A Mechanism of Basal Spacing Reduction in Sodium Smectitic Clay Materials in Contact with DNAPL Wastes

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Abstract

There has been concern regarding the possible attack of clays in aquitards, slurry walls and landfill liners by dense nonaqueous phase liquid (DNAPL) wastes, resulting in cracking. Despite the fact that a reduction in basal spacing in sodium smectitic clay materials has been linked to cracking, no plausible mechanism by which this reduction occurs in contact with waste DNAPLs has been formulated. To elucidate a mechanism, screening studies were conducted that showed that the combination of an anionic surfactant (AOT), a nonionic surfactant (TritonX-100) and a chlorinated solvent, tetrachloroethylene (PCE), could replicate the basal spacing reduction and cracking behavior of water-saturated bentonite caused by two waste DNAPLs obtained from the field. FTIR measurements of this system showed a displacement of the H-O-H bending band of water symptomatic of desiccation. Sorption measurements showed that the uptake of AOT by bentonite increased eight fold in the presence of TritonX-100 and PCE. The evidence presented here supports a mechanism of syneresis, involving the extraction of water from the interlayer space of the clay through the synergistic sorption of a nonionic and anionic surfactant mixture. It is speculated that the solvation of water in reverse micellar aggregates is the process driving the syneresis.

Keywords: clay; cracking; syneresis; DNAPL; surfactant, hazardous waste

1. Introduction

Tetrachloroethylene (PCE) and trichloroethylene (TCE) are chlorinated dense nonaqueous phase liquids (DNAPLs) that are commonly identified at hazardous waste sites (Oolman et al., 1995, Dwarakanath et al., 2002; Dou et al., 2008; Parker et al., 2008). The migration of DNAPLs in the subsurface may be constrained by the presence of clay lenses and aquitards, or by the installation of engineered slurry walls. The low permeability of these materials results from the presence of clay; in the case of slurry walls, the clay is bentonite, or primarily sodium montmorillonite. However, there has been concern that bentonite may be attacked by chlorinated solvents (Abdul et al., 1990; McCalou and Huling, 1999). Studies investigating this phenomenon have used changes in hydraulic conductivity as their measure of the degree of alteration, citing that the permeation of the clay with a chlorinated solvent resulted in an increase of up to two orders of magnitude. The explanation given was that the solvent displaced water, causing double-layer compression because of the low dielectric constant of the solvent. The shrinkage resulted in the formation of a network of cracks, which facilitated the flow of the solvent through the clay. Similar behavior was not observed in cases where water saturated with the solvent was used as the permeating fluid.

More recently, interest in the interactions between chlorinated solvents and smectitic clays has surfaced in the context of mass storage in clay lenses and aquitards. Due to the long-term contact between DNAPLs in the subsurface and these geologic strata, the latter can accumulate a significant mass of contamination over time, essentially becoming contaminant storage zones (Sale et al., 2008; Stroo et al., 2012). Field work has documented high concentrations of TCE and PCE in clay lenses and aquitards at waste sites (Ball et al., 1997; Parker et al., 2008). Once the original source is removed, these zones slowly release the accumulated contaminants back into the surrounding groundwater, significantly extending remediation times (Chapman and Parker, 2005).

It has been speculated that interactions between DNAPLs and the clay minerals in these layers may play a role in the mass accumulation (Matthieu et al., 2013; Ayral et al., 2014). One possible mechanism by which mass accumulation due to clay-waste interactions may occur is through cracking. If contact with DNAPLs causes a contraction in the basal spacing leading to cracking, the cracks may fill with DNAPL in a manner similar to that hypothesized for naturally-occurring fractures (Kueper and McWhorter, 1991). However, to substantiate such a hypothesis,

a clearer mechanistic understanding of crack formation due to contact with DNAPLs is necessary. In the studies showing an increase in hydraulic conductivity of bentonite exposed to neat chlorinated solvents, the clays were subjected to high hydraulic gradients, and it is unclear if the bentonite would have been permeated otherwise, given that water-saturated smectites are negatively-charged (Meunier, 2005), hydrophilic (van Oss and Giese, 1995) and have high entry pressures due to the small size of their pores (Marshall et al., 1996). Furthermore, Ayrat et al. (2014) found that passive contact of up to 319 days with laboratory-grade PCE and TCE did not cause cracking, and the few reported measurements of basal spacing of water-saturated smectitic clays in contact with chlorinated solvents are similar to those measured with water, suggesting that these solvents are unable to penetrate into the interlayer space of these materials when they are saturated with water (Griffin et al., 1984; Ayrat et al., 2014).

