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Sorption of Perchloroethylene by Surfactant-Modified Zeolite as Controlled by Surfactant Loading

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The sorption of nonpolar hydrophobic organic compounds by soil organic matter has long been attributed to a partitioning mechanism, with the sorption coefficient proportional to the fractional organic carbon content of the soil. However, deviations from this linear proportionality have been observed and reported in the literature by many authors. In our study a natural zeolite was modified with a cationic surfactant to achieve different fractional organic carbon contents and different surfactant molecule configurations on the surface. The sorption of perchloroethylene (PCE) by the surfactant-modified zeolite (SMZ) was found to be dependent on the bound surfactant molecule configuration as well as on the fractional organic carbon content. Below monolayer coverage by the surfactant, the PCE sorption coefficient on SMZ was proportional to the fractional organic carbon content. Above monolayer coverage, increasing fractional organic carbon content resulted in minimal further increase in the PCE sorption coefficient. The change in PCE sorption behavior was attributed to the structural differences between sorbed surfactant monolayers and bilayers. The surfactant surface configuration has a significant impact on the effective volume and density of the bound organic phase that is responsible for partitioning nonpolar organic compounds. The ratio of the organic carbon-based distribution coefficient (K_{oc}) for the monolayer versus that for the bilayer systems was 1.7, similar to the estimated bilayer to monolayer hydrocarbon density of 1.3. Our results reinforce the notion that the structure of natural organic matter as well as its quantity controls the sorption of nonpolar organics to soils and sediments.

Introduction

The fate of nonpolar hydrophobic organic compounds (NOCs) in natural water systems is highly dependent on their sorptive behavior. Under most circumstances the sorption of NOCs on soils and sediments follows a linear isotherm (1–4). Karickhoff et al. (1) studied the sorption of NOCs on natural sediments and found that the linear sorption coefficient was proportional to the fractional organic carbon content. Chiou et al. (2–3), in studying the equilibrium of NOCs between soil organic matter and water, found that the sorption coefficient was dependent on the water solubility of the solute and suggested that sorption of NOCs from water by soil is primarily due to the partitioning of NOCs into the

soil organic phase. In essence, the soil organic matter functions as an organic solvent and NOCs distribute themselves between water and this organic phase.

Deviations from equilibrium partitioning behavior have been observed by many authors. Hamaker and Thompson (5) observed that the values of K_{oc} (the organic-carbon-based partition coefficient of an NOC between soil organic matter and water) for soils with high organic carbon contents are usually lower than K_{oc} values for “normal” soils and soils with very low organic carbon contents. Chiou et al. (3, 6) stated that the K_{oc} value of a compound in different soils can vary to some extent since the composition of the organic matter is not constant. Chiou et al. (3) suggested that K_{oc} is affected by the structure and polarity of soil organic matter but did not give any details on how configuration of organic matter in soil could affect the K_{oc} . Schwarzenbach et al. (7) replotted the pyrene sorption data of Means et al. (4) and clearly showed that the sorption coefficient is not a simple linear function of fractional organic carbon content. Yu and Lobban (8) studied the adsolubilization of trimethyl orthobenzoate and its reaction product methyl benzoate by admicelles of sodium dodecyl sulfate (SDS) bound to porous activated acidic alumina. They found that the sorption coefficients of these compounds increased linearly with the concentration of bound SDS up to a certain value, beyond which there was little increase in sorption with SDS loading. All the above observations indicate that NOC sorption coefficients are dependent not only on the solid’s organic carbon content but also on the composition and configuration of the bound organic phase.

Natural clay minerals such as smectite have high cation exchange capacities due to the isomorphous substitution of cations in their crystal structure. This exchange capacity enables these minerals to be modified by cationic surfactants, such as hexadecyltrimethylammonium (HDTMA), for environmental contaminant remediation (9–12). Due to the two-dimensional platelike structure of clay minerals, it is difficult to differentiate interlayer sorption from external surface sorption of surfactant molecules. Zeolites also have high cation exchange capacities but have rigid three-dimensional structures free of shrink–swell behavior. Long-chain cationic surfactants such as HDTMA are too large to enter the zeolite pores (13). Thus, the sorption of HDTMA is exclusively on the external surfaces of zeolite particles. Progressive surface modification by HDTMA results in different fractional organic carbon contents with different surface configurations of sorbed surfactant molecules.

