Clays and Clay Minerals, Vol. 53, No. 1, 45–54, 2005.

SORPTION OF A NONIONIC POLYOXYETHYLENE LAURYL ETHER SURFACTANT BY 2:1 LAYER SILICATES

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Abstract—To better predict the fate and mobility of surfactants in the environment, sorption and desorption of a nonionic polyoxyethylene lauryl ether surfactant (Brij 35) by two smectites (Wyoming montmorillonite and Panther Creek smectite) and two interstratified mica-vermiculites (IMVs) were investigated by batch techniques, X-ray diffraction, and infrared spectroscopy. Maximum surfactant sorption by smectites ranged from 196 to 256 g kg^{-1}, whereas the maximum sorption by the IMVs was indeterminate over the range of concentrations employed. Sorption by smectites was best described by the Langmuir model, but sorption by the IMVs showed an S-shaped isotherm, suggesting that cooperative sorption occurred. The surfactant was more readily desorbed from the IMVs than from the smectites in an initial wash with water. After two water washes, 65–75% of the initially sorbed surfactant was retained by the smectite, and 44–51% of the surfactant sorbed to the IMVs remained with the solid phase. In this study, basal spacing of the smectites increased to ~17.5 Å near the sorption maximum, suggesting intercalation of surfactant molecules in the interlamellar regions of the clay. X-ray data also suggested that the surfactant molecules were oriented horizontally in the interlayer spaces. Greater surfactant sorption by the Ca-smectites gradually diminished the intensity of the 1630 cm^{-1} infrared band dues to hydration water, indicating that some water had been displaced by the surfactant. The surfactant was also sorbed by the IMV clays, but only on external surfaces and probably via interactions of micelles with the solid phase.

Key Words—Brij 35, Desorption, Interlayer, Polyoxyethylene.

INTRODUCTION

Surfactants find their way into the soil environment through agrochemical formulations, detergents, cosmetics, textiles and other additives (Krogh *et al.*, 2003). They are employed to enhance the solubility of sparingly water-soluble compounds (such as pesticides) by decreasing the surface tension of the aqueous system. Surfactant application has also been used to remediate sites contaminated by hydrophobic organic compounds in pump-and-treat remediation of groundwater (Pennell *et al.*, 1993). Surfactants can enhance both the bioavailability (Willumsen and Arvin, 1999; Pinto and Moore, 2000) and the transport of organic pollutants in soils (Lee and Fountain, 1999; Noordman *et al.*, 2000; Rodríguez-Cruz *et al.*, 2004).

Surfactants are also used in the synthesis of organoclays to improve the sorptive capacities of clay minerals for nonionic organic contaminants (Xu and Boyd, 1995). For example, Sheng *et al.* (1999) grafted a carboxylic group-bearing surfactant, carboxydecyltriethyl-ammonium $[(HOOC)\text{-}C_{10}H_{20}N(C_2H_5)_3]^+$ (CDTEA) to a montmorillonite to enhance retention of both organic and inorganic contaminants by the clay. Deng *et al.* (2003) added two nonionic polymeric surfactants, Brij 56 and Igepal CO720, to a smectite and observed unit-cell-scale expansion of the clay by intercalation of the surfactants in interlayer positions. They noted that smectite-surfactant composites were effective in retaining heavy metal ions and chlorophenols.

Improved knowledge of the reactions between nonionic surfactants and clay minerals will provide insight into the fate of nonionic surfactants in soil systems and could extend the scope of contaminant remediation strategies. Practically, soil remediation efforts must consider the co-existence of mixtures of various clay minerals whose unique surface properties will dictate the degree of clay-surfactant interactions. Hence, generalizations regarding the mechanism of interaction with clay minerals may not be relevant over the wide range of clays of different chemical and electrical properties.

Here we report the intercalation of a polyoxyethylene lauryl ether surfactant, Brij 35 ($C_{12}H_{25}[C_2H_4O]_{23}OH$), with 2:1 clays and test the reversibility of its retention by clay surfaces. Our hypothesis was that interactions between the nonionic surfactant and a clay mineral might be governed by the clay's charge density, charge location, and cation saturation. We also hypothesized that the surfactant could enter clay interlayer regions by coordinating with interlayer cations. The objectives of the present study were (1) to compare the sorption behavior of Brij 35 on smectites and interstratified mica-vermiculites (IMVs), (2) to determine if the surfactant could be retained in interlayer regions of smectites and IMVs, and (3) to measure desorption of the surfactant from the clays.

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DOI: 10.1346/CCMN.2005.0530106

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https://doi.org/10.1346/CCMN.2005.0530106 Published online by Cambridge University Press

MATERIALS AND METHODS

Clay samples and treatments

Our study utilized four clays: Wyoming montmorillonite (SWy-1), Panther Creek smectite (PC), and two interstratified mica-vermiculites (IMV1 and IMV2). These layer silicates were chosen to represent multiple values of layer charge and its distribution between octahedral and tetrahedral sheets. Wyoming montmorillonite was purchased from the Source Clays Repository of The Clay Mineral Society whereas the PC, IMV1 and IMV2 came from the A.D. Scott reference mineral collection, Agronomy Department, Iowa State University, Ames, IA. The interstratified mica-vermiculites were originally obtained from the Zonolite Co. of South Carolina, USA. Clay fractions (<2 μm) were collected following standard sedimentation procedures after dispersion of bulk samples in 1 M NaCl. The clay samples were saturated with K or Ca by using chloride salts, dialyzed free of excess salt, and freeze dried. Hereafter, K-saturated clays are designated as K-SWy, K-PC, K-IMV1 and K-IMV2. Calcium-saturated clays are referred to as Ca-SWy, Ca-PC, Ca-IMV1 and Ca-IMV2.