Although the passive contact of smectitic clays with neat chlorinated solvents did not have an impact, contact with two chlorinated DNAPLs recovered from the field reduced the basal spacing of bentonite from about 19 Å to 15 Å and caused the formation of cracks of up to 1 mm in aperture in a time frame of weeks (Ayrat et al., 2014). While the predominant organic component in a chlorinated DNAPL may be PCE or TCE, DNAPLs contain a range of solutes, added to enhance their performance (Jackson and Dwarakanath, 1999; Linn and Stupak, 2009), obtained through their use (Jackson and Dwarakanath, 1999) or acquired during their residence in the subsurface (Harrold et al., 2003). Additives to degreasing and drycleaning solvents include alcohols, aliphatic ketones, carboxylic esters, glycol ethers, and surfactants (Earnest et al., 1997; Jackson and Dwarakanath, 1999; Linn and Stupak, 2009); organic components identified in actual PCE and TCE field wastes include carboxylic esters, fuel hydrocarbons and phthalates (Dou et al., 2008), and nonionic and anionic surfactants (Hsu, 2005). In fact, Jackson and Dwarakanath (1999) point out that any chlorinated solvent in the subsurface will contain solutes that may significantly influence its behavior.

One hypothesis of how the basal spacing reduction and the ensuing cracking may occur in smectitic clays is that water-soluble organic compounds present in the waste dissolve in the water present in the interlayer spacing of the clay, enhancing the dissolution of the chlorinated solvent within the clay. Matthieu et al. (2013) cite evidence that the intercalation of TCE in sodium montmorillonite is possible. Furthermore, the ability of a cosolvent to increase the solubility of hydrophobic organic compounds is well documented (Schwarzenbach et al., 2003).

81 The solubility of PCE can be increased by orders of magnitude by the presence of an alcohol, for
82 example (Imhoff et al., 1995; Ladaa et al., 2001). Whether a mixture comprising a chlorinated
83 solvent and an alcohol would result in a reduction of the basal spacing, however, is unclear.
84 Contact of water-saturated bentonite with an aqueous solution of TCE at the solubility limit
85 yielded a basal spacing similar to that in contact with water (18.2 Å [Matthieu et al., 2013] vs.
86 18.0 -18.2 Å [Brown and Thomas, 1987; Li et al., 1996]). But, aqueous mixtures containing on
87 the order of 10% ethanol have been shown to expand the basal spacing beyond that in contact
88 with water alone (Griffin et al., 1984; Brown and Thomas, 1987).

89 Other hypotheses may be based on surfactant content. An explanation centered on
90 altered wettability by surfactants is not supported, however, as the DNAPL systems examined in
91 Ayral et al. (2104) were water-wet (Hsu, 2005), similar to the situation with the DNAPL waste
92 from the Savannah River site (Dou et al., 2008). Alternatively, studies of organobentonites show
93 that cationic surfactants can sorb in the interlayer space, increasing the basal spacing (e.g., Lee et
94 al., 2004; Hu et al., 2013) and the sorption of hydrophobic organic chemicals (e.g., Boyd et al.,
95 1988; Zhu et al., 1998). However, the increased sorption of hydrophobic chemicals was related
96 to the sorption of cationic surfactants, and Hsu (2005) identified nonionic and anionic surfactants
97 in the DNAPL waste samples. Work examining the sorption of nonionic surfactants documents
98 a lesser expansion of the clay structure (Shen, 2001; Deng et al., 2003) and the intercalation of
99 this type of surfactant did not seem to enhance the sorption of hydrophobic organic compounds
100 such as toluene or cyclohexane (Deng et al., 2003). In fact, Deng et al. (2003) speculated that
101 nonionic surfactants were not fully penetrating the interlayer space and that the sorption that did
102 occur was primarily confined to the interlayer margins. Similarly, Sanchez-Martin et al. (2008)
103 concluded that the minimal sorption of sodium dodecylsulfate (SDS), an anionic surfactant, to
104 montmorillonite, probably also occurred on the margins, due to the lack of change in the basal
105 spacing.

