

Cosorption of Atrazine and a Lauryl Polyoxyethylene Oxide Nonionic Surfactant on Smectite

MARK A. CHAPPELL,^{*,†} DAVID A. LAIRD,[‡] MICHAEL L. THOMPSON,[†] AND
 V. P. EVANGELOU[§]

Department of Agronomy, Agronomy Hall, Iowa State University, Ames, Iowa, 50011, and National Soil Tilth Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Ames, Iowa, 50011

Commercial atrazine formulations commonly contain nonionic surfactants that serve as solubilizing and wetting agents for enhancing the stability and efficacy of the herbicide. The fate of atrazine in soils has been extensively investigated; yet, few studies have considered the effects of formulation components on the fate of atrazine in soils. In this study, we investigated the influence of the nonionic surfactant, Brij 35 (Brij), on the sorption of atrazine on Ca- and K-saturated samples of a reference smectite, Panther Creek (PC). In general, Brij concentrations of 50 and 200 mg L⁻¹ had little effect on atrazine sorption, but sorption was substantially inhibited by Brij concentrations of 2100 mg L⁻¹. For Brij concentrations of 6300 mg L⁻¹, atrazine sorption was intermediate between that observed for the 200 and 2100 mg L⁻¹ Brij systems. Brij molecules themselves were very strongly sorbed by PC, with sorption maxima exceeding 200 g kg⁻¹. X-ray diffraction analysis of Brij-treated PC indicated that the sorbed Brij was intercalated into interlayers of the smectite. At Brij concentrations of 2100 mg L⁻¹, Brij competed with atrazine for interlayer sorption sites. In contrast, at the initial Brij concentration of 6300 mg L⁻¹, the clay interlayers were largely filled with Brij, and excess Brij probably accumulated on external surfaces of the clay as surface micelles. We hypothesize that atrazine partitioning into surfactant micelles on external surfaces of the clay led to enhanced retention by the solid phase.

KEYWORDS: Pesticide formulations; atrazine; PEO surfactants; Brij 35; smectite; crystalline swelling; sorption

INTRODUCTION

Pesticide formulations contain adjuvants, a heterogeneous collection of substances that promote the distribution and bioactivity of the toxicant. Depending on the type of formulation, adjuvants may include solvents, cosolvents, emulsifiers, wetting agents, dispersing agents, antifreezing agents, and inert support materials (1). Next to the solvents, nonionic surfactants make up the largest group of adjuvants in pesticide formulations (2 and references therein).

Surfactants and other adjuvants may influence the sorption of pesticides. A number of studies published over the past decade demonstrated the impact of surfactants on sorption of nonpolar organic compounds (NOC) on clays. Jaynes and Boyd (3) and Sheng et al. (4) showed that sorption of NOCs by smectites could be enhanced by loading the clay with cationic, alkylammonium surfactants. NOC sorption on these organically modified smectites was related to the extent of surface coverage

by the cationic surfactant as well as to the orientation of the surfactant on the surface. In contrast, conflicting evidence suggests that nonionic surfactants both enhanced (5, 6) and suppressed (6) NOC sorption. NOC sorption may be inhibited by competition from nonionic surfactant micelles in solution if the quantity of surfactant in solution exceeds its critical micelle concentration or CMC (6). However, mechanistic explanations and experimental evidence documenting conditions under which nonionic surfactants could either enhance or suppress NOC sorption is lacking.

Atrazine [2-chloro-4-(ethylamino)-6-isopropylamino-1,3,5-triazine] is applied to soils for preemergent control of weeds in corn and sorghum production. The worldwide use of atrazine has prompted a substantial amount of research on its sorption by clays and soils (see a comprehensive review by 7). However, most of this research involved reagent-grade atrazine prepared in aqueous solutions or aqueous solutions with cosolvents (such as ethanol). The effects of the nonionic surfactants found in herbicide formulations on sorption have only rarely been considered, and studies are inconclusive. For example, Abu-Zrieg et al. (8) and Iglesias-Jiminez et al. (9) reported enhanced atrazine sorption by soil in the presence of nonionic surfactants

* To whom correspondence should be addressed. E-mail: machap@iastate.edu.

[†] Iowa State University.

[‡] U.S. Department of Agriculture.

[§] Deceased.

(Rexonic, Rexol, and Tween 80). However, other studies have shown that nonionic surfactants enhanced atrazine's mobility in soils and clays (10–12), suggesting that the surfactant inhibited sorption. In part, these apparent discrepancies may arise from the sequence of atrazine and surfactant addition (10), i.e., whether atrazine and the surfactant are added simultaneously or sequentially. Clearly, there is a need for greater understanding of how nonionic surfactants influence the fate of atrazine in soils.

