Sm from aqueous solutions and the corresponding $d_{001}$ spacings of resultant surfactant-smectite composites.

of smectite from ~1.5 nm to higher values (Figure 1). In the lower surfactant concentration range (0 to 0.3 mM), the $d_{001}$ spacing increased with the concentration of the surfactants. For Brij 56-adsorbed smectite, the *d* spacing increased from 1.53 to 1.74 nm. For Igepal CO 720-adsorbed smectite, the *d* spacing increased from 1.54 to 1.62 nm. The expansion of the $d_{001}$ spacing indicated that the two non-ionic surfactants intercalated and expanded smectite. The *d* spacings were not further increased even when four times more surfactants were added to the suspension. The adsorption of Brij 56 increased gradually yet the XRD spacing was constant. In other words, the intercalation and expansion of smectite by the surfactants were limited. The limited expansion of the $d_{001}$ spacing implies that only a certain number of layers of surfactant can access the interlayer space of the smectite. In this experiment, the $d_{001}$ spacing did not reach 1.8 nm. The expansion by the two surfactants is very similar to the expansion by glycerol, no more than two layers of glycerol can form in the interlayer spacing of smectite with a maximum $d_{001}$ spacing of ~1.8 nm . It is likely that the surfactants are also limited to two molecular layers in the interlayer galleries of smectite.

### *XRD of surfactant-smectite composite*

In this experiment, the composites prepared by repeated surfactant treatments were used. The $d_{001}$ spacing of the Brij 56-smectite composite was 1.73 nm (Figure 2). The Igepal CO 720-smectite composite had a slightly larger $d_{001}$ spacing than the maximum $d_{001}$ spacing of 1.62 nm from the adsorption isotherm

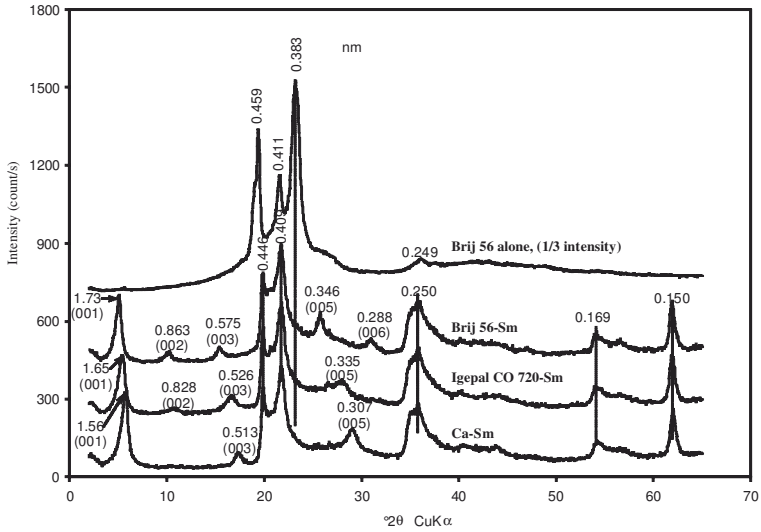



Figure 2. XRD patterns of surfactant Brij 56 and powder-mounted smectite and surfactant-smectite composites.

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experiment. Like the starting Ca-Sm, the higher diffraction orders, 003 and 005 of the two surfactant-smectite composites appeared in the XRD patterns. The 002 diffraction peaks of the two composites and the 006 diffraction feature of Brij 56-smectite also showed in the patterns. The additional higher-order diffraction peaks suggested regularity of the surfactants in the interlayer of smectite.

The repeated surfactant treatments with a high concentration surfactant (27 mM) did not further expand smectite. The $d_{001}$ values were still <1.8 nm. Surfactant Igepal CO 720 expanded smectite less than surfactant Brij 56 (Figure 2). Surfactant Brij 56 is a wax-like solid material at room temperature with melting point of 32–34ºC and produced strong XRD peaks at 0.459, 0.411 and 0.383 nm (uppermost pattern in Figure 2). The 0.383 nm peak did not occur in the XRD patterns of the Brij 56-smectite composites indicating a lack of free surfactant. These results suggest that the surfactants did not precipitate as separate crystalline phases on the mineral. In other words, the surfactant-smectite composites were not physical mixtures of the mineral with the surfactants.

