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Sorption Characteristics, Mechanism(s), and
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Sorption Characteristics, Mechanism(s), and Surface Heterogeneity of Organo-Clays

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ABSTRACT

Sorption Characteristics, Mechanism(s), and Surface Heterogeneity of Organo-Clays

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The sorptive characteristics of organoclays were compared in terms of magnitude and mechanism to those of natural soil organic matter. It has been demonstrated that multimechanisms control the sorption of aqueous phase neutral organic contaminants (NOCs) by organoclays including solvation of the cationic ammonium centers, the alkyl chains of HDTMA and the mineral surfaces, and solute partitioning. In contrast, solute partitioning appears to be the singular mechanism for the sorption of aqueous phase NOCs by natural soil organic matter. Organic contaminant sorption by the surfactant derived organic matter of organoclays is substantially higher than by natural soil organic matter due to the existence of multiple sorptive mechanisms for organoclays and the greater solvency of their organic phases.

Sorption of NOCs by organophilic organoclays is either enhanced or depressed by the presence of the second solute depending on the solubility parameters of both solutes. Aliphatic solutes either increase or decrease the solvency of the surfactant derived organic matter for NOCs. Aromatic molecules expand the swelling organoclays by solvating the cationic centers and alkyl chains of surfactant cations and the mineral

surfaces. They also increase the solvency of the organic phase of organoclays for NOCs. It appears that sorption of multiple organic contaminants in complex environmental systems by organoclays generally produces a synergistic effect.

Organic cations in adsorptive organoclays (layer silicate clays modified with small quaternary ammonium cations such as trimethylphenylammonium (TMPA)) take a partially random distribution in the interlayers of organoclays. These cations function as non-hydrated pillars and adsorption of organic molecules occurs predominantly on the adjacent siloxane surface, which is hydrophobic in nature. In mixed Ca/TMPA-smectites, the presence of TMPA and its partially random distribution result in far less water associated with the clay. The interspersing of TMPA and Ca^{2+} ions prohibits the formation of a network of large hydration shells around Ca^{2+} rendering the siloxane surface available for the adsorption of NOCs. The partially random distribution also creates an energetically (energy distribution) and structurally (fractal dimension) heterogeneous surface in organoclays. The effect of such heterogeneity on adsorption of organic molecules depends on the size of probe molecules. This heterogeneity is largely generated by the microporosity of organoclays.

To my mother

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Abstract

Layer silicate clays modified with cationic surfactants ("organoclays") such as hexadecyltrimethylammonium (HDTMA) are effective sorbents for neutral organic contaminants (NOCs), and may be useful for *in-situ* and *ex-situ* remediation of contaminated soils and waters. In this study, the sorptive characteristics of organoclays were compared in terms of magnitude and mechanism to those of natural soil organic matter. The data presented here support multiple mechanisms controlling the sorption of aqueous phase NOCs on organoclays including solvation of the cationic ammonium centers, the alkyl chains of HDTMA and the mineral surfaces, and solute partitioning. In contrast, solute partitioning appears to be the singular mechanism for the sorption of aqueous phase NOCs by natural soil organic matter. Organic contaminant sorption by the surfactant derived organic matter of organoclays is substantially higher than by natural soil organic matter due to the existence of multiple sorptive mechanisms for organoclays and the greater solvency of their organic phases.

Key Words - mechanism, sorption, organoclay, solvation, partition.

Introduction

Earlier studies have demonstrated that replacing the native inorganic exchange cations of clay minerals, soils and subsoils with organic cations of the form $[(CH_3)_3NR]^+$ results in greatly enhanced abilities of the materials to remove organic contaminants from water *(Boyd et al., 1988a,b,c; Brixie et al., 1994; Jaynes et al., 1990, 1991a,b; Lee et al., 1989a,b, 1990; Mortland et al., 1986; Wagner et al., 1994)*. The impressive sorptive capabilities of surfactant modified clays suggested their potential utility for treating contaminated waters, as extenders for activated carbon, and as components of clay containment barriers, for example, in clay slurry walls, hazardous waste landfills and petroleum tank farms *(Boyd et al., 1991)*. These studies also suggested that aquifer materials or subsoils could be modified *in-situ* via injection of cationic surfactants to create sorptive zones that could intercept and immobilize advancing contaminant plumes *(Boyd et al, 1988a, 1991; Burris et al., 1992; Lee et al., 1989a)*. Coupling contaminant immobilization with *in-situ* biodegradation would provide a comprehensive restoration technology to permanently eliminate target contaminants *(Burris et al., 1992; Nye et al., 1994)*.

Elucidating the mechanistic function of organoclays as sorbents for organic contaminant molecules is important for understanding, predicting and maximizing their sorptive capabilities, and for designing new families of organoclays. In the case where the organic cations comprising the organoclay contain a large hydrophobic alkyl chain (e.g., HDTMA), the interlamellar spaces of expandable clay minerals (e.g., smectite) are almost fully occupied by the alkyl chains *(Jaynes et al., 1991b)*. A conglomeration of the alkyl chains on the clay surfaces and interlayer regions results in the formation of an organic phase that controls the sorptive removal of organic contaminants from water.