Panther Creek (PC) smectite is a reference smectite similar to smectites commonly found in many soils. In a previous paper (13), atrazine sorption was found to be much larger for K-saturated PC (K-PC) than for Ca-saturated PC (Ca-PC) samples. Furthermore, more atrazine was sorbed by K-PC samples that had been air-dried and rehydrated than by K-PC samples that had never been dried. Enhanced sorption of atrazine with K saturation and the drying treatments was attributed to collapse of the smectite interlayers, which created a more favorable environment for atrazine. The purpose of this paper is to elucidate the mechanisms by which a nonionic surfactant, similar to that used in pesticide formulations (14), influences atrazine sorption by PC.

MATERIALS AND METHODS

Reagents. Atrazine (99% purity) was obtained from Chem Service (West Chester, PA). The nonionic surfactant was a polydisperse, lauryl polyoxyethylene (PEO) known as Brij 35 (Brij). Brij has a hydrophobic aliphatic group ($-\text{CH}_2-$)_n and a hydrophilic linear chain containing an average of 23 ethylene oxide (EO, where EO = OCH_2CH_2) groups. Brij (>99% purity, specific gravity = 1.02 g cm^{-3}) was obtained from Sigma Chemical Co. (St. Louis, MO) and stored at -20°C after opening to limit oxidation. Both chemicals were used as received. ACS-certified dimethyl sulfoxide (DMSO), methanol (MeOH), and acetonitrile were obtained from Fisher Scientific (Madison, WI). MeOH and acetonitrile were high-performance liquid chromatography (HPLC) quality.

Clay Preparation. The PC bentonite ore was obtained from the A. D. Scott collection at Iowa State University. Details of the procedures used to prepare the PC samples were given elsewhere (13). To summarize, the clay fraction ($<2 \mu\text{m}$) of a Na-saturated PC suspension was dialyzed against 100 mM CaCl_2 or 200 mM KCl to saturate clay samples with Ca^{2+} or K^+ . Then, the suspensions were dialyzed against 5 mM CaCl_2 and 10 mM KCl to remove excess salt. One portion of each Ca-PC or K-PC sample was stored as a suspension at 4°C until used; these samples are referred to in this paper as the “never-dried” (ND) samples. Another portion of the Ca-PC and K-PC samples was air dried, crushed in an agate mortar, resuspended in water, and finally dialyzed against dilute 5 mM CaCl_2 or 10 mM KCl solutions. This second sample was stored as a suspension at 4°C until used and is referred to in this paper as the “air-dried” (AD) sample.

Influence of Brij on Atrazine Sorption. Before the sorption experiments were conducted, aqueous atrazine/atrazine-Brij solutions were prepared as follows: 3 mg of solid atrazine was dissolved in 4 mL of MeOH. Portions of the dissolved atrazine solution were added to 100 mL volumetric flasks, containing either deionized water or different concentrations of aqueous Brij, and then diluted to volume with deionized water. Aqueous atrazine/atrazine-Brij emulsions were prepared at least 2 h before use.

Cation-saturated PC clay suspensions and dilute electrolyte were added to 30 mL Teflon tubes to achieve a solid–solution ratio of 12.5 mg mL^{-1} (or 250 mg of solids) and 10 mM CaCl_2 or 20 mM KCl background electrolyte. Aqueous or Brij-emulsified atrazine was added to the tubes, giving initial atrazine concentrations ranging from 2.1 to 10.5 mg L^{-1} and initial surfactant concentrations of 0, 50, 200, 2100, and $6300 \text{ mg Brij L}^{-1}$. The systems were equilibrated on a rotary shaker (70 rpm) for 24 h at room temperature. The clay suspensions were centrifuged (6722g for 10 min), and the clear supernatant was analyzed for atrazine by HPLC as described below. The amount of atrazine sorbed was calculated as the difference between the amount of atrazine

initially added to the system and the amount of atrazine found in the solution phase at equilibrium.

To assess whether any of the sorbed atrazine was degraded during the equilibration, the clay samples were extracted with a 60:40 mixture of DMSO and 10 mM CaCl_2 [adjusted to pH 9.5 using saturated $\text{Ca}(\text{OH})_2$]. The clay samples were resuspended in the extractant by vortexing for 30 s and then equilibrated for 1 h on a rotary shaker. After centrifugation (6722g for 10 min), the supernatant was decanted and analyzed by HPLC for atrazine and atrazine degradation products (hydroxyatrazine, desethylatrazine, and desisopropylatrazine). The extraction procedure was repeated three times for each sample. The recovery of atrazine by this procedure was only qualitative (average recovery of 77%, ranging from 27 to 148%); however, the only purpose of the procedure was to look for evidence of atrazine degradation, and no degradation products were detected in the extracted solutions.

Atrazine Analysis. Atrazine concentrations were quantified by reverse phase (RP) HPLC as detailed previously (13). Analysis of standards prepared with Brij 35 concentrations both above and below the CMC demonstrated that the surfactant had no impact on the separation and detection of atrazine by this method.