*Thermal reactions of surfactant-smectite composites*

Both of the Brij 56- and Igepal CO 720-smectite composites were thermally stable at 100ºC. When the oriented samples were heated to a higher temperature (*e.g.* 150ºC), their XRD peaks showed slight increases in intensity and sharpness. In addition, the $d_{001}$ spacing of the Igepal CO 720 also appeared a little higher at 100 to 200ºC than the $d_{001}$ value at room temperature (Figure 3). The Brij 56-smectite composite began to collapse when the sample was heated at 150ºC and higher temperatures. The Igepal CO 720-smectite composite was slightly more resistant to heat treatment showing no collapse until 250ºC. Both of the polymeric surfactant-smectite composites kept $d_{001}$ values >1.40 nm when heated to 300ºC. With the same heat treatments, the homoionic Ca-smectite showed early collapse with $d_{001}$ reduced to 1.0 nm when the temperature was raised to 300ºC. The differences among the $d_{001}$ values of the smectite and surfactant-smectite composites suggested that the surfactants were not completely expelled from the interlayer galleries of smectite even when the temperature was raised to 300ºC. The greater $d_{001}$ spacing of the surfactant-smectite composites at high temperature confirmed that the surfactants could enter the interlayer of smectite.

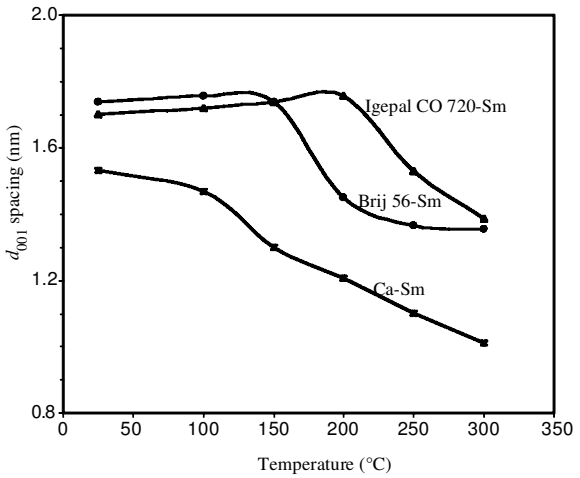



Figure 3. Temperature dependence of the $d_{001}$ spacing of smectite and surfactant-smectite composites.

The surfactant-smectite composites had consistently larger spacings than Ca-Sm throughout the range of heat treatments indicating persistence of the intercalating molecules. There were no peaks in the surfactant-smectite composite XRD patterns at the position corresponding to the 001 peaks of the unintercalated smectite. The single 001 peak suggested that all of the smectite layers were intercalated and expanded during the repeated surfactant treatments.

*Solvation of surfactant-smectite composites*

The $d_{001}$ spacing data of the surfactant-smectite composites have confirmed that the polymeric surfactant can enter the interlayer of smectite. As the structures of the surfactants have shown (Table 2), polymeric surfactants contain hydrophilic PEO segments and hydrophobic hydrocarbon chains. A question arose as to whether the whole surfactant molecule or only part of it could migrate into the interlayer space of smectite. To answer this question, the surfactant-smectite composites were exposed to five solvents with different polarity. It was expected that the surfactants would increase the hydrophobicity of the interlayer spaces of smectite if the whole surfactant molecules could move into the interlayer galleries. Therefore, some non-polar organic molecules should be able to access the galleries of the surfactant-smectite composites by hydrophobic bonding. The XRD patterns of smectite and surfactant-smectite composites exposed to the solvents showed nearly identical reaction to the polarity of the solvents. The non-polar solvents hexane and toluene and the weakly polar solvent octanol did not change the $d_{001}$ spacing distinctively. Polar solvent glycerol caused all of the samples to expand to 1.8 nm and water caused them to expand to >1.9 nm (Figure 4). The identical solvation reaction suggested that the interlayer galleries of surfactant-smectite composites were still hydrophilic.