In analogy to the mechanistic function of natural soil organic matter *(Chiou et al., 1979, 1983)*, the sorption of nonionic organic contaminants (NOCs) from water by organoclays such as HDTMA-smectite was originally viewed as a partitioning process involving the organic cation derived organic phase *(Boyd et al., 1988b; Jaynes et al., 1991b)*. The partition coefficients for the sorption of aqueous phase hydrocarbon contaminants (e.g., benzene, toluene, ethylbenzene) from water over a limited range of solute concentrations were estimated using a simple linear relationship between the amount sorbed and the equilibrium aqueous concentration to describe the sorption isotherms, in accordance with the concept of solute partitioning *(Chiou et al., 1979, 1983)*. The general observation was that sorption coefficients for contaminant sorption by organoclays were considerably higher (10 to 30 times) than those for soil organic matter *(Boyd et al., 1988a; Lee et al., 1989a)*. This was attributed to the nonpolar nature of the organic cation (e.g., HDTMA) derived phase as compared to soil organic matter which contains an abundance of polar functional groups (e.g., -OH, -COOH).

In the present study, we have examined in greater detail the sorptive characteristics of HDTMA-clays for aqueous phase NOCs in an attempt to define the operative sorptive mechanism(s). Sorption was characterized over a wide range of solute concentrations approaching their water solubilities. Changes in the d-spacing (d_{001}) of HDTMA-clays due to contaminant sorption were also quantitated using X-ray diffraction (XRD). The sorptive characteristics of organoclays were compared in terms of magnitude and mechanism to those of natural soil organic matter. The data presented here support multiple mechanisms controlling the sorption of aqueous phase NOCs on organoclays including solvation of the cationic ammonium centers, the alkyl chains of HDTMA and the mineral surfaces, and solute partitioning. In contrast, solute partitioning appears to be the singular mechanism for the sorption of aqueous phase NOCs by natural soil organic matter.

Experimental Section

The muck soil used in this study was collected from Michigan State University Muck Farm (Lainsburg, MI). The clays used in this study were illite from Fithia, Illinois, low-charge smectite (mostly low-charge montmorillonite, SAC) from Wyoming (American Colloid Company, Chicago, IL), and high-charge smectite (high-charge montmorillonite, SAz-1) from Arizona (the Source Clays Repository of the Clay Minerals Society). The <2μm clay fractions were obtained by wet sedimentation and subsequently saturated with Ca^{2+} cations by washing the clay repeatedly with $CaCl_2$ solution (0.1 mol/l). HDTMA bromide (Aldrich Chemical Co.) was dissolved in warm distilled water and used to prepare HDTMA organoclays. A portion of clay suspensions containing 25 g of clays was treated by adding HDTMA bromide solution (0.03 mol/l) in an amount just equal to the cation-exchange capacity of the clays (224 $mmol_c$/kg for illite, 900 $mmol_c$/kg for SAC, and 1200 $mmol_c$/kg for SAz-1). The mixtures were agitated overnight on a magnetic stirrer at room temperature. The HDTMA-illite (IH), HDTMA-SAC (SACH) and HDTMA-SAz-1 (SAzH) suspensions were then washed with distilled water repeatedly until free of bromide ions as indicated by $AgNO_3$. The HDTMA organoclays were then stored in bottles for later use. Organic carbon contents of the HDTMA organoclays were determined using Dohrmann DC-190 high temperature TOC analyzer

(Rosemount Analytical Inc., Santa Clara, CA).

Sorption of benzene, nitrobenzene, chlorobenzene, trichloroethylene, and carbon tetrachloride (Aldrich Chemical Co.) on muck soil and HDTMA organoclays was conducted using a batch equilibration technique. A weight of 1 g of muck soil, 0.8 g of IH, 0.2 g of SACH or 0.2 g of SAzH and 25 ml of distilled water were placed in Corex glass centrifuge tubes. Organic solutes were added neat using a Hamilton microliter syringe to produce a range of initial and final concentrations. The tubes were capped immediately with teflon-backed septa. The tubes were shaken for 24 hours on a rotator at room temperature. Preliminary experiments showed that sorption reached equilibrium within 18 hours. After equilibration, the tubes were centrifuged at 8000 rpm (RCF=4302 g) for 10 minutes to separate liquid and solid phases. A volume of 5 ml of supernatant was extracted with 10 ml of carbon disulfide in a glass vial.

Analysis of organic solutes in the carbon disulfide extracts was made by gas chromatography. A Hewlett-Packard 5890A gas chromatograph fitted with a flame ionization detector and a packed column (Alltech Co.) was used; N_2 was the carrier gas. Peak areas were recorded by a Hewlett-Packard 3392A integrator, and compared to external standards to determine the concentrations of organic solutes. The recovery of organic solutes in blanks not containing organoclays was about 90%. The amount of organic solutes sorbed was calculated from the differences between the amount of organic solutes added and that remaining in the final equilibrium solutions. Sorption isotherms were made by plotting the amount sorbed versus the equilibrium concentration in solution. All sorption isotherms were normalized to organic carbon content of the corresponding sorbents.