106 In the context of a DNAPL waste, possible synergistic interactions must also be
107 considered (Hsu and Demond, 2007). For example, the sorption of an anionic surfactant onto
108 kaolinite from a mixture of anionic-nonionic surfactants could be greater than that in the
109 presence of the anionic surfactant itself (Xu et al., 1991). Hydrophobic chain-chain interactions
110 of the surfactants and the reduction of the repulsive force of the negatively-charged head of the
111 anionic surfactant by the nonionic surfactant were offered as a possible explanation for such

synergy (Xu et al., 1991; Zhang and Somasundaran, 2006). It should be noted that all of these studies examined sorption from aqueous solutions; comparable sorption studies from nonpolar solvents are not available. However, studies of surfactant behavior in nonpolar solvents show that surfactants can form mixed reverse micelles (Fendler, 1976; Moulik, 1996), based on interactions between the hydrophilic moieties of the anionic and nonionic surfactants. Furthermore, these reverse micelles solubilize water in their core (Silber et al., 1999), a phenomenon that is exploited in the dry cleaning industry for the removal of water-based stains (Linn and Stupak, 2009).

Although solutes present in the DNAPL wastes may play a critical role in the contraction of the basal spacing of bentonite, and consequently, possibly in the mass accumulation of contaminants by aquitards or in the deterioration of slurry walls and landfill liners, the mechanism by which this occurs is unknown. Previous studies evaluating the possible degradation of bentonite in contact with chlorinated solvents hypothesized that the DNAPL enters the clay, causing double-layer compression and subsequent cracking, without offering supporting evidence. But, how the DNAPL actually enters the clay, or whether it even does, is a matter of speculation. Thus, the objective of this study was to delineate a plausible mechanism by which chlorinated DNAPL wastes can cause a contraction of the structure of water-saturated bentonite.

2. Screening Experiments

A preliminary step in obtaining this objective was to perform two sets of screening experiments to ascertain which components of the waste were the causative agents of the reduction in basal spacing. Two DNAPLs, one a PCE-based DNAPL obtained from a dry cleaner (Ann Arbor, MI), and the other a TCE-based DNAPL obtained from Operable Unit 2 at Hill Air Force Base (UT), both of which Ayral et al. (2014) found to reduce the basal spacing of sodium smectites and cause cracking, served as the representative wastes. Both wastes had contact angles on quartz in the presence of water at neutral pH of approximately 30°. The interfacial tension of both waste was about 2-3 dyn/cm, attributed to the presence of nonionic and anionic surfactants (Hsu, 2005). To ascertain whether water-soluble organic components in the DNAPL wastes were enhancing the aqueous solubility of the chlorinated solvent, the wastes were contacted with water at a waste-to-water volume ratio of 4:1 for 56 days. After this period

of equilibration, the aqueous phase was extracted with toluene, which was then analyzed for concentrations of PCE and TCE by gas chromatography. The PCE concentration in the aqueous phase contacted with the PCE-based waste was measured to be 9500 mg/L, with no measurable concentrations of TCE. The concentrations in the aqueous phase contacted with the degreasing TCE waste were 125 mg/L and 500 mg/L, of PCE and TCE respectively. The aqueous solubilities of PCE and TCE at 25°C are 150 mg/L and 1370 mg/L, respectively (Riddick et al., 1986). Thus, the components in the PCE-based waste increased the aqueous phase concentration of PCE significantly, but the components in the TCE-based waste reduced the TCE concentration below solubility. Since both the PCE and TCE wastes caused similar basal spacing contraction and cracking (Ayrál et al., 2014), but the aqueous solubility increased only in the case of the PCE waste, an enhancement of the solubility of the chlorinated compounds in the interlayer water was eliminated as a likely mechanism.

The second set of screening experiments involved setting up a suite of 18 20-mL glass vials. One gram of commercial Wyoming Na-bentonite (Southwestern Materials, Austin, TX) was put into each vial and contacted with 10 mL of a 0.005 M CaSO₄ solution to saturate it. After two weeks, the surficial excess water was removed. Then both aqueous and PCE solutions were made up containing various combinations of organic solutes hypothesized to be present in dry cleaner and degreasing wastes, at concentrations given in Table 1. Then, 15 mL of one of these solutions was added on top of the clay. The vials were capped, stored at room temperature and observed over time. No cracking was observed for over 75 days in the vials containing an individual or a combination of the lower-molecular weight organic solutes dissolved in PCE. Moreover, vials containing a single surfactant dissolved in PCE did not show evidence of rapid cracking. Yet, cracking occurred in less than two weeks in the vials containing the anionic and nonionic surfactants and PCE. Therefore, it was concluded that a surfactant combination was vital to the cracking process. As the same surfactants dissolved in water did not cause cracking, the implication was that the chlorinated solvent was also an indispensable constituent.