In aqueous solution surfactant molecules form micelles if the concentration exceeds the critical micelle concentration (cmc). When the initial concentration exceeds the cmc, cationic surfactant micelles sorb on negatively charged surfaces to form admicelles or a bilayer (14). The first surfactant layer is anchored to the surface by cation exchange while the outer layer is retained by hydrophobic interactions and stabilized by counterions (15–16). The ratio of surfactant in “bilayer” versus “monolayer” configuration is dependent on the total amount of surfactant in solution and the characteristics of the counterions (15–16). When the surfactant concentration is less than the cmc, only monomers exist in solution. At low surface coverage the surfactant molecules sorb primarily as monomers on the negatively charged surface. A second layer may or may not form by self-assembly depending upon the equilibrium surfactant concentration (14). A desired surfactant configuration on the surface can be achieved by controlling the initial and final surfactant concentrations in the system.

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In this study, we investigated sorption of the model nonpolar organic solute perchloroethylene (PCE) by the model organic surface surfactant-modified zeolite (SMZ). We focused on the effects of bound surfactant concentration on PCE sorption, with particular emphasis on the variability of K_{oc} with surfactant loading.

Materials and Methods

Zeolite. The zeolite used in this study is a natural clinoptilolite from the St. Cloud mine in Winston, New Mexico. The material is approximately 74% clinoptilolite, 5% smectite, 10% quartz and cristobalite, 10% feldspar, and 1% illite (17). K^+ and Ca^{2+} are the major exchangeable cations. The external cation exchange capacity (ECEC) is 90–110 mequiv/kg (16), and the external surface area is 15.7 m²/g (17), resulting in an external surface charge density of about $-e/26 \text{ \AA}^2$. High molecular weight surfactants such as HDTMA are too large to enter the Ångström-scale internal zeolite channels and thus have access only to the external surface area and ECEC (13). The raw zeolite was sieved to yield particles (aggregates) in the range 0.42–0.83 mm (20–40 mesh). The fundamental clinoptilolite particles are micron-sized (17) but are bound together in stable aggregates by amorphous zeolite and other minerals. The sieved zeolite was used without pretreatment for HDTMA modification and the subsequent PCE sorption experiments. Previous research showed that the HDTMA sorption capacity on this zeolite is 210 mmol/kg for HDTMA-Br and 150 mmol/kg for HDTMA-Cl (16).

SMZ Preparation. The SMZ was prepared by treating zeolite with HDTMA-Br (>99% purity) or with HDTMA-Cl (30% active ingredient in water) both from Aldrich (Milwaukee, WI) to yield varying surface coverages up to 200 mmol/kg and 150 mmol/kg for HDTMA-Br and HDTMA-Cl, respectively. The cmcs of HDTMA-Br and HDTMA-Cl are 0.9 mM and 1.3 mM at 25 °C (16). The zeolite was modified using HDTMA initial concentrations both less than the cmc and greater than the cmc. For the <cmc treatment, 400 mL of 0.45 mM HDTMA-Br solution and varying amounts of zeolite (ranging from 0.9 to 9.5 g) were put into 500-mL bottles and shaken on a shaker table at 25 °C for 8 h at 150 rpm. The mixtures were centrifuged at 14500g for 25 min, the supernatants were removed, and the samples were air-dried. For the >cmc treatment, 30 g of zeolite and 180 mL of HDTMA-Br or HDTMA-Cl solution in the concentration range 10–67 mM were put into 500-mL bottles and shaken for 8 h. The supernatants were removed, and the samples were washed with two portions of Type I water and air-dried. For each treatment the equilibrium HDTMA concentration was analyzed using a chromatographic method described earlier (16). The amount of HDTMA sorbed on the zeolite surface was determined by difference. The target HDTMA loading levels for the SMZ were 25, 50, 75, 100, 150, and 200 mmol/kg when HDTMA-Br was used and 19, 38, 75, 113, and 150 mmol/kg when HDTMA-Cl was used.