Brij Adsorption Experiments. Aliquots of cation-saturated ND or AD PC suspensions were added to triplicate 30 mL Teflon tubes containing 10 mM CaCl_2 or 20 mM KCl (to produce a solid–solution ratio of 12.5 mg mL^{-1}). A 2% (w/v) micellar Brij stock solution was prepared and stored at 4°C when not in use. Aliquots of the stock solution were added to the Teflon tubes to give Brij concentrations ranging from 500 to 6500 mg L^{-1} in 20 mL. Tubes were then capped and equilibrated on a rotary shaker at 70 rpm for 24 h. Afterward, the tubes were centrifuged at 10000 rpm (6486g) for 10 min. The quantity of surfactant in the supernatant was determined as described below. The mass of Brij in solution was calculated from the mole ratio of carbon in the surfactant. Sorbed Brij was calculated by the difference.

Brij Analysis. Aqueous Brij concentrations were determined by dissolved carbon analysis (15, 16). Carbon in solution was measured from HCl-acidified samples using a Shimadzu TOC 5050 dissolved C analyzer (Shimadzu Scientific Instruments, Inc., Columbia, MD) by Pt-catalyzed oxidation at 680°C with high-quality, carbon-free air. Samples were not sparged during analysis to prevent the surfactant from foaming and spilling into the sample chamber. Analytical tests demonstrated that the form of Brij polymers in solution, whether in monomers or micellar, did not impact dissolved carbon analysis.

X-ray Diffraction (XRD) Analysis. Aqueous suspensions of Ca-PC equilibrated with 0, 2100, and 6300 mg L^{-1} Brij were vacuum-filtered onto ceramic tiles, oven-dried at 100°C for 2 h to remove interlayer water, and cooled in a desiccator over anhydrous silica desiccant. Afterward, the samples were analyzed by XRD under a gentle stream of desiccated air to prevent rehydration. XRD analysis was performed using a Siemens D5000 diffractometer operating at 40 kV and 30 mA with $\text{CuK}\alpha$ radiation, a solid state detector, and θ – θ goniometer. Measurements were carried out in step-scanning mode; each step of $0.05^\circ 2\theta$ was counted for 2 s.

In separate analyses, the aqueous suspensions of cation-saturated PC equilibrated with 0– 6000 mg L^{-1} Brij were analyzed by suspension XRD using a liquid sample cell mounted in transmission mode (17). The analysis was performed as described previously except that the scanning rate was 0.1 and $0.05 \text{ deg min}^{-1}$ for Ca-PC and K-PC samples, respectively.

Calculating Interlayer Volumes Filled with Brij. The total surface area ($619 \text{ m}^2 \text{ g}^{-1}$) was calculated using the PC structural formula (18) and elemental concentrations given by Laird et al. (19). The structural formula of PC was determined as $\text{Ca}_{0.34}^{2+}\text{K}_{0.13}^{+}(\text{Si}_{7.59}^{4+}\text{Al}_{0.41}^{3+})(\text{Al}_{2.72}^{3+}\text{Fe}_{0.76}^{3+}\text{Mg}_{0.40}^{2+}\text{Ti}_{0.09})\text{O}_{20}(\text{OH})_4$.

The interlayer volume of the various PC samples was calculated by multiplying surface area by the measured *d*-spacing (in the absence of Brij) less the unit-layer thickness (0.96 nm) and dividing by 2. The volume of sorbed Brij was calculated by dividing the quantity of sorbed Brij (mg kg^{-1}) by the specific gravity of Brij (1.02 g cm^{-3}). Here, the specific gravity of Brij was used to represent the upper limit of Brij packing density in the smectite interlayers. An approximate value for the relative interlayer volume filled was estimated from the ratio of the volume occupied by the sorbed Brij to the interlayer volume.