The elemental compositions of Ca-saturated clay samples were determined by inductively coupled plasma-atomic emission spectroscopy by using the suspension-nebulization technique of Laird *et al.* (1991). Structural formulae and specific surface areas for the smectites were calculated by standard techniques (Gast, 1977). Structural formulae for mica and vermiculite phases in the IMV samples were calculated by a similar approach in which the micaceous phase was assumed to be biotite and to contain all nonexchangeable K. Additional assumptions were that Si/Al and Mg/Fe ratios in the biotite phase were the same as those of the whole IMV sample. (Details of these calculations and spreadsheets are available from the corresponding author.) Structural formulae, layer charge and other calculated parameters of the clays are given in Table 1.

The two smectites had lower layer charge than the IMV samples, and most of the Wyoming montmorillonite's charge originated in the octahedral sheet. The two IMV samples had much greater charge density than did the smectite samples, but they differed in the proportion of vermiculite present. Calculated from the elemental analyses, ~54% of the mass of IMV1 was composed of vermiculite layers whereas ~75% of the mass of IMV2 was composed of vermiculite.

Brij 35

Brij 35 (CAS # 9002-92-0) is a polyether surfactant with an aliphatic carbon chain and has a formula weight of 1198 g mol^{-1}. Brij 35 is thought to be biodegradable in natural environments (Shen, 2001) and has a low critical micelle concentration (CMC) that is reported to range from 4.3×10^{-5} mol L^{-1} (~52 mg L^{-1}) (Choy and Chu, 2001; Zhu and Feng, 2003) to 6.2×10^{-5} mol L^{-1} (~75 mg L^{-1}) (Yuan and Jafvert, 1997). Its toxicity is reported as 1000 mg kg^{-1} (oral rat LD_{50}) on the material safety data sheet of Sigma-Aldrich Chemical Company (www.sigmaaldrich.com). Brij 35 was obtained from the Sigma-Aldrich Chemical Company and used without further modification. A stock solution of 20 g L^{-1} was prepared by dissolving the surfactant in distilled,

Table 1. Calculated parameters of Ca-saturated smectites and interstratified mica-vermiculite samples.

Clay	Total layer charge	Tetrahedral charge	Octahedral charge	Formula weight	Calculated surface area	Surface charge density	Cation exchange capacity
	—— (moles(-)/formula unit) ——			(g mol^{-1})	(m^2 g^{-1})	(μmol(-) m^{-2})	(cmol(+)/kg)
Wyoming montmorillonite	0.36	0.10	0.26	365	764	1.31	100
$Ca_{0.18}(Si_{3.90}Al_{0.10})(Al_{1.55}Fe_{0.20}Mg_{0.24})O_{10}(OH)_2$							
Panther Creek smectite	0.34	0.15	0.19	370	757	1.28	96
$Ca_{0.17}(Si_{3.85}Al_{0.15})(Al_{1.44}Fe_{0.35}Mg_{0.21})O_{10}(OH)_2$							
IMV1 vermiculite	0.67	0.87	−0.20	391	751	2.39	174
$Ca_{0.34}(Si_{3.13}Al_{0.87})(Al_{0.39}Fe_{0.70}Mg_{1.46})O_{10}(OH)_2$							
IMV1 biotite	1.00	1.12	−0.12	402	N/A	N/A	N/A
$K_{1.01}(Si_{2.88}Al_{1.12})(Al_{0.03}Fe_{0.97}Mg_{2.05})O_{10}(OH)_2$							
IMV2 vermiculite	0.60	0.85	−0.25	390	765	2.06	151
$Ca_{0.30}(Si_{3.15}Al_{0.85})(Al_{0.32}Fe_{0.58}Mg_{1.79})O_{10}(OH)_2$							
IMV2 biotite	1.00	1.06	−0.06	410	N/A	N/A	N/A
$K_{1.00}(Si_{2.94}Al_{1.06})(Al_{0.02}Fe_{0.73}Mg_{2.27})O_{10}(OH)_2$							

N/A: not applicable

https://doi.org/10.1346/CCMN.2005.0530106 Published online by Cambridge University Press

deionized H_2O. Surfactant solutions with concentrations ranging from 0.020 to 5 g L^{-1} were made by volumetric dilution of the stock solution.

Sorption experiments

Sorption of the surfactant by clay minerals was carried out following batch equilibration procedures. Cation-saturated SWy and PC clays (100 mg) were weighed into 35 mL centrifuge tubes and a 10 mL aliquot of solution (0, 24, 61, 85, 168, 348, 500, 719, 896, 1205, 1816, 2554, 3767, 4448 mg L^{-1}) was added. For IMV samples, the mixtures comprised 50 mg of cation-saturated clay and 5 mL of surfactant solution. The suspensions were equilibrated on a reciprocating shaker at 180 cycles min^{-1} at room temperature (~22ºC) for 24 h. After equilibration, the mixtures were centrifuged for 10 min at $5989 \times g$, and clear supernatant liquids were collected; 3 mL aliquots of clear supernatant liquid were analyzed for surfactant concentration by a spectrophotometric iodine-iodide assay, which is based on the change in absorbance when ethylene oxide units form complexes with both I_2 and I_3^- ions in solution (Brown and Jaffe, 2001). The amount of surfactant adsorbed by clay was calculated as the difference between the initial and final surfactant concentrations. Clay remaining in the centrifuge tubes was reserved for the succeeding desorption experiment. Each experiment was replicated three times.