PCE Sorption. Two grams of SMZ and 10 mL of aqueous PCE solution spiked with ¹⁴C-labeled PCE (specific activity 6.0 mCi/mmol, radiochemical purity >98%) from Sigma (St. Louis, MO) were put into 12-mL crimp-top vials and sealed with Teflon-lined septa while eliminating any headspace. Initial PCE concentrations ranged from 0 to 200 mg/L. Each mixture was placed on a shaker table and shaken at 25 °C and 150 rpm for 24 h (determined in preliminary experiments to be sufficient to attain sorption equilibrium) then centrifuged at 3600g for 30 min to yield a clear supernatant solution. Parallel experiments showed that less than 0.3 mM or less than 0.003 mmol of HDTMA (representing about 8% of the sorbed HDTMA at the lowest loading rate of 19 mmol/kg, and a smaller percentage at higher HDTMA loadings) desorbed from the SMZ during the equilibrations. One milliliter of the equilibrium solution was withdrawn using a

glass 2.5-mL gastight syringe, injected into 6 mL of scintillation cocktail (Ecolite from ICN Biomedicals, Inc., Costa Mesa, CA), and analyzed by ¹⁴C counting for equilibrium PCE concentration using a Packard Tri-Carb liquid scintillation counter. Duplicates and appropriate blanks were prepared for each concentration. Preliminary experiments proved that there was no PCE degradation during the equilibration and negligible PCE volatilization from the liquid scintillation cocktail.

Measurement of ζ -Potential. The ζ -potential of SMZ was measured using a Delsa-400 from Coulter Corp., Miami, FL. Duplicate measurements were performed for each HDTMA treatment level. Since the method requires colloidal-sized particles, zeolite aggregates were wet ground prior to HDTMA treatment; otherwise, SMZ was prepared as described above. Preliminary experiments showed that maximum HDTMA sorption differed by less than 10% between ground and unground samples; since individual zeolite crystals are in the submicron to micron size range (17), HDTMA sorption is not a strong function of aggregate size.

Results and Discussion

It is often assumed that the sorption of NOCs to an organic-rich substrate obeys a linear sorption isotherm:

$$C_s = K_d C_w \quad (1)$$

where C_s is the amount of solute sorbed per unit mass of sorbent, C_w is the equilibrium aqueous solute concentration, and K_d is the linear sorption coefficient. K_d is related to f_{oc} , the fractional organic carbon content of the sorbent, and K_{oc} , the organic carbon-based-partition coefficient of the NOC, by the following equation:

$$K_d = K_{oc} f_{oc} \quad (2)$$

For a given NOC, K_{oc} is reasonably constant and thus K_d increases linearly with respect to f_{oc} .

In a partitioning process the NOC distributes itself between two immiscible phases. The partition coefficient K_{oc} reflects the ratio of NOC concentrations in the organic phase (C_{oc}) and the aqueous phase (C_w).

$$K_{oc} = C_{oc} / C_w \quad (3)$$

Since f_{oc} is dimensionless and K_{oc} has the same units as K_d , C_{oc} has the units of (mass of NOC)/(mass of bound organic carbon).

Sorption of PCE by SMZ at the maximum HDTMA-Br loading of 200 mmol/kg, prepared from both <cmc and >cmc solutions, can be seen in Figure 1. The linear sorption of PCE was the same regardless of the method of SMZ preparation, indicating that both systems had equilibrated to the same final surfactant configuration. The sorbed surfactant molecules created an organic environment into which PCE molecules could partition (13). Results from Figure 1 indicate that SMZ, like surfactant-modified clay minerals, is an effective sorbent for organic compounds and can be used to remove NOCs from water.