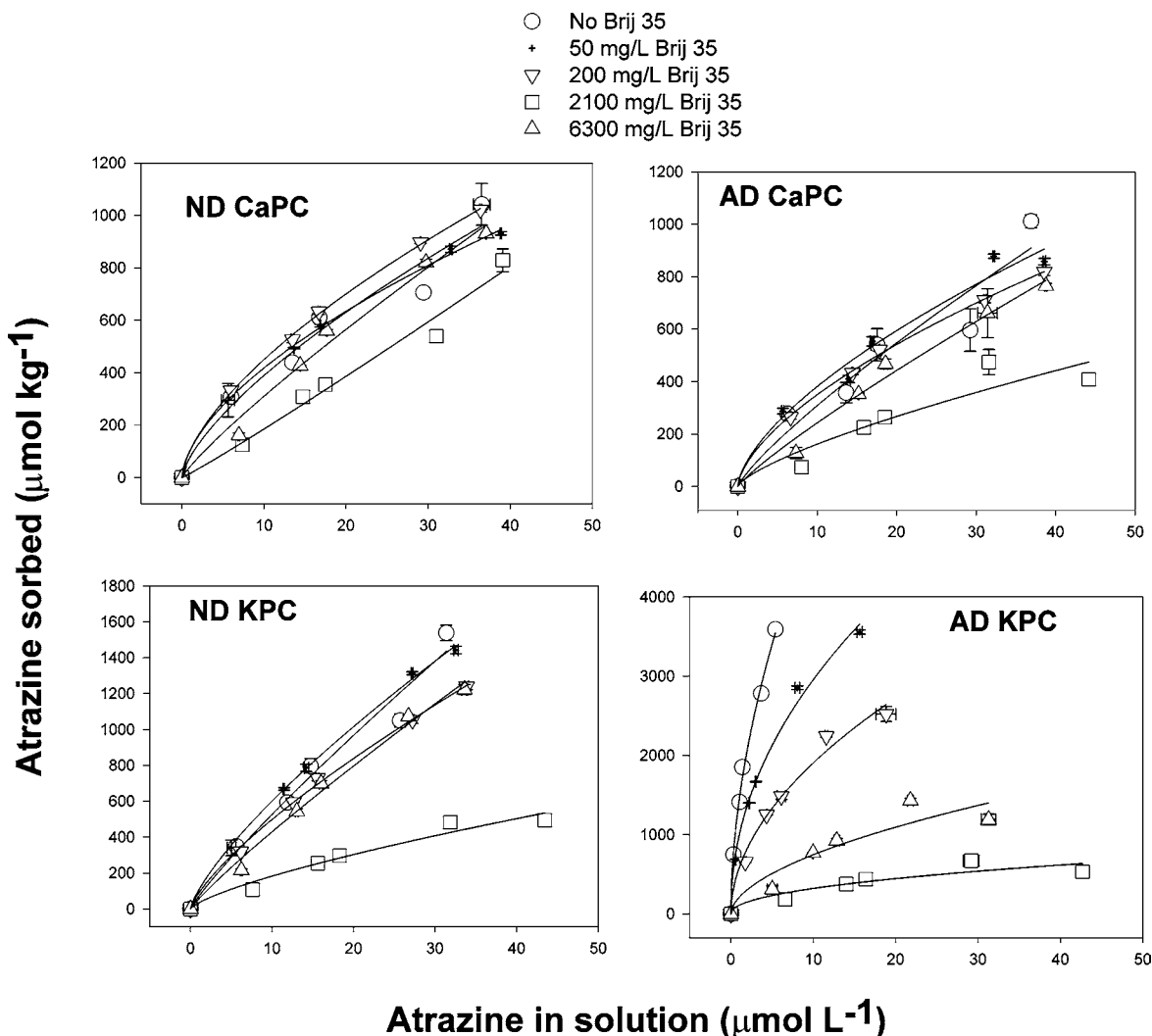


Figure 1. Atrazine sorption on AD or ND Ca-PC and K-PC as affected by different additions of Brij 35. Error bars are for triplicate samples. Error bars cannot be seen when the error is smaller than the symbol.

CMC Measurement. A CMC of 63 mg L⁻¹ was measured for Brij using an iodine assay (20–22). Literature values for the CMC of Brij range from 60 to 120 mg L⁻¹ (23–27) and depend on the analytical technique used and the extent to which the Brij EO groups have oxidized.

RESULTS AND DISCUSSION

The presence of Brij in the clay–atrazine systems substantially impacted atrazine sorption by PC (**Figure 1**). In general, there was little effect on atrazine sorption for Brij concentrations up to 200 mg L⁻¹, substantial inhibition of atrazine sorption for Brij concentrations of 2100 mg L⁻¹, and enhanced atrazine sorption for Brij concentrations of 6300 mg L⁻¹ (relative to the amount of atrazine sorbed in the 2100 mg L⁻¹ Brij systems). The effect of Brij on atrazine sorption was most evident for the AD K-PC, as additions of even small amounts of Brij caused a dramatic decrease in sorption affinity of AD K-PC for atrazine (**Figure 1**). We have previously shown that air-drying treatments substantially increase the affinity of K-PC for atrazine due to an irreversible collapse of the smectite interlayers (13). Calculated constants (K_F and n) for fit of the sorption data to Freundlich isotherms are presented in **Table 1**. All but one of the Freundlich n values were between 0.47 and 0.88, indicating substantial positive curvature for the sorption isotherms.