*Incomplete water displacement from FTIR evidence*

The IR spectra of the surfactant-smectite composites will be discussed in detail elsewhere. Part of the normalized spectra are shown in Figure 5. To compare the water bands of the spectra, the bands at 3624 $cm^{-1}$ were normalized to the same heights. The 3624 $cm^{-1}$ band arose from the inner OH group of the smectite and it was not altered by surfactant adsorption and therefore

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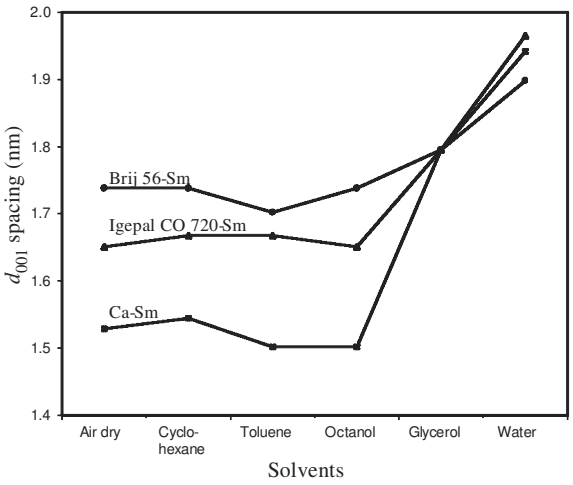



Figure 4. Effect of solvation on the $d_{001}$ spacing of smectite and surfactant-smectite composites.

can be regarded as a reference band. The bands in the range 3000–3600 $cm^{-1}$ arise from the stretching vibration of adsorbed $H_2O$ molecules and the end OH group of the surfactants. The bands at ~1640 $cm^{-1}$ are caused mainly by the bending vibration of the water molecules. The 1608 and 1575 $cm^{-1}$ bands of Igepal CO 720-smectite arose from the symmetric and asymmetric stretching vibrations of the aromatic ring respectively. As the IR spectra show, after surfactant adsorption, there are still strong IR adsorptions corresponding to the water bands, indicating that the water molecules on smectite were not completely replaced by the surfactant molecules. According to the area calculation of the water-bending bands at ~1640 $cm^{-1}$ after deconvoluting the aromatic bands of Igeapl CO 720, the relative water ratios of Brij 56-smectite and Igepal CO 720-smectite to the starting smectite are 47% and 56%, respectively. The adsorbed water molecules were apparently associated with the exchangeable cation on the mineral and thus the interlayer galleries of the surfactant-smectite composites were still partly occupied by water molecules.

Table 4. $d_{001}$ spacing of surfactant-smectite composites after washing with water.

| No. of washings | $d_{001}$ spacing after washing (nm) | |
|---|---|---|
| | Brij 56-Sm | Igepal CO 720-Sm |
| 0 | 1.738 | 1.651 |
| 1 | 1.757 | 1.603 |
| 2 | 1.738 | 1.619 |
| 3 | 1.775 | 1.603 |
| 4 | 1.738 | 1.588 |
| 5 | 1.757 | 1.573 |

*Washing resistance of surfactants on smectite*

*Washing resistance to distilled water.* The Brij 56-smectite composite kept almost identical $d_{001}$ spacing values (1.74 nm) during the washing process (Table 4). The Igepal CO 720-smectite composite had a slight reduction in the $d_{001}$ spacing when it was washed with distilled water. Five repeated washings with 0.005 M $CaCl_2$ solution removed ~30% of the adsorbed Igepal CO 720 and 70% of the surfactant was still associated with the mineral (Figure 6).