Desorption experiment

To explore the desorbability of surfactant from the clay samples, deionized, distilled water was added to each clay sample from the sorption study (10 mL for SWy and PC clays; 5 mL for IMV1 and IMV2). The samples used in the desorption study were selected from the high end of the adsorption isotherms, where sorption was close to the maximum obtained in the experiments. The suspension was shaken briefly with a Vortex mixer, and then equilibrated on a reciprocating shaker at 180 cycles min^{-1} for 24 h. After centrifugation, surfactant concentrations were measured in the supernatant liquids by the I-I assay. The washing procedure was repeated once more. The amount of surfactant desorbed in each washing step was subtracted from the amount of surfactant initially sorbed. Corrections to the amount of surfactant in the entrained solution not removed in the previous step were included in the calculations.

X-ray diffraction

For X-ray diffraction (XRD) studies, clays were equilibrated with selected concentrations of surfactant at the same time as the sorption experiments. After shaking for 24 h, suspensions were mounted by suction onto ceramic tiles, air dried for ~3 h, and transferred to a desiccator over a saturated solution of $Mg(NO_3)_2$ for equilibration at 54% relative humidity prior to XRD analysis. The d_{001} basal spacings of the clays with or without surfactant treatment were measured by using a Siemens D500 diffractometer operating at 50 kV and 27 mA with CuKα radiation. Measurements were carried out in step-scanning mode; each step of 0.05º2θ was counted for 2 s.

Fourier transform infrared (FTIR) analysis

Clays equilibrated with various concentrations of surfactant were air dried and powdered in a Wig-L-Bug (Crescent Dental Manufacturing Co., Chicago Ill.). The Wig-L-Bug was thoroughly washed and rinsed with acetone between samples to avoid cross contamination. Clay samples were mixed with spectroscopic grade KBr on a 1:10 weight ratio (clay:KBr), weighed into FTIR micro sampling cups, and analyzed using a Nicolet Magna-IR spectrometer in the diffuse-reflectance infrared Fourier transform (DRIFT) mode. The optical bench was constantly flushed with a stream of dry air to purge the system of CO_2 and moisture. Each sample was run at 300 scans with a resolution of 4 cm^{-1}.

RESULTS

Adsorption isotherms

The adsorption characteristics of Brij 35 varied among the clay samples. The adsorption isotherms for SWy and PC smectites could be fit to the linearized Langmuir adsorption model:

$$\frac{Ce}{(x/m)} = \frac{1}{ab} + \frac{1}{a} Ce \qquad (1)$$

where Ce is the equilibrium concentration of surfactant in solution (g L^{-1}), x/m is the amount of surfactant sorbed per unit weight of sorbent (g kg^{-1}), a is a constant that reflects the sorption capacity (g kg^{-1}), and b is an index of sorption energy (L g^{-1}).

The capacity and intensity of sorption by SWy clay varied with the type of cation saturating the clay. Brij 35 sorption was greater by Ca-SWy than by K-SWy (Figure 1a), with calculated sorption maxima at 232 and 196 g kg^{-1}, respectively (Table 2). In both systems, there was a sharp increase in adsorption at low equilibrium surfactant concentrations ($\leqslant$ 0.20 g L^{-1}), but eventually sorption reached a plateau.

The ideal Langmuir adsorption model assumes that there is no interaction between sorbate molecules on the surface and that sorption occurs in a monolayer on the surface. It is further assumed that once the surfactant occupies a site, no further sorption can take place at that site. According to Rosch (1967), polyoxyethylene surfactants normally occur in either the extended-chain (zig-zag) morphology (<9 ethoxide links in the chain) or in the coiled 'meander' configuration (>9 ethoxide links). In the meander configuration, each oxyethylene unit has an average length of ~2 Å and width of ~4 Å. Thus, in the meander configuration, the length of the

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Table 2. Langmuir sorption parameters for the isotherms of Brij 35 sorption on smectites.

Clay	Maximum adsorption (a) (g kg^{-1})	Sorption intensity (*b*) (L g^{-1})	Regression coefficient (R^2)
K-SWy	196	5.7	0.96
Ca-SWy	232	7.2	0.95
K-PC	238	5.2	0.94
Ca-PC	256	5.6	0.96

ethoxy portion of a surfactant homolog with 23 oxyethylene units would be ~46 Å, and the total length (including the alkyl chain (~1.25 Å per CH_2 unit)) would be ~62 Å. The calculated surface area of the SWy clay was 764 m^2 g^{-1} (Table 1). Given these dimensions and the formula weight of the surfactant, a monolayer of surfactant on all SWy basal surfaces would require 613 g surfactant kg^{-1} clay. The maximum sorption capacity estimated from the Langmuir model for Ca-SWy was only 232 g kg^{-1}, so surface coverage was <40% of the total surface area at the calculated sorption maximum for the meander configuration.