We investigated the sorption behavior of Brij by PC in the absence of atrazine (**Figure 2**). Brij was very strongly sorbed

Table 1. Regression Coefficients Calculated from the Nonlinear Fit of the Freundlich Equation to the Atrazine Sorption Data

saturation cation	sample handling	Brij 35 (mg L ⁻¹)	K_F	n	R^2
Ca	ND	0	79	0.70	0.96
		50	105	0.60	1.00
		200	104	0.64	1.00
		2100	16	1.06	0.99
		6300	43	0.86	0.99
Ca	AD	0	46	0.83	0.96
		50	87	0.64	0.99
		200	82	0.63	1.00
		2100	31	0.73	0.94
		6300	33	0.87	0.99
K	ND	0	70	0.88	0.99
		50	105	0.76	1.00
		200	89	0.75	1.00
		2100	34	0.73	0.98
		6300	55	0.90	1.00
K	AD	0	1430	0.54	1.00
		50	990	0.48	1.00
		200	580	0.52	0.99
		2100	110	0.47	0.93
		6300	210	0.55	0.94

by the PC, with sorption maxima between 250 and 350 g kg⁻¹, similar to the results reported by Sonon and Thompson (27) for sorption of Brij by PC clay. Nearly 100% of added Brij

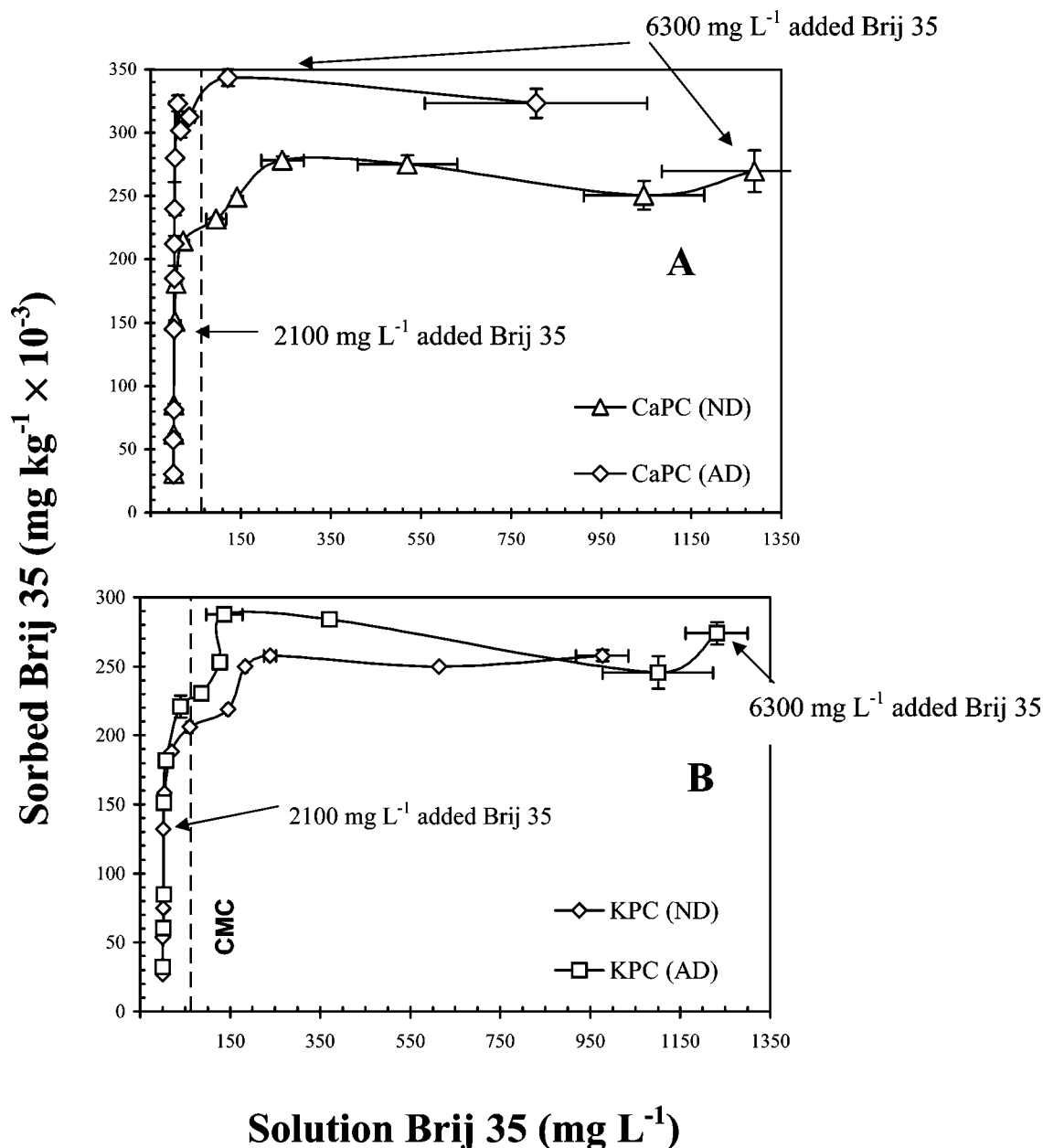


Figure 2. Brij 35 sorption isotherms on (A) Ca-PC and (B) K-PC. Brij 35 concentrations ranged from 500 to 6000 mg L^{-1} , except for AD Ca-PC, which ranged from 500 to 6500 mg L^{-1} . Arrows indicate the portion of the sorption isotherms representing 2100 and 6300 mg L^{-1} added Brij 35.

was sorbed up to 200 g kg^{-1} . Sorption maxima for Brij were higher for the AD clays than for the ND clays. Uncertainty in determining solution concentrations of nonsorbed Brij increased at high levels of Brij addition. Most likely, variability increased because at high levels of added Brij some micelles that incorporated sorbed clay remained suspended, resisting the centrifugation that separated solid and solution phases. However, there was little variability in the amounts of Brij sorbed at lower concentrations, below and near the sorption capacity of the clay.