*Washing resistance of interlayer surfactants to salt solutions.* Both Brij 56 and Igepal CO 720 showed high resistance to salt solution washing. Three washings with 1 N chloride solution of $Na^+$, $Mg^{2+}$, $Cu^{2+}$ and $Cr^{3+}$ did not reduce the $d_{001}$ values of the surfactant-smectite (Figure 7). Indeed, when the Brij 56-smectite composite

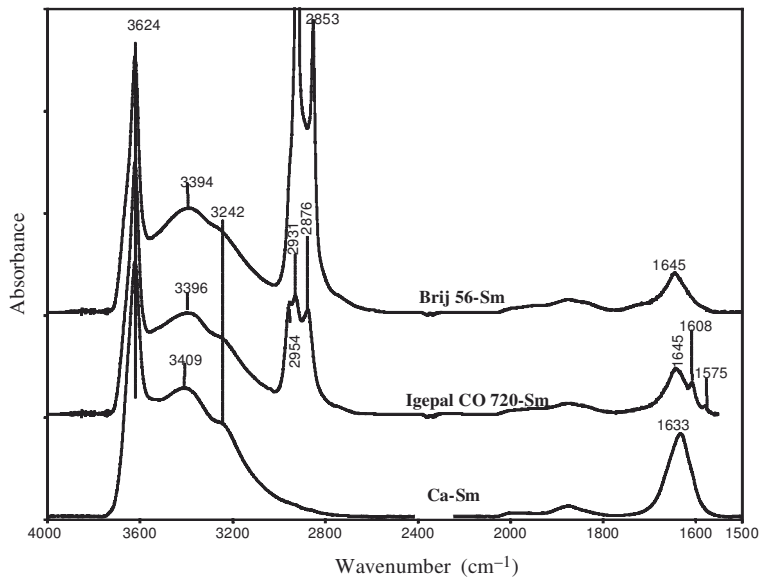



Figure 5. Normalized IR spectra of smectite and surfactant-smectite composites.

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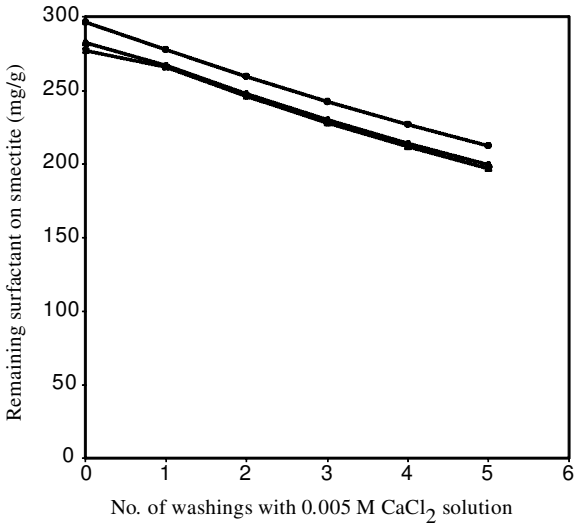



Figure 6. Desorption of Igepal CO 720 from smectite by washing with 0.005 M $CaCl_2$ solution.

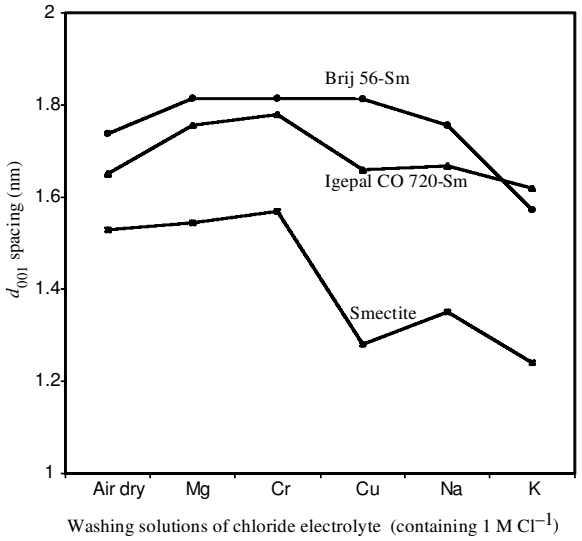



Figure 7. Effects of electrolyte solutions on the $d_{001}$ spacing of smectite and surfactant-smectite composites.