3. Experimental Methods

Once the minimum necessary system components were determined, x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and sorption measurements were made to gain additional insight into the mechanism. Water-saturated bentonite samples were prepared

Table 1. Concentrations of Compounds in Screening Experiments

Chemical group	Compound	Chemical Formula	Concentration
Alcohol	Propanol	C ₃ H ₈ O	50 mg/L
Aliphatic ketone	Acetone	C ₃ H ₆ O	10 mg/L
	Methyl isobutyl ketone	C ₆ H ₁₂ O	2550 mg/L
Aliphatic carboxylic ester	Amyl acetate	C ₇ H ₁₄ O ₂	525 mg/L
	n-Butyl acetate	C ₆ H ₁₂ O ₂	528 mg/L
Glycol ether	2-Butoxyethanol	C ₆ H ₁₄ O ₂	8992 mg/L
Nonionic surfactant	TritonX-100 [†]	C ₁₄ H ₂₂ O(C ₂ H ₄ O) _n (n = 9-10)	3.3 mM
	C ₁₂ E ₆ [‡]	C ₂₄ H ₅₀ O ₇	6.7 mM
Anionic surfactant	AOT	C ₂₀ H ₃₇ NaO ₇ S	3.3 mM

Aqueous solutions were made up using water with a resistivity of 18.3 MΩ·cm made by passing deionized distilled water through a series of four cartridges (Milli-Q, EMD Millipore) to remove additional impurities. PCE solutions were made up using HPLC grade PCE (>99.9%, Sigma Aldrich). All other chemicals were laboratory grade from Fisher Scientific, unless noted. [†]ICN Biomedicals; [‡]Sigma Aldrich.

as in the screening experiments by adding 10 mL of 0.005 M CaSO₄ to one gram of bentonite in glass vials. After two weeks, the excess water was removed and the clay was mixed for homogeneity. Two grams of the clay were then transferred into a 30-mL centrifuge tube and 20 mL of a solution containing combinations of TritonX-100, AOT and C₁₂E₆ as solutes, dissolved in either water or PCE, were added into the tubes. The first set of tubes was rotated for four days followed by passive contact of at least one week; the second set of tubes was rotated for three weeks. The clay-solution mixture was centrifuged and the solid phase was analyzed using an X-ray diffractometer (Rigaku, The Woodlands, TX) equipped with a rotary anode source (CU) with a 12 kW X-ray generator, a graphite monochromator and two wide angle horizontal goniometers (2°-138°). As the samples containing chlorinated solvent had diffuse peaks, they were analyzed using a step size of 0.04° and a count time of 20 sec over the range of 4-8° 2θ. JADE (Version 10; Materials Data, Livermore, CA) was used to analyze the data. A background curve was fitted automatically and, after determining the portion of the profile attributable to the background, the PseudoVoigt profile function was used to fit the profile and determine the location of the peaks.

Samples were also analyzed using FTIR spectroscopy (Spectrum BX, Perkin Elmer, Boston, MA) with a MIRacle attenuated total reflectance (ATR) accessory. First, the background was scanned in a range of 650 cm⁻¹ to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. Then, the sample was placed on the ATR crystal, and data was collected in the transmission mode. The

spectra were corrected using the background scan and the peaks on each spectrum greater than the threshold (5% of transmission) were labeled. The bentonite clay samples were rotated for four days and then were left sitting for almost six months. For comparison, scans were also made for dry and wet clay, clay in contact with aqueous solutions of surfactants, and for solvents and solutions in the absence of clay.