The Brij sorption data shed light on interactions among the surfactant, the atrazine, and the clay. In the 2100 mg L^{-1} treatment, over 99% of added Brij was sorbed, leaving less than 5 mg L^{-1} of surfactant in solution (well below the CMC). Although atrazine may associate in solution with individual surfactant molecules, surfactants typically do not solubilize nonpolar solutes (i.e., "remove" atrazine from the aqueous solution) until aggregated into micelles (25, 28). Therefore, the data imply that an insufficient quantity of Brij remained in solution to form micelles and compete with the surface for

atrazine. However, at the initial concentration of 6300 mg L^{-1} of added Brij, approximately 1400 mg L^{-1} of surfactant was left in solution, a concentration well above CMC (Figure 2). At these large solution concentrations of surfactant, it was expected that surfactant in the equilibrium solution would readily form micelles and that the micelles would compete with the clay surfaces for atrazine, keeping atrazine in the solution phase. Instead, atrazine sorption was enhanced relative to the 2100 mg L^{-1} of added Brij. Hence, we infer that the patterns in atrazine sorption cannot be explained by competition of solution-phase surfactant micelles for atrazine molecules.

XRD studies of oven-dried, oriented PC samples provided direct evidence that Brij can be sorbed in smectite interlayers (Figure 3). The broad 1.06 nm XRD peak for the control (no Brij added, peak A) indicated that the Ca-PC was fully collapsed and dehydrated during oven drying and that adequate precautions had been taken to prevent the clay from rehydrating during the XRD analysis. Therefore, increases in *d*-spacing of clay samples to 1.44 and 1.73 nm with the 2100 and 6300 mg L^{-1} Brij

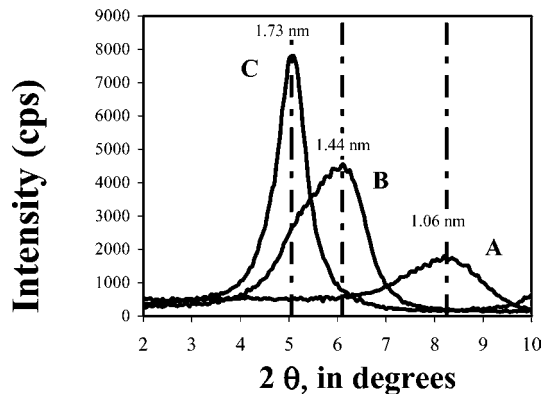


Figure 3. XRD patterns of oriented, oven-dried Ca-PC clay films after equilibrating the samples with 0 (A), 2100 (B), and 6300 (C) mg L⁻¹ of Brij 35.

treatments, respectively, are consistent with the intercalation and lateral orientation of two or three layers of surfactant molecules that have polyethylene chain widths of ~0.2 nm in the zigzag configuration (29). The relatively high intensity and symmetrical nature of the 1.73 nm peak suggest that nearly all interlayers contained multiple layers of Brij for the sample given the 6300 mg L⁻¹ Brij treatment. In contrast, the position and the asymmetrical nature of the 1.44 nm XRD peak for the sample given the 2100 mg L⁻¹ Brij treatment indicate interstratification of clay layers with monolayers and bilayers of interlayer Brij molecules. This information suggests that the Brij 35 micelles ruptured when exposed to the clay and that the Brij molecules

were readily sorbed into the clay interlayers. The results of the XRD analysis of the oven-dried Ca-PC–Brij systems (**Figure 3**) together with the Brij sorption isotherms (**Figure 2**) suggest that there was not enough Brij in the system at the 2100 mg L⁻¹ Brij level to completely fill the interlayers with a bilayer of Brij molecules.

Having demonstrated that Brij could intercalate the smectite quasicrystals, we conducted transmission XRD analyses using PC suspensions loaded with different concentrations of surfactant (**Figure 4**). These studies were performed to determine if Brij intercalation modified clay swelling in suspension. The broad nature of the XRD peaks was caused by the random orientation of clay quasicrystals in the suspensions and by disorder in the layer-stacking sequence. Brij sorption decreased peak *d*-spacings of ND and AD Ca-PC suspensions from 1.92 to 1.88 nm (**Figure 4A,B**). For the K-PC, an initial Brij concentration of 1000 mg L⁻¹ had little effect on the *d*-spacing (as compared to the absence of Brij), while higher levels increased the *d*-spacing to 1.6–1.8 nm. These trends for the K-PC indicate that in an aqueous suspension Brij entered the interlayers and displaced most if not all of the interlayer water, such that the interlayer K ions became solvated with Brij EO groups rather than with water. By contrast, water appears to coexist in the interlayers of Ca-PC. From the results presented in **Figure 3**, it is clear that Brij can enter the interlayers of Ca-PC, forming a bilayer with a desiccated *d*-spacing of 1.73 nm. Hence, the stable 1.92 nm *d*-spacing observed for the Ca-PC–Brij suspensions (**Figure 4A,B**) indicates that Brij and water coexist in the interlayers of Ca-PC in aqueous systems.