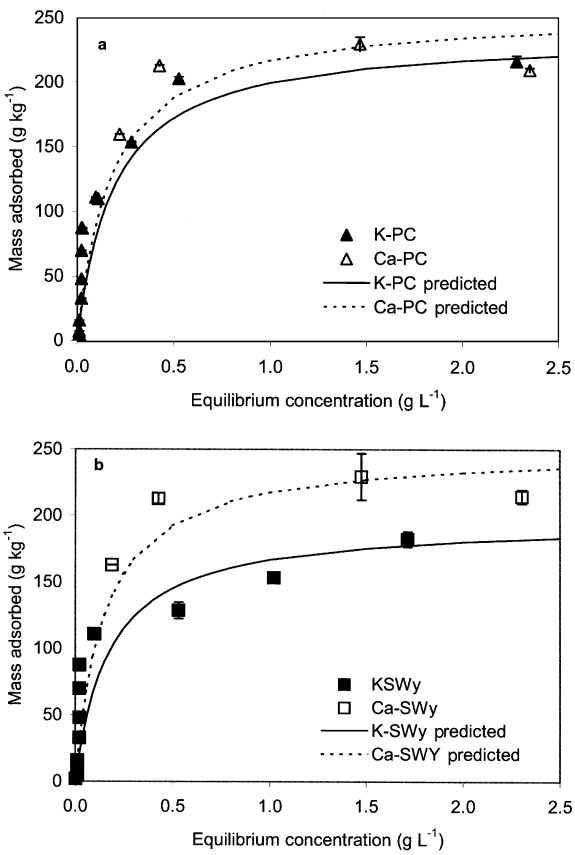


Figure 1. Adsorption of Brij 35 on K- and Ca-saturated SWy (a) and PC (b). Solid lines are predicted sorption values using the linearized Langmuir adsorption model. Error bars represent the standard deviation from the mean.

Surfactant sorption isotherms for K-PC and Ca-PC clay were similar to those of the SWy clay (Figure 1b), with sorption maxima of 238 and 256 g kg^{-1}, respectively (Table 2). Isotherms of both cation saturations fit well with the Langmuir equation, with a goodness of fit >94% (Table 2). The L-type isotherms indicated strong interaction between the surfactant and the surface and suggested that sorption was dependent on the properties of both the sorbent (clay) and sorbate (Giles *et al.*, 1960; McBride, 1994).

Sorption isotherms of Brij 35 on IMV1 and IMV2 are depicted in Figure 2. Over the range of concentrations used, the largest amounts of surfactant sorbed by K- and Ca-saturated IMV clays were about 100 and 150 g kg^{-1}, respectively (Figure 2a). Surfactant sorption by K- and

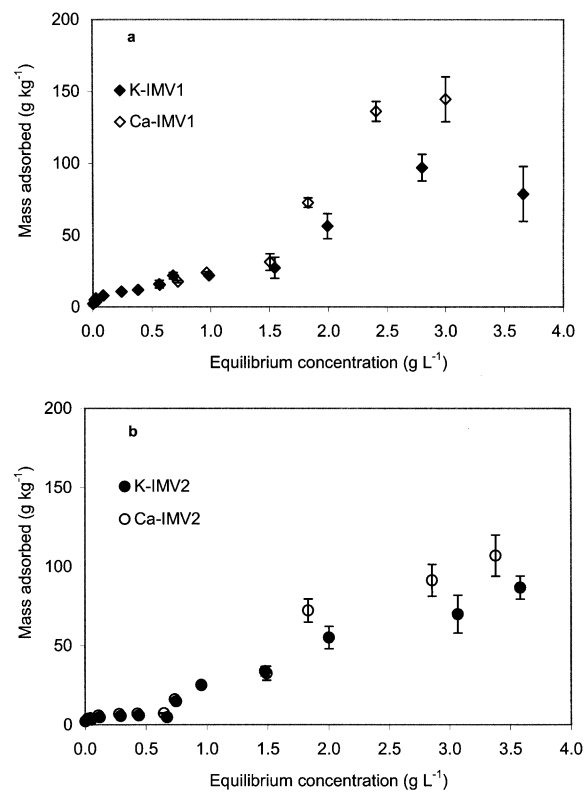


Figure 2. Adsorption of Brij 35 on K- and Ca-saturated IMV1 (a) and IMV2 (b). Error bars represent the standard deviation from the mean.

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Table 3. Desorbability of Brij 35 from clays with distilled, deionized water.

Clay	Surfactant initially sorbed (g kg^{-1})	Surfactant removed First wash (g kg^{-1})	Surfactant removed Second wash (g kg^{-1})	Surfactant remaining with clay* (%)
K-SWy	153	24	23	69
Ca-SWy	213	30	45	65
K-PC	203	21	38	71
Ca-PC	213	26	28	75
K-IMV1	97	46	1	51
Ca-IMV1	145	67	1	53
K-IMV2	87	48	1	44
Ca-IMV2	108	54	2	49

* after the second wash and relative to amount of surfactant initially sorbed

Ca-saturated IMV2 was ~80 and 100 g kg^{-1}, respectively, at the high end of the concentration range studied (Figure 2b). The roughly S-shaped sorption isotherms in the IMV systems indicated that sorbent-sorbate interaction did not conform to the Langmuir model. S-shaped isotherms describe stronger interactions among surfactant molecules than between surfactant molecules and clay surfaces (cooperative sorption) (McBride, 1994).