For the sorption measurements, vials were made up containing one gram of Wyoming Na-montmorillonite clay (SWy-2; Clay Minerals Society, Chantilly, VA) that was contacted with 10 mL of 0.005 M CaSO₄ solution for two weeks. Similar to the protocol in the basal spacing measurements, excess surficial water was removed from the surface and the clay was mixed. Then, two or four grams of the clay were transferred to a 30-mL centrifuge tube. Surfactant solutions containing the same concentrations as in the screening experiments (Table 1) were prepared in 50 mL volumetric flasks, and in the case of the surfactant solutions prepared in PCE, 0.06 mL ¹³C-labeled TCE (>98%; Cambridge Isotope Laboratory, MA) was also injected into the volumetric flasks. 20 mL of the surfactant solutions were then added to the centrifuge tubes. Following one week of rotation, the tubes were centrifuged. The supernatant phase was sampled to determine the concentration of surfactant and ¹³C-labeled TCE left in the solution, from which the degree of sorption was calculated by mass balance.

The surfactant concentrations in both the aqueous phase and PCE were analyzed using high-performance liquid chromatographs (HPLC) (Hewlett Packard), equipped with evaporative light scattering detectors (ELSD) (Sedere Sedex), as detailed in Ayral (2015). The concentration of ¹³C-labeled TCE in PCE was measured using a gas chromatograph (Hewlett-Packard 5890) equipped with a mass selective detector (Hewlett-Packard 5972) to differentiate between bulk TCE and ¹³C-labeled TCE, based on a shift of the base peaks. Ions at m/z values of 131, 133, and 135 were extracted and used to determine the concentration of ¹³C-labeled TCE.

4. Results and Discussion

The screening experiments suggested that a mixture of anionic and nonionic surfactants dissolved in a chlorinated solvent was necessary in order to observe a magnitude and rate of cracking comparable to the DNAPL wastes. The XRD results (Table 2) show that an aqueous solution of TritonX-100 reduced the basal spacing of water-saturated bentonite from 19.0 Å to

17.5 Å; the combination of TritonX-100 and AOT had the similar impact. In contrast, contact with an aqueous solution of all three surfactants (TritonX-100, AOT, and C₁₂E₆) caused the basal

Table 2. Basal Spacing of Bentonite (Initially Saturated with 0.005 M CaSO₄) in Contact with Various Surfactant Solutions

Surfactant	Basal spacing (Å) (4 days of rotation and one week passive contact)		Basal spacing (Å) (3 weeks of rotation)	
	Dissolved in water	Dissolved in PCE	Dissolved in water	Dissolved in PCE
No surfactant	19.0	19.0	NM	NM
TritonX-100 (3.3 mM)	17.5	17.5	17.4	15.6
TritonX-100 (3.3 mM) and AOT (3.3 mM)	17.9	15.4	17.1	12.7
TritonX-100 (3.3 mM) and C ₁₂ E ₆ (6.7 mM)	NM	18.8	NM	NM
TritonX-100 (3.3 mM), AOT (3.3 mM) and C ₁₂ E ₆ (6.7 mM)	20.2	15.8	NM	NM

NM: not measured.

spacing to increase to 20.2 Å. But, water-saturated bentonite in contact with the same surfactant mixture in PCE showed a reduction in the basal spacing to 15.8 Å, similar to that observed when water-saturated bentonite was contacted with DNAPL waste. Similarly, the basal spacing of water-saturated bentonite in contact with a PCE solution of TritonX-100 and AOT decreased to 15.4 Å, suggesting that the second nonionic surfactant C₁₂E₆ was not necessary. The basal spacing of water-saturated bentonite in contact with PCE containing these surfactants decreased even further to 12.7 Å after three weeks of rotation, to almost air-dry values. These results showed that the minimum mixture needed to reproduce the basal spacing measurements reported in Ayral et al. (2014) for DNAPL wastes was a combination of TritonX-100, AOT, and PCE.

Figure 1 shows the XRD pattern of water-saturated bentonite contacted with the mixture of AOT and TritonX-100 dissolved in PCE. The average basal spacing is 15.4 Å, but in fact, the pattern appears to be comprised of three overlapping peaks: one peak corresponding to a basal spacing of 18.9 Å (25% of the total area as calculated by the profile fitting software), another one to 15.5 Å (50% of the total area), and a third to 11.5 Å (25% of the total area). These values

suggest that about 25% of the interlayer space was still fully hydrated, 50% of the interlayer space was partially hydrated and 25% of the interlayer space of bentonite was dehydrated up to

Figure 1. XRD pattern of water-saturated bentonite contacted with PCE containing 3.3 mM AOT and 3.3 mM TritonX-100 for one week following four days of rotation.

air-dry conditions, as 11.5 Å is the basal spacing of air-dry bentonite (Brown and Brindley, 1980; Moore and Reynolds, 1989).