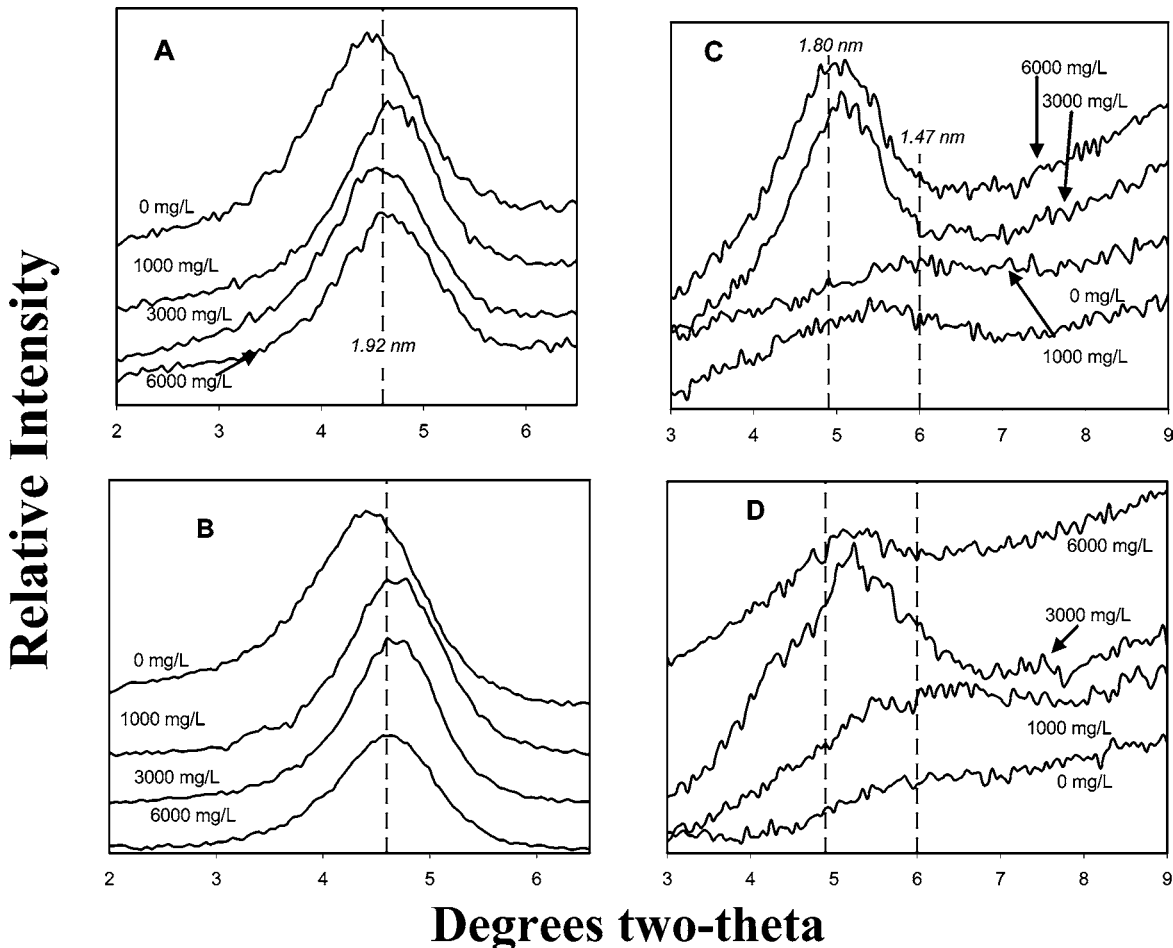


Figure 4. Transmission XRD data showing basal spacings *d*(001) in PC clay suspensions with various levels of added Brij 35. Shown are patterns for (A) ND Ca-PC, (B) AD Ca-PC, (C) ND K-PC, and (D) AD K-PC clay suspensions.