was washed with $Mg^{2+}$, $Cu^{2+}$ and $Cr^{3+}$ solutions, its $d_{001}$ spacing showed a slightly higher value (1.8 nm). When the Igepal CO720-smectite composite was washed with the salt solutions, the $Mg^{2+}$, $Cr^{3+}$ salts also slightly increased its $d_{001}$ spacing from 1.64 to 1.75 nm or more. The KCl solution washing showed different effects on the two surfactant-smectite composites: for Brij 56, the $d_{001}$ spacing collapsed to 1.6 nm while the Igepal CO 720 kept its 1.63 nm spacing. It is not certain why the KCl solution washing could reduce the $d_{001}$ values, one cause may be related to the low hydration energy of the $K^+$ ion. The surfactant-smectite composites always have higher $d_{001}$ spacings than the corresponding smectite samples washed with the same electrolyte solutions even though they showed changing $d$ spacings with different cations. The persistence of the $d_{001}$ values of the composites suggested that the interlayer surfactant molecules were resistant to electrolyte solution washings.

*Surface properties of surfactant-smectite composites*

*Charge properties.* The non-ionic surfactant-smectite composites preserved >80% of the initial CEC whereas the cationic surfactant BDTA-treated smectite lost almost all of the surface charge (Table 5). The CEC differences of the two types of surfactant-treated smectite are attributed to their different bonding mechanisms. The BDTA molecules were adsorbed by ionic bonding between the cationic ammonium and the negative charge of smectite. The organic ammonium surfactants were irreversibly adsorbed. The surface charges were neutralized and thus not available for other cations. Brij 56 and Igepal CO 720 are non-ionic surfactants. They cannot have ion-exchange reactions with the mineral. Therefore, no smectite charge neutralization resulted from their adsorption. The slight reduction of the CEC implied steric hindrance to the exchangeable sites by the surfactant molecules. Since most smectite surface charge sites are in the interlayer galleries, the preservation of the CEC demonstrated accessibilities of inorganic cations.

Table 5. CEC values of smectite and surfactant-smectite composites.

| Sample | CEC (cmole(c)/kg) | Percentage relative to smectite |
|---|---|---|
| Smectite | 82.7 | 100 |
| Brij 56-Smectite | 64.3 | 77.8 |
| Igepal CO 720-smectite | 73.8 | 89.3 |
| BDTDA-Sm | 6.1 | 7.4 |

The availability of the interlayer charge sites for cations was further confirmed by their sorptive capacities for removing $Cu^{2+}$ and $Cr^{3+}$ from solution (Figure 8a). Activated carbon and BDTDA-smectite were used to compare their efficiencies. The graph illustrated that the activated carbon and BDTDA-smectite composite had the least removal capacity for heavy metal contaminants. The non-ionic surfactant-smectite composites kept >80% of the capacity compared with the untreated Ca-Sm. Apparently, the adsorption differences of the activated carbon and the surfactant-smectite composites were related to the surface-charge properties. The adsorption of the $Cu^{2+}$ and $Cr^{3+}$ were through ion-exchange reactions.

*Hydrophobicity of the surfactant-smectite composites.* Hydrophobicity was evaluated by determining the adsorption of three chlorophenols that differ in solubility in water and comparing them with the untreated Ca-Sm