Figure 2 summarizes the FTIR results. The H-O-H bending band of water (Madejova and Komadel, 2001) is located at 1652 cm^{-1} for air-dry clay and at 1636 cm^{-1} for water-saturated bentonite. This figure shows that six months of contact with TritonX-100 dissolved in PCE did not change the location of the H-O-H bending band relative to that for water-saturated clay, suggesting that the interlayer water was not impacted by the presence of the nonionic surfactant and chlorinated solvent. This observation agrees with the results of the screening experiments and basal spacing measurements since neither cracking nor a reduction in the basal spacing was observed for this system. However, contact with a mixture of TritonX-100, AOT and PCE caused the wavenumber of the H-O-H bending band to shift to 1652 cm^{-1} , similar to the location for air-dry clay. This shift in wavenumber towards that for air-dry clay suggests a displacement

of water molecules from the interlayer space, similar to the process of desiccation (Russell and Farmer, 1964; Johnston et al., 1992). Although evidence was found suggesting an interruption of the hydration layers in clay, surfactant specific bands were not detected. In previous studies

Figure 2. FTIR spectra of water-saturated bentonite in contact with different fluids compared to the spectrum of air-dry bentonite. Wavenumbers indicated correspond to the H-O-H bending band of water.

using FTIR to examine surfactants in clays, the clays were exposed to high concentration surfactant solutions and then dried. Here, the clays were exposed to relatively dilute concentrations of surfactants and were analyzed wet. Because of these differences in measurement conditions, surfactant specific bands, such as those reported by Del Hoyo et al. (2008), could not be observed.

Figure 3 summarizes the results from the sorption experiments conducted in both water and PCE. Figure 3a shows that that 65% of TritonX-100 was sorbed from an aqueous solution of TritonX-100, whereas the degree of sorption of TritonX-100 decreased slightly to 57% if the aqueous solution contained both TritonX-100 and AOT. On the other hand, the degree of AOT sorption increased from 7% to 14% if AOT and TritonX-100 were present in the aqueous solution together. Thus, the presence of TritonX-100 increased the sorption of AOT two fold, giving a sorbed molar ratio of TritonX-100:AOT of around 5:1 from the aqueous solution.

Figure 3. Percent sorption of solutes from aqueous and PCE solutions onto Na-montmorillonite. A: TritonX-100; B: AOT; C: ¹³C-labeled TCE. ND = below detection.

Similar experiments were conducted with the surfactants dissolved in PCE. The results, presented in Figure 3b, showed that the degree of TritonX-100 sorption increased slightly, from 72% to 85%, in the presence of AOT. On the other hand, the degree of AOT sorption increased almost eight fold, from 7% to 58%, in the presence of TritonX-100. In the case of sorption from PCE, the sorbed molar ratio of TritonX-100:AOT was 3:2. Although AOT is an anionic surfactant, its sorption increased considerably through its association with a chlorinated solvent and a nonionic surfactant. Measurements of the sorption of ^{13}C -labeled TCE (Figure 3c) show that, in the absence of surfactant, the degree of sorption was nondetectable. In the presence of surfactants, the sorption of TCE is higher, but the increase is considerably less than that observed in the case of AOT. Thus, the fundamental difference noted in the presence of the chlorinated solvent is increased sorption, in particular, that of the anionic surfactant AOT.

The sorption results suggested that there was increased sorption in the presence of PCE, with about 85% of the nonionic surfactant, TritonX-100, and nearly 60% of the anionic surfactant, AOT, sorbed onto water-saturated Na-montmorillonite, giving a sorption ratio of 3:2. The location and orientation of the surfactant molecules relative to the clay surface of the interlayer space will depend, in part, on the size of the molecules (Table 3). The basal spacing for sodium montmorillonite is the sum of the tetrahedral-octahedral-tetrahedral (TOT) layer and the interlayer space. The TOT structure of smectite clay minerals has a thickness of around 9.6 Å (Moore and Reynolds, 1997); thus, the interlayer space has a thickness of around 5.5 Å, if the basal spacing is 15 Å. TritonX-100 can conceivably penetrate and sorb in the water-filled interlayer space since it is nonionic, miscible in water, and has a width of about 4 Å (based on the diameter of a phenyl group). But, due to its length, TritonX-100 probably lies essentially parallel to the interlayer surfaces, as also hypothesized by Deng et al. (2003). Conversely, AOT is less likely to enter into the interlayer space because it has a negatively-charged head, whose diameter is 5 Å. AOT's enhanced sorption in the presence of TritonX-100 suggests that AOT interacts with TritonX-100, most likely through their hydrophilic moieties because of the nonpolar nature of the surrounding solvent (Moulik, 1996). Furthermore, if there is water present on the exterior surfaces, this may contribute to the association of AOT with the surface, as AOT shows preferential partitioning into water over PCE ($K_{\text{PCE,water}} = 0.001$) (Hsu, 2005). Assuming a 3:2 ratio of sorption, that interactions between TritonX-100 and AOT occur through