Table 2. Calculations to Determine the Percent Volume of Interlayer Filled by Brij 35 Sorption

clay and handling	Brij 35 added (mg L ⁻¹)	<i>d</i> -spacing (Å)	specific interlayer volume (m ³ g ⁻¹ × 10 ⁻⁷) ^a	sorbed Brij 35 (g kg ⁻¹)	specific volume of sorbed Brij 35 (m ³ g ⁻¹ × 10 ⁻⁷)	interlayer filled ^a (%)
Ca-PC (ND)	0	19.8	3.9	0.0	0.0	0
	1000	18.6	3.5	61.5	0.6	17
	3000	19.2	3.7	214.7	2.1	57
	6000	19.0	3.6	269.6	2.6	72
Ca-PC (AD)	0	20.1	4.0	0.0	0.0	0
	1000	18.8	3.5	57.2	0.6	17
	3000	18.8	3.5	212.4	2.1	60
	6000	19.0	3.6	343.6	3.4	94
K-PC (ND)	0	<i>b</i>				
	1000					
	3000	17.5	3.0	188.4	1.8	60
	6000	17.7	3.1	257.7	2.5	81
K-PC (AD)	0	<i>b</i>				
	1000					
	3000	16.8	2.8	220.8	2.2	71
	6000	16.8	2.8	274.0	2.7	96

^a Unit layer thickness for smectite = 9.6 Å. ^b *d*-Spacing could not be accurately determined.

Transmission XRD also revealed qualitative information about the size of PC clay quasicrystals in aqueous suspension. In the Ca-PC suspensions, the XRD peaks became sharper with the addition of Brij, indicating that the surfactant promoted an increase in the size and/or order of the coherent scattering domains of the suspended quasicrystals. The XRD pattern of the control (no Brij) for the K-PC suspensions indicated small and/or highly disordered quasicrystals. The sharper peak for the 3000 mg L⁻¹ treatment indicated that Brij intercalation in K-PC promoted the formation of larger, more ordered quasicrystals.

We attempted to quantify the interaction between the Brij and the clay by estimating the fraction of interlayer volume that was occupied by Brij in the clay suspensions. The interlayer volume was calculated from the modal *d*-spacings (determined by XRD, **Figure 4**) in the absence of Brij, the layer thickness (0.96 nm), the total surface area of the clay, and the mass of clay in each suspension. The volume of sorbed Brij, estimated from the mass of Brij sorbed by the clay in each suspension and the specific density of Brij, represents the upper limit for the density of sorbed Brij (the actual density may be much lower). On the basis of these calculations (**Table 2**), the sorption maximum of Brij (see **Figure 2**) corresponds with substantial filling of the clay interlayer. These data suggest that competition between Brij and atrazine for sorption sites on the clay was responsible for suppressing atrazine sorption for the 2100 mg L⁻¹ Brij systems.

Other research (4, 30) has shown that sorption of cationic, alkylammonium surfactants by smectites may enhance the sorption of weakly polar and NOCs. Sorption of NOC was shown to occur by partitioning into hydrophobic regions created by the long alkyl tails of the sorbed surfactant. In contrast, our data show that the presence of Brij molecules can suppress atrazine sorption (at 2100 mg L⁻¹ of added Brij). Brij has a long EO chain that makes the molecule very hydrophilic and strongly sorbed by the clay. Perhaps the presence of these large hydrophilic groups masks hydrophobic nanosites on the clay that might have affinity for atrazine, making the interlayers more hydrophilic and, consequently, a less favorable environment for atrazine (19).

With the 6300 mg L⁻¹ Brij treatment, the clay–Brij–atrazine systems behaved very differently. This concentration of Brij exceeded the Brij sorption capacity of PC; hence, a large amount of Brij (exceeding the CMC) was present in the aqueous phase (**Figure 2**). While the 2100 mg L⁻¹ treatment suppressed

atrazine sorption by the PC, the 6300 mg L⁻¹ treatment increased atrazine sorption by PC (relative to the 2100 mg L⁻¹ treatment) (**Figure 1**). An opposite trend would be expected if micelle competition were controlling atrazine sorption. The formation of micelles at the external surfaces of the smectite quasicrystals is a possible explanation for increased atrazine sorption at 6300 mg L⁻¹ of added Brij. Modeling studies predict that long-chained PEO molecules, sorbed onto silica, self-assemble into a disklike aggregates, which have hydrophobic cores (31). Such surface micelles would provide a nearly ideal environment for adsorption of weakly polar compounds such as atrazine. By contrast, Brij sorbed in the interlayers is both sterically constrained by the limited interlayer volume and compelled to simultaneously interact with interlayer cations, negatively charged surface sites, and hydrophobic nanosites. These steric constraints within the interlayers prevent the formation of micelles with hydrophobic centers as represented by CMC.

This work demonstrated the ability of a nonionic surfactant to strongly influence atrazine sorption by a reference smectite. There is no evidence that micelle competition inhibited atrazine sorption; indeed, the sorption trend is opposite of that which would be expected were micelle competition significant. At lower concentrations, Brij was capable of inhibiting atrazine sorption by blocking interlayer sorption sites. Once the interlayer filled with Brij, we hypothesize that the surfactant enhanced atrazine sorption, apparently through the formation of micelles at the clay surface. These results demonstrate that the effect of formulation components must be considered to reliably predict the molecular-scale fate of atrazine in soil systems.

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