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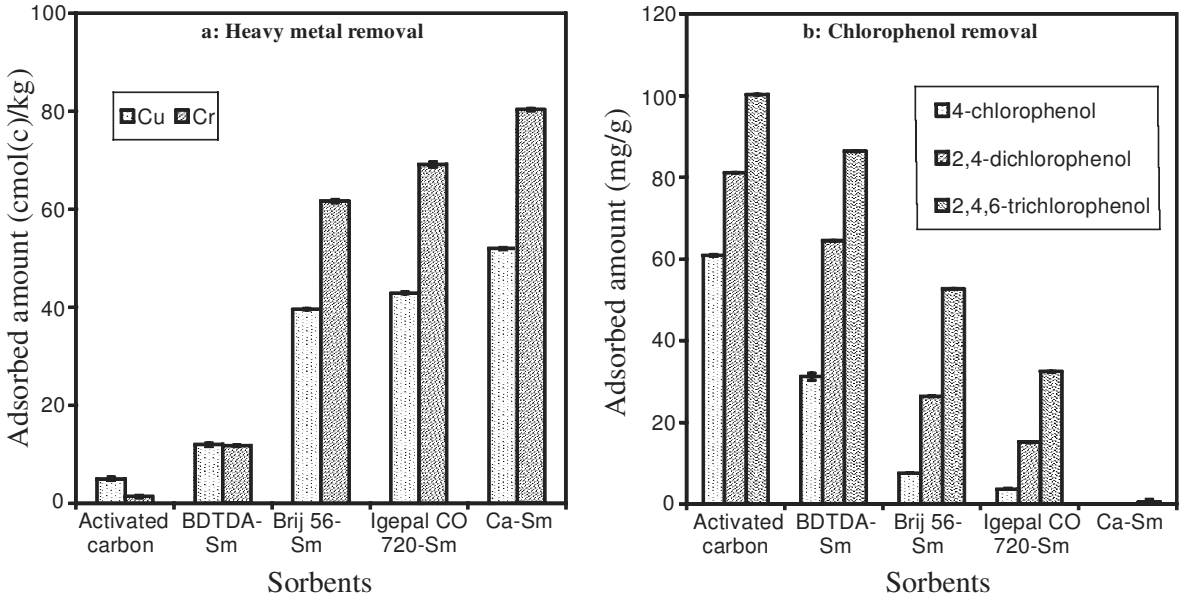



Figure 8. Removal capacities for $Cu^{2+}$ and $Cr^{3+}$ (a), and chlorophenols (b) by activated carbon, smectite, and surfactant-smectite composites.

and two other sorbents (Figure 8b). The Ca-Sm was essentially inactive as an adsorbent of the chlorophenols reflecting its hydrophilic surface characteristics. The solubility of the phenols decreases and hydrophobicity increases with increased chlorination. The adsorption of the chlorophenols on the composites and activated carbon reference showed a stepwise increase with their hydrophobicity. For example, the solubility of the mono 4-chlorophenol is 24.0 g/L and it had the least adsorption (7.6 mg/g on Brij56-smectite); the solubility of 2,4,6-trichlorophenol is 0.80 g/L and it had the greatest adsorption (52.7 mg/g on Brij56-smectite). Because the pH of the solutions was buffered at pH 4.9 with Na acetate in this study, all of the chlorophenols molecules should exist as neutral species. Their adsorption was mainly determined by the hydrophobicity of the surfaces. The greater adsorption of chlorophenols by the composites than by smectite alone illustrated that the surfactants greatly increased the hydrophobic character of the smectite by providing the hydrophobic segments accessible to the chlorophenols for bonding.

## DISCUSSION

### *Limited expansion of smectite by non-ionic surfactants*

The adsorption of non-ionic surfactants on smectite, and the $d_{001}$ spacing of surfactant-smectite composites did not increase with excess surfactant. These facts indicate that the surfactants did not develop a micelle structure in the interlayer of smectite after the adsorption reached its maximum value. This adsorption characteristic is different from that of cationic surfactant adsorption onto smectite minerals. When cationic surfactants are grafted onto clay minerals, it has often been observed that minerals can adsorb more organic cations than suggested by their CEC. Adsorption above the CEC of the minerals is due to the hydrophobic bonding between the aliphatic tails of the surfactants (Mortland, 1986; Deng and Dixon, 2002). The hydrophobic bonding can induce the formation of surfactant aggregates in the interlayer galleries of expanding minerals even at the low levels of adsorption. For example, the maximum adsorption of hexadecyl-trimethyl-ammonium (HDTMA) reached 1.6 times the CEC of a montmorillonite (Jaynes and Boyd, 1991), and the maximum adsorption of benzyl-dimethyl-tetradecyl-ammonium (BDTDA) might even reach three times the CEC of a Na-montmorillonite (Koh and Dixon, 2001). The interlayer cationic surfactant can have one layer, two layers, pseudo three layers and paraffin multiple structures.