Since the organic environments created by sorbed surfactant monomers and admicelles on the zeolite surface may be different, the efficiency of partitioning of NOCs into such environments may also be different. To test this hypothesis, SMZ was prepared at different surface loadings and with different initial HDTMA concentrations to test the influence of fractional organic carbon content on the PCE sorption coefficient. The plot of K_d versus HDTMA surface coverage (or f_{oc}) can be seen in Figure 2. It is clear that the K_d versus f_{oc} correlation follows a straight line only when the HDTMA loading is less than 100% of the ECEC of about 100 mmol/kg,

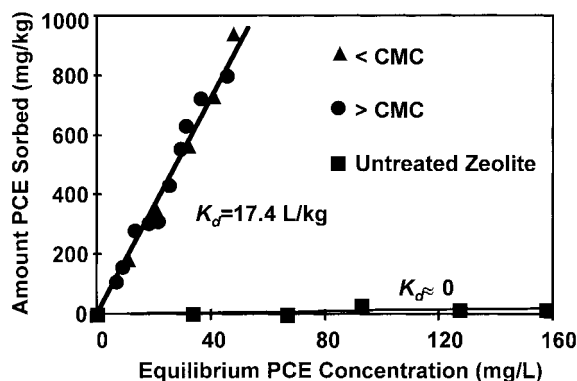


FIGURE 1. Sorption of PCE on SMZ prepared from solutions with the initial HDTMA-Br concentrations $<cmc$ and $>cmc$. In each case HDTMA was loaded to a coverage of 200 mmol/kg. For comparison the negligible PCE sorption by untreated zeolite is also plotted.

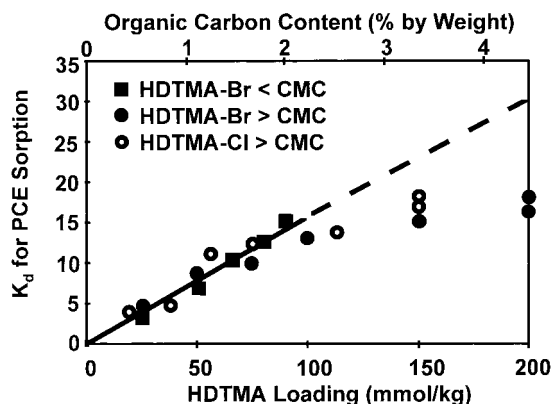


FIGURE 2. K_d for PCE sorption by SMZ as a function of HDTMA loading. SMZ was prepared using HDTMA solution concentrations both $<cmc$ and $>cmc$. The straight line is fitted to the data corresponding to HDTMA loadings of 0–100% of the ECEC.

that is, when surfactant molecules are expected to exist primarily in monolayer or submonolayer configuration on the zeolite surface. Further increases in surfactant loading resulted in progressive admicelle or bilayer coverage but caused little further increase in K_d (Figure 2). Thus, K_{oc} for PCE is not constant for the SMZ but is related to the level of surfactant loading on the surface. A similar trend in the K_d versus f_{oc} relationship was found for benzene sorption by SMZ (data not presented).

Figure 2 shows no evidence of a threshold for PCE sorption at low HDTMA loading levels, indicating that hydrophobic environments exist on the surface even when it is incompletely covered by HDTMA monomers. This lack of a sorption threshold suggests that HDTMA monomers associate together in patches at low loadings, rather than distributing themselves uniformly over the surface. Such patchlike associations of HDTMA molecules at low loading rates are supported by molecular investigations. Using atomic force microscopy, Sullivan et al. (17) showed the presence of "islands" of HDTMA at low loading rates, which expanded and ultimately coalesced as HDTMA surface coverage increased.

There is no clear change in HDTMA sorption behavior on clinoptilolite at the transition from equivalent monolayer to bilayer coverage. The entire HDTMA sorption isotherm is well-described by a Langmuir isotherm up to maximum surfactant sorption (16). This monotonic and strong sorption of HDTMA is also reflected by thermodynamic calculations which indicate higher free energies of sorption for HDTMA in bilayer versus monolayer configuration (18).