their hydrophilic moieties, that TritonX-100 can penetrate into the interlayer space, but AOT cannot, a schematic can be constructed (Figure 4).

With the sorption of TritonX-100, some of the water molecules at the margins of the interlayer space of the clay particle may be displaced. In addition to this displacement of water

Table 3. Dimensions of Molecules in Model DNAPL Waste System

Head diameter of AOT	5.0 Å	Moulik and Mukherjee, 1996
Tail length of AOT	12.6 Å	Moulik and Mukherjee, 1996
Width of TritonX-100 [§]	4.2 Å	Zhang et al., 2005
Length of TritonX-100 [¶]	48 Å	Paradies, 1980
Width of PCE molecule	3.6 Å	Zhou, 1994
Width of water molecule	2.8 Å	Cheng et al., 2001

[§]Taken as the diameter of the phenyl group. [¶]Taken as effective hydrodynamic radius of the micelle at 20°C.

Figure 4. Schematic representation of possible arrangement of AOT and TritonX-100 in PCE in contact with water-saturated bentonite.

by TritonX-100, it is speculated that the association of the AOT molecules in close proximity with the interlayer space stimulates further reductions in the quantity of the interlayer water. AOT is known to spontaneously form thermodynamically stable premicellar aggregates and reverse micelles in nonpolar solvents, with water being an essential component in their formation. These aggregates can solubilize substantial amounts of water, reaching molar ratios of water to micellized surfactant of up to 40-60, depending on the temperature and the nature of the nonpolar solvent (Silber et al., 1999). Thus, AOT's association with TritonX-100 may facilitate its attraction of water from the interlayer structure to fulfill its need for aqueous solvation. As the displacement of water molecules from the interlayer space is not uniform,

there is a range of basal spacings; this is reflected in the XRD pattern (Figure 1) as a very broad peak which actually represents overlapping peaks, with each peak indicating interlayer space with different thicknesses.

The explanation of how bentonite cracks in contact with organic solvents that has been put forth previously is one of intercalation, involving the entrance of the chlorinated compound into the interlayer space. The evidence presented here supports a mechanism primarily of syneresis, involving the extraction of water from the interlayer space by the synergistic sorption of nonionic and anionic surfactants. Burst (1965) documented the cracking of clay layers containing as little as 10% bentonite due to syneresis, driven by high salinity levels in the surrounding aqueous solution. The evidence presented in this study suggests that cracking may be similarly precipitated by the solvation of the clay's interlayer water in surfactant aggregates. The cracks formed by passive contact with DNAPL wastes reported by Ayral et al. (2014) were up to 1 mm in aperture. Considering the DNAPL pool depths reported at hazardous waste sites (Oolman et al., 1995; Parker et al., 2003; Parker et al., 2004), the hydrostatic head of these pools may be greater than the entry pressure of such cracks, allowing the waste to enter. Consequently, penetration into cracks formed by contact with DNAPL waste could be a means by which chlorinated solvents may accumulate in aquitards.

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Figure 1. XRD pattern of water-saturated bentonite contacted with PCE containing 3.3 mM AOT and 3.3 mM TritonX-100 for one week following four days of rotation.

Figure 2. FTIR spectra of water-saturated bentonite in contact with different fluids compared to the spectrum of air-dry bentonite. Wavenumbers indicated correspond to the H-O-H bending band of water.

Figure 3. Percent sorption of solutes from aqueous and PCE solutions onto Na-montmorillonite. A: TritonX-100; B: AOT; C: ^{13}C -labeled TCE. ND = below detection.

Figure 4. Schematic representation of possible arrangement of AOT and TritonX-100 in PCE in contact with water-saturated bentonite.