The limited expansion of the *d* spacing by the non-ionic surfactants also implied that the surfactant did not orient vertically or inclined relative to the silicate (001) surface whereas cationic surfactants are often tilted. Since the expansion of the smectite along the *c* axis was <0.8 nm, and the length of the surfactants can be >5.6 nm, the surfactants cannot develop the conformation with the chain axis perpendicular or inclined to the (001) surface of smectite. The only possible orientation is that the chain axis of the surfactant molecules were parallel or nearly parallel to the basal surface.

The slight $d_{001}$ spacing increment when the surfactant-smectite was heated (Figure 3) can be attributed to a conformation change of the surfactant in the interlayer of the mineral when the samples were heated. Similar small increases in $d_{001}$ spacings have been reported for a smectite loaded with Triton TX100 (Breen *et al.*, 1999).

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The small $d_{001}$ spacing change was observed when TX100-smectite was heated in the temperature range 100–200ºC, and the increases were attributed to either the reordering of the surfactant molecules within the clay interlayer or to the fact that more surfactants migrated into the galleries and completed the filling of the interlayer space at elevated temperatures (Breen *et al.*, 1999). Several studies on clay nanocomposites have shown conclusively that annealing clay polymer mixtures at elevated temperatures can encourage the expansion of clay galleries from the pool of external polymer (Lan and Pinnavaia, 1994; Shi *et al.*, 1996).

*Surfactant location and orientation in the interlayer of smectite*

The reactions of $d_{001}$-spacing with respect to the solvent treatments suggested that the interlayer space of surfactant-smectite composites were identical or nearly identical to untreated smectite: they are inert to non-polar hydrophobic solvents but accessible to polar solvents (*e.g.* glycerol and water in this experiment). It appears reasonable to conclude that the surfactant mostly stayed in the marginal area of the interlayer gallery. The inner or central area of the interlayer gallery would be much less accessible to the polymeric surfactants (Figure 9). The surfactant molecules probably formed an annular ring between neighboring smectite platelets. It is possible that some surfactant molecules migrated to the central area of the interlayer spaces, but the concentration in the center would be less than the margin area. The annular ring non-ionic surfactant-smectite structure proposed here is different from cationic-smectite organoclays. In the cationic-smectite organoclay, it is assumed that the surfactants were distributed homogeneously in the galleries when they started to occupy the interlayer spaces. Water cannot expand the cationic surfactant-smectite organoclays, even though small alcohol molecules such as methanol or ethanol may solvate them (Slabaugh and Hiltner, 1968). We found that cyclohexane and octanol solvated the cationic surfactant BDTDA-smectite and even removed the cationic surfactant from the interlayer of the composite causing the collapse of the $d_{001}$ spacing from 2.08 nm to 1.8 nm (data not shown). It has been reported that when smectite and vermiculite were intercalated with the cationic surfactant decylammonium, their adsorption for herbicide 2,4-D increased and the interlayer became accessible to the herbicide. The $d_{001}$ spacing of the decylammonium-smectite complex was increased from 2.1 nm to 2.9 nm, and the decylammonium-vermiculite was expanded from 2.4 nm to 3.3 nm by 2, 4-D (Hermosin and Cornejo, 1993).

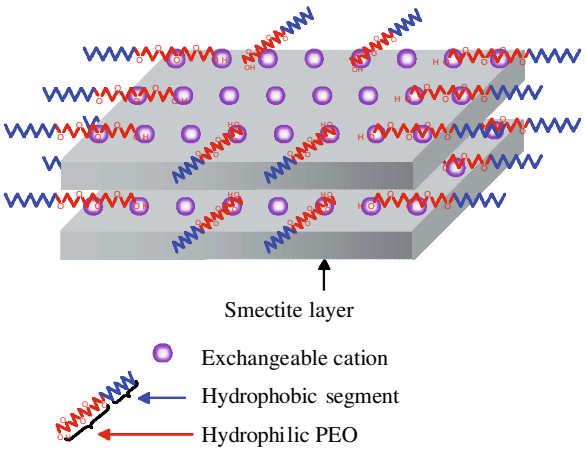



Figure 9. Proposed non-ionic surfactant-smectite composite model. The hydrophilic PEO segments of the surfactants can access the interlayer galleries of smectite whereas the hydrophobic tails tended to extend away from the mineral. The non-ionic surfactants concentrated in the margin area of the interlayer galleries and formed an annular ring between two neighboring smectite sheets.