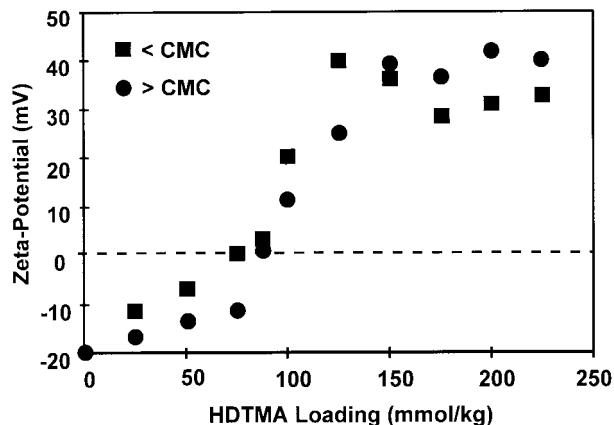


FIGURE 3. SMZ zeta potential versus HDTMA loading. SMZ was prepared using HDTMA solutions both $<cmc$ and $>cmc$.

TABLE 1. Sorption of PCE by SMZ as a Function of HDTMA Surface Coverage^a

HDTMA surface coverage (mmol/kg)	K_d (L/kg)	f_{oc} (%)	K_{oc} (L/kg)
<100	0–12.4	0.0–1.9	660 ± 63^b
100	13.4 ± 0.6	2.3	588
113	13.5 ± 0.3	2.6	524
150	17.5 ± 0.5	3.4	512
200	17.4 ± 0.8	4.6	382

^a K_{oc} was obtained from eq 2. ^b Based on linear regression of the data for PCE sorption at HDTMA surface coverages <100 mmol/kg.

Zeta potential is a reflection of surface potential. Zeta potential changes with respect to different HDTMA loadings reflect the transition between monolayer and bilayer coverage on the SMZ (Figure 3). The same trend in ζ potential resulted no matter whether the initial HDTMA concentrations were $<cmc$ or $>cmc$. The zero point of charge (zpc) was 80–90 mmol/kg (Figure 3), in agreement with the zeolite's ECEC of 90–110 mequiv/kg (16). Therefore, the zpc may correspond to a complete monolayer surface coverage by HDTMA and may be a good indicator for a surface exhibiting maximum hydrophobicity. Visual observations showed rapid flocculation of SMZ suspensions when the HDTMA loading was equal to 100% of the ECEC. The surface progressively loses its negative charge with increasing HDTMA loading and becomes more hydrophobic as the zpc is approached. Above the zpc, a second layer of HDTMA molecules reverses the surface charge. This reversal of surface charge is responsible for the sorption of anions by SMZ (16, 17). Upon bilayer sorption of HDTMA the surface again becomes hydrophilic and the colloidal particles re-disperse.

The K_d values from Figure 2 along with the corresponding K_{oc} values are listed in Table 1. K_{oc} is approximately constant (660 ± 63 L/kg) for HDTMA surface coverages below the zeolite ECEC of about 100 mmol/kg. At HDTMA surface coverages above 100 mmol/kg, K_{oc} progressively decreases, dropping to a value of 382 L/kg when the HDTMA loading on the zeolite is 200 mmol/kg. Clearly, the configuration of HDTMA on the zeolite surface, not just the total amount of HDTMA (or organic carbon), controls PCE sorption on SMZ. PCE is more efficiently partitioned into HDTMA when it is present in submonolayer or monolayer configuration (below the ECEC) than when it is present as admicelles or in a bilayer (above the ECEC).

In studying the solubilizing power of sorbed bilayers in the presence of solution micelles, Mukerjee et al. (19) found that bilayers were more effective solubilizers for Orange OT than were the micelles. They attributed these results to

differences in the geometries of surfactant molecules in the planar bilayer versus in the spherical micelles. This suggests that the specific volume of the sorbed surfactant molecules (equivalently, the density of the bound hydrocarbon phase) must play an important role in NOC sorption. Yu and Lobban (8) also noted changes in K_{oc} with surfactant loading when they studied the adsolubilization of trimethyl orthobenzoate and its reaction product methyl benzoate by SDS sorbed on porous activated acidic alumina. Yu and Lobban (8) attributed the variation in K_{oc} to changes in the surface configuration and packing of SDS molecules on the surface. We suggest that Yu and Lobban (8) were observing the same decrease in K_{oc} with SDS coverage that we observed for HDTMA.