Desorption of surfactant from clays

Desorption of surfactant from the clays was studied by washing the surfactant-treated clays with deionized water twice (Table 3). During the first wash, the surfactant was more resistant to desorption from SWy and PC clays than from the IMV clays. After the first wash, the smectites retained $\geqslant$85% of the initially sorbed surfactant. Surfactant retention decreased to 65–75% after the second wash. In the IMV clays, the first wash desorbed ~50% of retained surfactant, but very little more was desorbed by the second wash.

X-ray diffraction

X-ray diffraction was used to investigate whether the surfactant could be intercalated in the interlayer region of each clay. The basal spacing values (d_{001}) of oriented, cation-saturated samples at various concentrations of Brij 35 are noted on the XRD patterns in Figures 3 and 4. The d_{001} values of both K-saturated smectites increased as more surfactant was sorbed. In K-SWy, the d_{001} value of the clay increased from 11.1 Å with no surfactant added to ~12 Å with 87 g kg^{-1}; it increased to 17.5 Å when the clay sorbed surfactant at 188 g kg^{-1} (Figure 3a). A similar gradual increase in d value occurred with the K-PC. In Ca-SWy, the d_{001} value without surfactant treatment and with 87 g surfactant kg^{-1} clay was invariant at 14.7 Å, but it increased to 17.5 Å when the clay sorbed ~229 g of surfactant kg^{-1}.

The basal spacings of the IMV samples were not altered by surfactant sorption (Figure 4). In the K-saturated IMV samples, the basal spacing remained at 10 Å regardless of the level of surfactant sorption. The Ca-IMV1 clays had a basal spacing of ~12 Å at all levels of sorbed surfactant (Figure 4a), and the Ca-IMV2 samples had d values of 14.4 and 12.4 Å (Figure 4b).

FTIR analysis

Infrared spectroscopy can detect interactions between nonionic surfactants and clay surfaces by providing information on the perturbation of functional groups of sorbed molecules. The FTIR pattern of Brij 35 in Figure 5 is consistent with the polyoxyethylene infrared (IR) peaks reported by Bailey and Koleske (1976). The IR bands at 2870–2900 cm^{-1} correspond to C–H

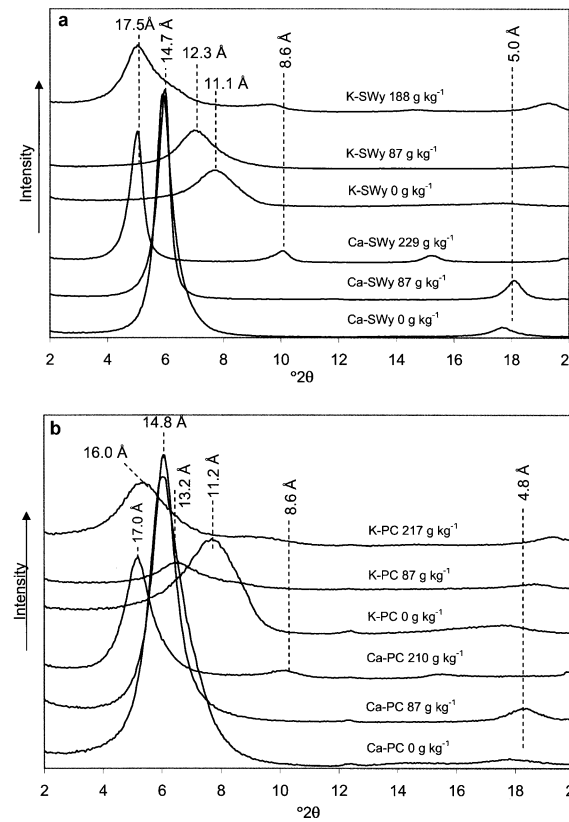


Figure 3. XRD patterns of K- and Ca-saturated SWy (a) and PC (b) at various levels of sorbed Brij 35.