The central areas of the non-ionic polymeric surfactant-smectite composites basically had the same properties as the untreated smectite. Water molecules may stay in the interlayer galleries, especially the central areas, as indicated by the IR data (Figure 5). The proposed annular orientation of the surfactant on the mineral caused the surfactant-smectite composites to respond similarly to the solvents as the untreated Ca-smectite. Since the hydrophobic segments of the surfactants would probably be extended away from the hydrated region, it is expected that the hydrophobic tails should increase the hydrophobicity of the mineral surfaces as indicated by the chlorophenol adsorption experiment.

*Stability of surfactant-smectite composites*

The amount of desorption suggested that the surfactants on the smectite were not as stable as big polymers such as polyacrylamide with a molecular weight of millions g/mol. In a similar washing experiment, Parfitt and Greenland (1970) found that only 15% of PEO with molecular weight of 2000 g/mol could be removed from Ca-montmorillonite, whereas >80% of the PEO with a molecular weight of 300 g/mol was desorbed. This was apparently due to the polymer size effect on the strength of binding between the polymer and smectite. High molecular weight polymers have stronger binding forces to the mineral. Therefore, it is expected that increasing the PEO chain length of the surfactant will induce more stable surfactant-smectite composites.

*Hydrophobicity of non-ionic surfactant-smectite composites*

The different removing capacities for cholorophenols are related to the hydrophobicity of the adsorbing surfaces, and thus are related to the loading and the structure of the surfactants on the mineral. In this experiment, the loading of BDTDA was expected to be higher than the non-ionic surfactant because of the higher affinity of cationic surfactant for smectite than

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the non-ionic surfactant (Rheinlander *et al.*, 1998). To increase the adsorbing capacity of surfactant-smectite composites for the hydrophobic compounds, it is necessary to increase the surfactant loading or increase the size of the hydrophobic segments of the surfactant. The goal of enhancing the loading could be achieved by increasing the chain length of the PEO segment of the surfactants. This idea will be tested in future research.

The data on removing chlorophenols and heavy metal cations suggest that non-ionic surfactant-smectite composites would be promising candidates for environmental applications because of their dual characteristic in removing both inorganic and organic contaminants. There is one additional advantage of the non-ionic surfactant-smectite composites over the cationic surfactant-modified smectite or vermiculite: the non-ionic surfactants are much less toxic than the cationic ones. They have been used increasingly in detergents, agrochemical formulations, cosmetics and textiles (Portet *et al.*, 1997; Portet *et al.*, 1998). The non-ionic surfactants are also biodegradable. Yet further investigations are needed to increase the efficiencies of these sorbents in removing contaminants, especially organic contaminants, in order to compete effectively with commonly used sorbents like activated carbon.

## CONCLUSIONS

Smectite can be intercalated and expanded by non-ionic polymeric surfactants but the expansion is limited. Only two or less layers of the surfactants can access the interlayer galleries. The interlayer surfactant molecules probably form an annular ring structure between neighboring smectite platelets. The hydrophilic PEO segments of non-ionic surfactants access the interlayer whereas the hydrophobic hydrocarbon tails tended to extend away from the mineral surfaces. The central areas of the interlayer galleries of smectite are probably less accessible to these surfactants and are more likely to be occupied by water molecules. The adsorbed non-ionic surfactants on smectite are relatively stable to heat or washing treatments. The composites preserved most negative charges of smectite and therefore are more efficient at removing heavy metal cations than activated carbon and cationic surfactant-treated smectite. The aliphatic hydrocarbon segments of the surfactants markedly increase the hydrophobicity of smectite surfaces and thus increase the retention of aromatic chlorophenols on the composites. Non-ionic surfactant-smectite composites are promising candidates for environmental applications because of their dual abilities to remove both organic and inorganic contaminants.

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