Since $C_{oc} = x_{oc}/(V_{oc}\rho_{oc})$, $C_w = x_w/(V_w\rho_w)$, where x_{oc} and x_w are the mole fraction concentrations of the NOC in the organic phase and in aqueous solution, respectively, V_{oc} and V_w are the molar volumes of the two phases, ρ_{oc} is the hydrocarbon density of the bound organic phase (or the density of the sorbed HDTMA in this study), and ρ_w is 1, eq 3 can be written as

$$K_{oc} = \frac{x_{oc}}{V_{oc}} \frac{V_w}{x_w} \frac{1}{\rho_{oc}} \quad (4)$$

Thus, K_{oc} is a function of ρ_{oc} which is in turn a function of surface configuration of the sorbed HDTMA molecules. Since the sorption of monomers is controlled primarily by cation exchange, ρ_{oc} for HDTMA sorbed below the zeolite's ECEC depends on the surface charge density. The data presented in Figure 1 and by Sullivan et al. (20) suggest that HDTMA monomers sorb in distinct patches, due to hydrophobic interaction, of equal ρ_{oc} , yielding a constant K_{oc} for NOC sorption until full monolayer coverage is achieved. Above monolayer coverage, the sorbed surfactant molecules associate to form patchy bilayers or a complete bilayer. Depending upon the configuration and interaction of the sorbed surfactant bilayer, the thickness of the bilayer may be twice the thickness of the surfactant monolayer. On the other hand, if strong hydrophobic bonding exists the surfactant molecules in the bilayer may be interfingered and the thickness shortened so as to maximize van der Waals interactions among HDTMA tail groups. Evidence from Raman spectroscopy of HDTMA sorbed on zeolite (20) suggests greater interdigitization of surfactant chains when HDTMA is sorbed as a bilayer rather than as a monolayer. Therefore, an increased hydrocarbon density may exist in the admicelle/bilayer system.

Potential configurations of sorbed surfactant molecules are shown in Figure 4. For submonolayer sorption below the ECEC, the distribution and hence the density of HDTMA is controlled by the charge density on the zeolite surface (Figure 4a). We can estimate the average thickness of surfactant in monolayer configuration from the length of an HDTMA molecule. According to Tanford (21), for an aliphatic surfactant hydrocarbon chain of n carbon atoms in a micelle, the length l can be estimated as $l(\text{\AA}) = 0.8(1.265n + 0.15)$. For HDTMA this yields an effective hydrocarbon length of 16.3 \AA. Assuming close-packing of monomers in patches on the surface, as indicated by the PCE sorption data at less than full monolayer coverage, we can thus assume an average monomer length of about 16 \AA. Alternatively, taking the volume of the hydrocarbon chain of an HDTMA molecule as $v(\text{\AA}^3) = 26.9n + 27.4$ (21), and the area occupied per molecule on the surface as 26\AA^2 (as described in the Materials and Methods section), we derive a similar value of 17 \AA for the monolayer thickness.

Due to the hydrophobic interaction between the HDTMA molecules in the upper and lower layers, the thickness of an HDTMA bilayer may be less than twice the monolayer

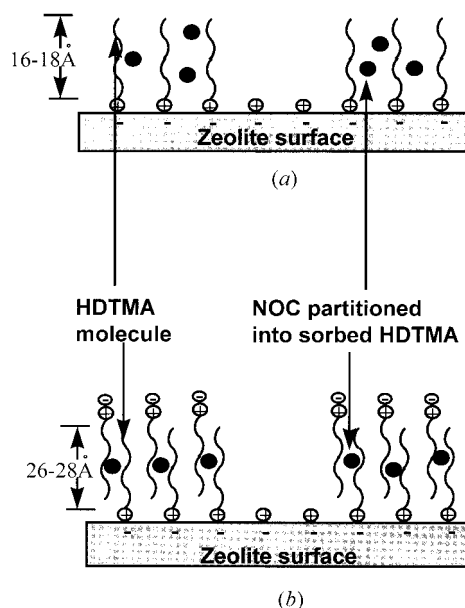


FIGURE 4. Schematic diagram of PCE partitioned into HDTMA in various configurations on the zeolite surface. (a) HDTMA sorbed as monomers below the ECEC. (b) HDTMA in an interfingered bilayer.