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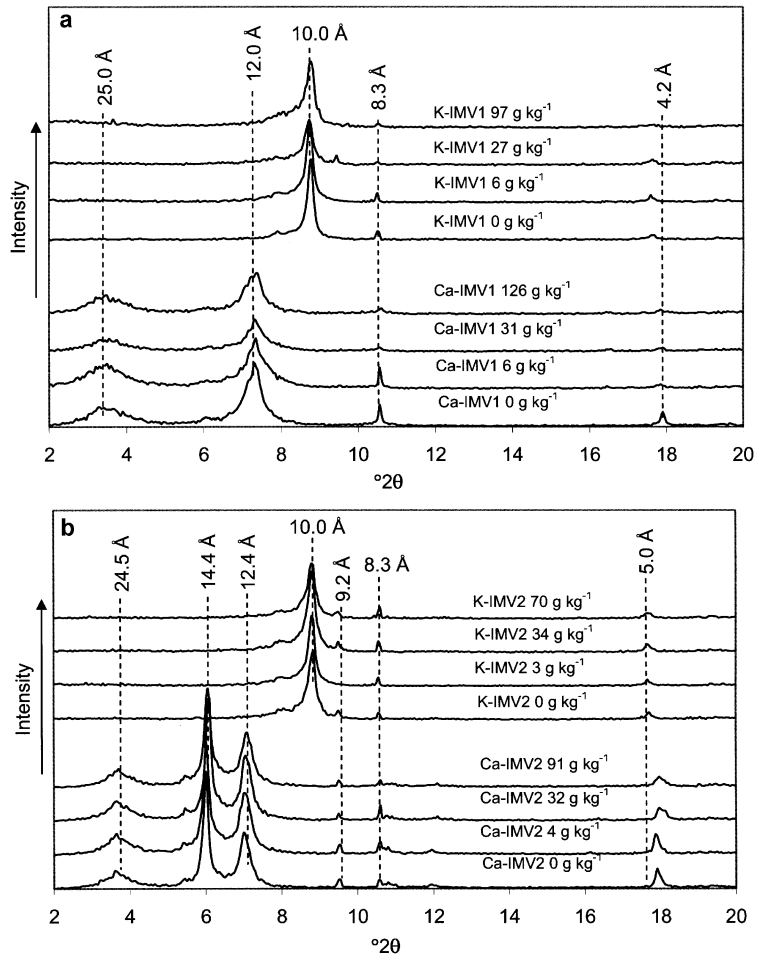


Figure 4. XRD patterns of K- and Ca-saturated IMV1 (a) and IMV2 (b) at various levels of sorbed Brij 35.

stretch of CH_2 groups, and a band at ~1470 cm^{-1} is associated with C–O stretching in the ethylene oxide chain of the surfactant. The small but distinct peak at ~3450 cm^{-1} is probably due to the stretching vibration of adsorbed water molecules and to the terminal OH group of surfactant molecules (Deng *et al.*, 2003).

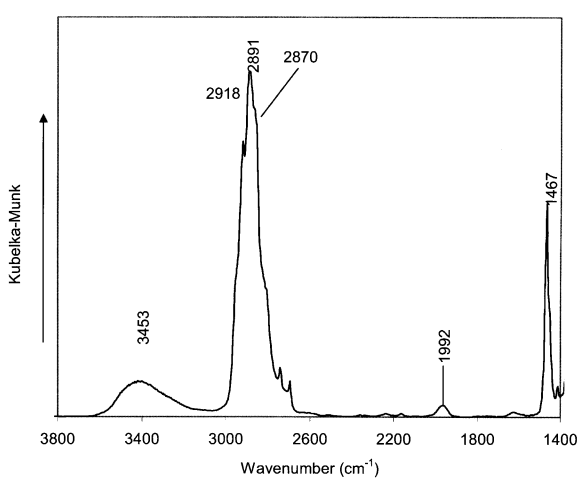


Figure 5. DRIFT spectrum of neat Brij 35.

The IR spectra of surfactant-treated SWy and PC clays are shown in Figures 6a and b, respectively. Distinct peaks occurred in the 2800–2950 cm^{-1} region in all the smectite samples that were treated with surfactant, reflecting the C–H stretch of the alkyl groups of the surfactant molecule. In the untreated Ca-saturated smectites, an IR band at ~1630 cm^{-1}, corresponding to the OH-bending vibration of water molecules solvating the interlayer cation was observed, but it did not occur in the K-saturated smectites. The greater intensity of the water deformation band in Ca systems indicated that these clays retained more interlayer water molecules, probably due to higher hydration energy of Ca^{2+} compared to K^+. The intensity of the 1630 cm^{-1} band diminished somewhat with surfactant adsorption, and the intensity of the 1470 cm^{-1} band increased, indicating replacement of water molecules by the EO groups of Brij 35 molecules. However, water displacement was apparently not complete, because small but distinct water-deformation bands were still evident at

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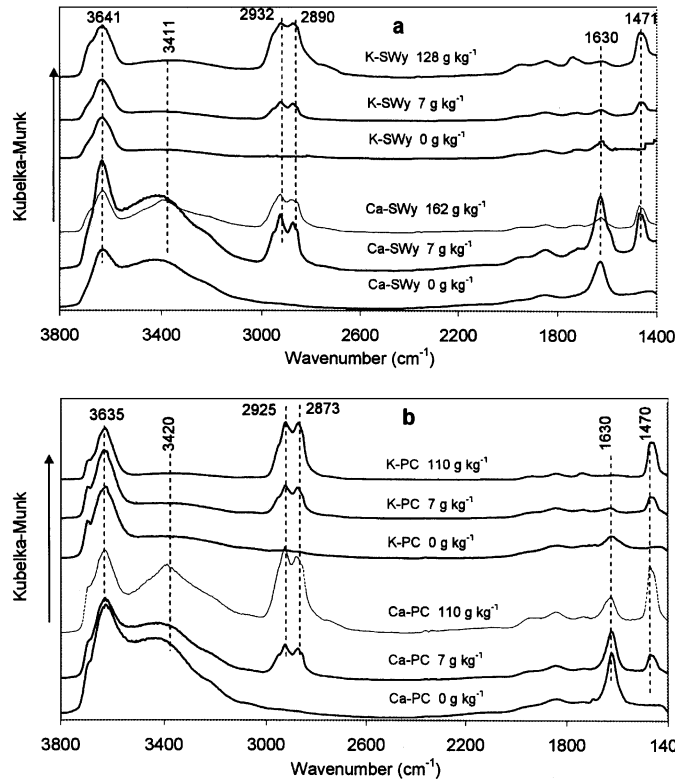


Figure 6. DRIFT spectra of K- and Ca-saturated IMV1 (a) and IMV2 (b) at various levels of sorbed Brij 35.

high levels of sorbed surfactant. Consistent with the formation of an incomplete monolayer on the smectite surfaces, surfactant molecules probably had limited access to interlayer regions distant from the layer edges, as also observed by Deng *et al.* (2003).