thickness. Studies of the sorbed layer of HDTMA-Br on quartz performed by McDermott et al. (22) using neutron reflection showed that the surface could be described by a three-layer mosaic having top and bottom layers 4 \AA in thickness (corresponding to the headgroups) with alkyl chains 26 \AA in thickness sandwiched in between. In a similar study Rennie et al. (23) measured a thickness of $28 \pm 4 \text{\AA}$ for the hydrocarbon chain portion of a sorbed HDTMA-Br bilayer on amorphous silica. Thus, the upper and lower HDTMA layers appear to be interfingered with an average hydrocarbon thickness of about 27 \AA (Figure 4b), resulting in a higher density than in the monomer system.

The hydrocarbon density is proportional to the thickness of the surfactant layer and f_{oc} . On the basis of the above measurements, the relative density of the bilayer system to the monolayer system (per mole of surfactant) is $17 \text{\AA}/[(27 \text{\AA})/2] = 1.3$. This ratio is close to the relative K_{oc} 's for PCE sorption by the monomer and full bilayer systems (Table 1) of $660/382 = 1.7$. The correlation between HDTMA density and partitioning ability suggests that, for a given f_{oc} , the NOC sorption is reduced when the density of the bound organic phase increases. Assuming x_{oc} , x_w , V_{oc} , and V_w in eq 4 are relatively constant, the density of sorbed HDTMA in a bilayer configuration is about 1.7 times greater than the density of sorbed HDTMA in a monolayer configuration.

Others have observed decreases in partition coefficients in bilayer systems. In studying lipid bilayer membranes De Young and Dill (24) observed that nonpolar solute partitioning into the bilayer was dependent not only on the solute's oil/water partition coefficient but also on the surface density of the bilayer chains. Increasing bilayer surface density led to solute exclusion: benzene partitioning decreased by an order of magnitude and hexane partitioning decreased by a factor of 9 as the surface density increased from 50% to 90% of its maximum value, a range readily accessible in bilayers and biomembranes under physiological conditions (24-25). De Young and Dill concluded that the partitioning of solute into bilayer membranes, which are interfacial phases, is of a fundamentally different nature than partitioning into bulk oil and octanol phases (24-25). Similarly, phenol sorption to a HDTMA-Cl sorbed layer on quartz and corundum also revealed a decrease in the partition coefficient as the equilibrium surfactant surface concentration increased (26).

These results from different investigators are consistent with our hypothesis that PCE sorption in our system was controlled by the density of the sorbed HDTMA layer.

The hypothesis of increased surfactant packing density in the HDTMA bilayer is supported qualitatively by the results of the Raman spectroscopic investigations noted above (20). This hypothesis could be confirmed quantitatively by measuring the thickness of sorbed HDTMA monolayers and bilayers using ellipsometry (27), neutron reflection (28–29), or other techniques. Such measurements are difficult on natural sedimentary zeolites such as the one examined here due to the small size (typically $< 1 \mu\text{m}$) of the zeolite crystals. Differences in monolayer versus bilayer environments may also be detectable by spectroscopic analyses of these systems in the presence of sorbed PCE or other nonpolar organics.

To summarize, surfactant-modified zeolite is an effective sorbent for removal of PCE from water. The sorption of PCE on SMZ is due to partitioning of PCE into the organic phase formed by the surfactant on the zeolite surface. The PCE sorption coefficient on SMZ is a function of the surfactant loading and resultant organic phase density. PCE is most efficiently sorbed by SMZ when surfactant is present at or below full monolayer coverage; at higher surfactant loading levels, PCE sorption appears limited by a reduced effective volume and an increased density of the hydrophobic core of the sorbed surfactant bilayer, resulting in a decreased K_{oc} . The greater hydrophobicity of the monolayer- versus the bilayer-modified surface may also add to the greater PCE sorption efficiency exhibited by the monolayer system. The results from this research indicate that for removal of NOCs from water the most economical treatment (in terms of moles of NOC sorbed per mole of surfactant) would be to produce a monolayer, rather than a full bilayer, of HDTMA on the zeolite surface.

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