In contrast to the smectite samples, the presence of very low concentrations of sorbed surfactant could not be detected by the FTIR analysis of the IMVs (Figure 7). But the alkyl bands of the surfactant as well as the C–O stretching band of the ethylene oxide chain were clear at sorbed concentrations >70 g kg^{-1}. The response of the water bending band to sorption of surfactant did not show a consistent trend in the IMV systems (Figure 7a,b).

DISCUSSION

Sorption of nonionic molecules such as Brij 35 by clay surfaces can arise by several mechanisms that are difficult to distinguish from one another. Surfactant moieties (such as electronegative oxygens in the oxyethylene groups) may coordinate directly with water molecules that surround the saturating cation (Ottewil, 1967). The ether oxygen gives the ethylene oxide chain a polar character because of its unpaired electrons, allowing coordination with cations.

Surfactant sorption could also involve either van der Waals interactions between the alkyl chain of the surfactant and portions of the clay surface with low charge density (where water molecules would be rare) or hydrogen bonding between the surfactant and basal plane oxygen atoms (Somasundaran *et al.*, 1991; Xu *et al.*, 1991). The increase in entropy that accompanies displacement of near-surface water molecules by long-chain polymers can itself be a major driving force for sorption (Bailey and Koleske, 1976; Theng, 1982).

Because these mechanisms occur at the same time and are closely related to one another, their relative importance is difficult to establish. The sorption of surfactants by clay surfaces is also complicated by the presence of surfactant micelles with structures in which the alkyl groups associate with each other while the polyoxyethylene tails interact with solvent water molecules (Chin *et al.*, 1996). Retention of intact micelles at clay surfaces or in nanopores between quasicrystals is thus possible.

At low initial concentrations of surfactant, sorption to both smectites was strong, yet it was unrelated to cation saturation (Figure 1). Moreover, at this stage, intercalation of the surfactant occurred only with the K-saturated clays (Figure 3). Had the primary mechanism of sorption been displacement of water molecules from the hydration sphere of the cations, we might have predicted that retention by the K-saturated clay would be greater than by the Ca-saturated clay because of the lower energy of hydration of K. The FTIR evidence in Figure 6 also

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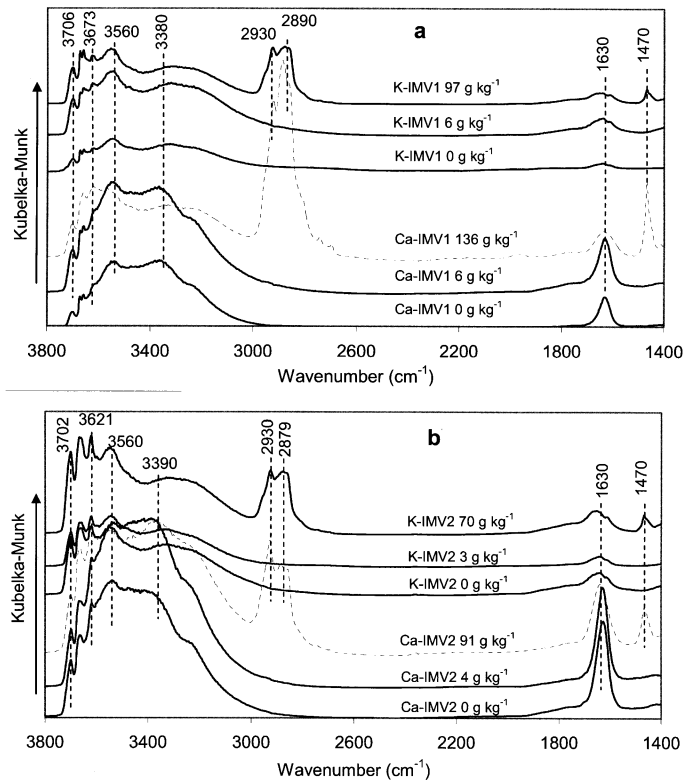


Figure 7. DRIFT spectra of K- and Ca-saturated SWy (a) and PC (b) at various levels of sorbed Brij 35.

suggests that at low sorption levels, water molecules were not significantly displaced by the surfactant. The lack of impact of the saturating cation favors the interpretation that van der Waals interactions, H bonding, or micelle entrapment were important mechanisms in sorption to smectites at low surfactant concentrations.

Inspection of Figure 1 indicates that ~30–50% of the sorption maximum of the smectites was reached before the sorption intensity started to level off at >90 g of surfactant kg^{-1} of clay. If physical entrapment of micelles played a major role in sorption, then we might predict that the desorption treatments would readily remove that portion of the sorbed surfactant. Yet only 23–30% of the surfactant was removed in the two desorption treatments, suggesting that some surfactant was retained by a mechanism stronger than physical entrapment. We hypothesize that the alkyl chains of the surfactant could be retained by van der Waals forces at locations on the smectite surfaces where charge was weakly expressed. The observation of greater sorption intensity by the smectite with the greater octahedral charge (SWy) is consistent with this hypothesis (Table 2).

In general, the maximum value of surfactant sorption was less for the two IMVs than for the smectites. In the case of the IMVs, d_{001} values were not altered with surfactant sorption, indicating that surfactant molecules did not enter the interlamellar regions of the clay, even at high surfactant concentrations. Diffusion of surfactant into the interlayers was physically constrained because the high layer charge maintained collapsed layers in both Ca- and K-IMV clays. Therefore, sorption must have occurred only at external surfaces.

Significant sorption to the IMV samples did not begin until the initial surfactant concentration was ~2000 mg L^{-1} (equilibrium concentrations of ~1.5 g L^{-1}). As noted above, the shape of the isotherms for the IMV samples suggested a cooperative mechanism by which significant sorption only occurred after a 'critical mass' of surfactant retained near the clay surface was large enough to attract more surfactant molecules to form sorbed micelles (Fuerstaneau, 1970).

Surfactant desorption was faster from the IMVs than from the smectites, and after two water washes the smectites retained a larger fraction of the initially sorbed surfactant than did the IMV clays. Still, the surfactant molecules that did remain with the IMV samples after one desorption treatment seemed to be strongly sorbed. Shen (2001) also noted retention of >80% of sorbed nonionic surfactants on bentonite after seven washes with deionized water. The stability of surfactant on clay surfaces could be influenced by the size of the Brij 35 molecules. Parfitt and Greenland (1970) suggested that high-molecular-weight polyethylene oxides (>2000 g mol^{-1}) are less likely than smaller molecules to be desorbed from Ca-saturated montmorillonite

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because the longer ethoxy chains afford more points of van der Waals contact between the polymer and the clay surface. In their study, polyethylene oxides with low molecular weight (300 g mol^{-1}) were easily desorbed. Having a formula weight of 1198 g mol^{-1}, the resistance of Brij 35 to being released from clay surfaces may be beneficial if surfactant-modified clays are employed in environmental applications because it may limit secondary release of residual, aqueous-phase surfactants.

By using the X-ray data and dimensions of the polyoxyethylene chain, we may postulate the arrangement and orientation of the surfactant on the smectite surfaces. After sorption, the basal *d* value of the Ca-smectites was 17–17.5 Å, reflecting an interlayer *z*-axis dimension of ~7.4–7.9 Å, assuming that the smectite layer is 9.6 Å thick. This space would be sufficient to hold as many as three layers of surfactant with the polyethylene chain in the zig-zag (extended) configuration (chain width = ~2 Å) but only one layer with the chain in the more compact meander configuration (chain width = ~4 Å). Although Theng (1982) reported that polymers tend to uncoil and spread out when sorbed at clay surfaces (favoring the zig-zag configuration of Brij molecules in the interlayer), maximum sorption by Ca-SWy corresponded to coverage of <40% of the total interlayer surface area by Brij 35 molecules. This observation favors the interpretation that the surfactant molecules retained the meander conformation upon sorption.

For the K-saturated smectites with intercalated surfactant, the broad XRD peaks with *d* values of <16 Å are assumed to represent random layer stacks with interlayers that are incompletely filled or filled with only one surfactant layer.

The FTIR data for both smectites and IMV clays showed diminishing intensity of water deformation bands with increasing surfactant sorbed; but the water bands did not totally disappear even at high levels of sorption. This observation indicates that surfactant molecules were not able to displace all water molecules. One plausible scenario is that the large molecules of sorbed Brij 35 blocked access of additional surfactant molecules to more interior interlayer binding sites. This interpretation would also be consistent with the calculation that <40% of the total surface area of the Ca-SWy was covered by surfactant molecules at maximum sorption.

CONCLUSIONS

The sorption behavior of clays with Brij 35 differed between the smectites and interstratified mica-vermiculites. Surfactant molecules intercalated in the smectite layers but interlayer sorption was not evident in the IMV clays. For the smectites, a combination of sorption mechanisms, including displacement of water molecules, van der Waals interactions, and H-bonding were probably involved over the entire range of the sorption isotherm. In contrast, sorption by IMV clays was attributed to the retention of surfactant micelles at clay surfaces. For environmental applications, knowledge about the interaction of surfactants such as Brij 35 with clay minerals is of special significance. Although the present study does not identify a single mechanism of interaction between Brij 35 and clay surfaces, our observations may further the understanding of the fate of this surfactant in the presence of different clays. It is important to note that in the soil environment, a variety of exchange and sorption sites will be present because an assortment of minerals is likely. Surfactant components are likely to interact differentially with these sites.

ACKNOWLEDGMENTS

We acknowledge the contribution of the late Dr V.P. Evangelou to the original conceptualization of this research project. We also recognize the analytical assistance of P. Fleming, D.A. Laird and S. Schlorholtz as well as useful discussions with M.A. Chappell. This work was supported by United Agri Products (UAP), Greeley, Colorado, and the Iowa Agricultural and Home Economics Experiment Station.

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(*Received 6 April 2004; revised 27 July 2004; Ms. 900; A.E. William F. Jaynes*)

https://doi.org/10.1346/CCMN.2005.0530106 Published online by Cambridge University Press