Sorption of trichloroethylene in the presence of a cosolute was performed by adding chlorobenzene into the glass centrifuge tubes containing either muck soil or SACH, distilled water and trichloroethylene. A volume of 10 μl of chlorobenzene was added to each tube. Immediately after addition of chlorobenzene, the experiments were continued following the procedure described above.

Partition of chlorobenzene and trichloroethylene between hexane (Aldrich Chemical Co.) and water was measured in glass centrifuge tubes containing 20 ml of water and 2 ml of hexane. Different amounts of chlorobenzene and trichloroethylene were added directly. Following addition, the tubes were immediately sealed, and shaken vigorously for 10 min. The aqueous phase was extracted with CS_2. The hexane phase was diluted to a proper concentration of chlorobenzene and trichloroethylene. The concentration of chlorobenzene and trichloroethylene in both the hexane phase and CS_2 extract was analyzed by gas chromatography. Hexane-water partitioning was normalized to the organic carbon content of hexane.

Basal spacings (d_{001}) of HDTMA organoclays, and of SACH and SAzH with chlorobenzene or trichloroethylene sorbed were determined by XRD analysis. HDTMA clay suspensions were dropped on glass slides, and immediately covered by teflon tape to prevent vapor loss. X-ray diffraction patterns were recorded using CuKα radiator and a Philips APD3720 automated X-ray diffractometer using an APD3521 goniometer fit with a θ-compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator, from 2 to $10^{0}2\theta$, in steps of $0.03^{0}2\theta$, 1 sec/step.

Results and Discussion

Sorption isotherms of benzene, nitrobenzene, chlorobenzene, trichloroethylene, and carbon tetrachloride from water onto IH, SACH and SAzH, and onto the muck soil are shown in Figure 1.1. Table 1.1 shows some properties of the HDTMA-clays and muck soil. The sorption isotherms of all five solutes tested were highly linear for the muck soil. In contrast, NOC sorption by the organoclays resulted in isotherms with distinct curvature which differed in shape and extent depending on the specific solute and sorbent. Isotherms of trichloroethylene and carbon tetrachloride on all three organoclays are type III which is convex to the abscissa commencing at the origin. Sorption of these two solutes is much lower on SACH than on SAzH and IH. The isotherms of benzene, nitrobenzene and chlorobenzene are more complex with a double-sigmoid shape. At low relative concentrations of these aromatic solutes, the amount sorbed on SACH is much lower than on SAzH and IH.

Table 1.1. Properties of muck soil and HDTMA-treated clays.

Sample	Source	Organic C (%)	Charge (mol$_c$/unit cell)	CEC (cmol$_c$/kg)	d-spacing (Å)
Muck Soil	Michigan State University Farm	49.0	-	-	-
Illite					
IH	Illinois	4.96	1.44	22.4	10.0
Smectites					
SAzH	Arizona	20.7	1.14	120	28.7
SACH	American Colloid Co.	16.5	0.64	90	21.6

The high linearity of isotherms on the muck soil is consistent with previous observations and with the concept of solute partitioning into soil organic matter *(Chiou et al., 1979, 1983)*. Similarly, partitioning is apparently the dominant sorptive mechanism for trichloroethylene and carbon tetrachloride sorption by HDTMA-clays. Here, the much higher degree of sorption into the HDTMA phase, as compared to soil organic matter, substantially changed the composition of the phase. This caused the solvency (i.e. the solubilization capability) of HDTMA phase for these solutes to increase so that the isotherms became convex to the abscissa, and hence are classified as type III. A similar phenomenon was observed for the partitioning of trichloroethylene and chlorobenzene between hexane and water (Figure 1.2).

The solubility parameter *(Barton, 1991; Hildebrand et al., 1970)* of the HDTMA phase after sorption of solute molecules can be expressed as:

$$\delta = (1-\phi_2)\delta_{HDTMA} + \phi_2\delta_2 \tag{1.1}$$

where ϕ_2 is the volume fraction of the solute; δ_{HDTMA} and δ_2 are the respective solubility parameters of the pure HDTMA phase and the solute. The change in solubility parameter of the HDTMA phase with solute content is:

$$\frac{d\delta}{d\phi_2} = \delta_2 - \delta_{HDTMA} \tag{1.2}$$

The term $\frac{d\delta}{d\phi_2}$ measures the ability of the solute to increase the solvency of the HDTMA phase, and is directly related to the difference of the solubility parameters of the two mixing phases. The solvency increase of the HDTMA phase is thus dependent on ($\frac{d\delta}{d\phi_2} \times Q \times f$) where Q is the amount of solute sorbed and f the conversion factor to convert Q in mmol/g to the volume fraction. The value of $\frac{d\delta}{d\phi_2}$ for the solutes used in this study (Table 1.2) indicates that

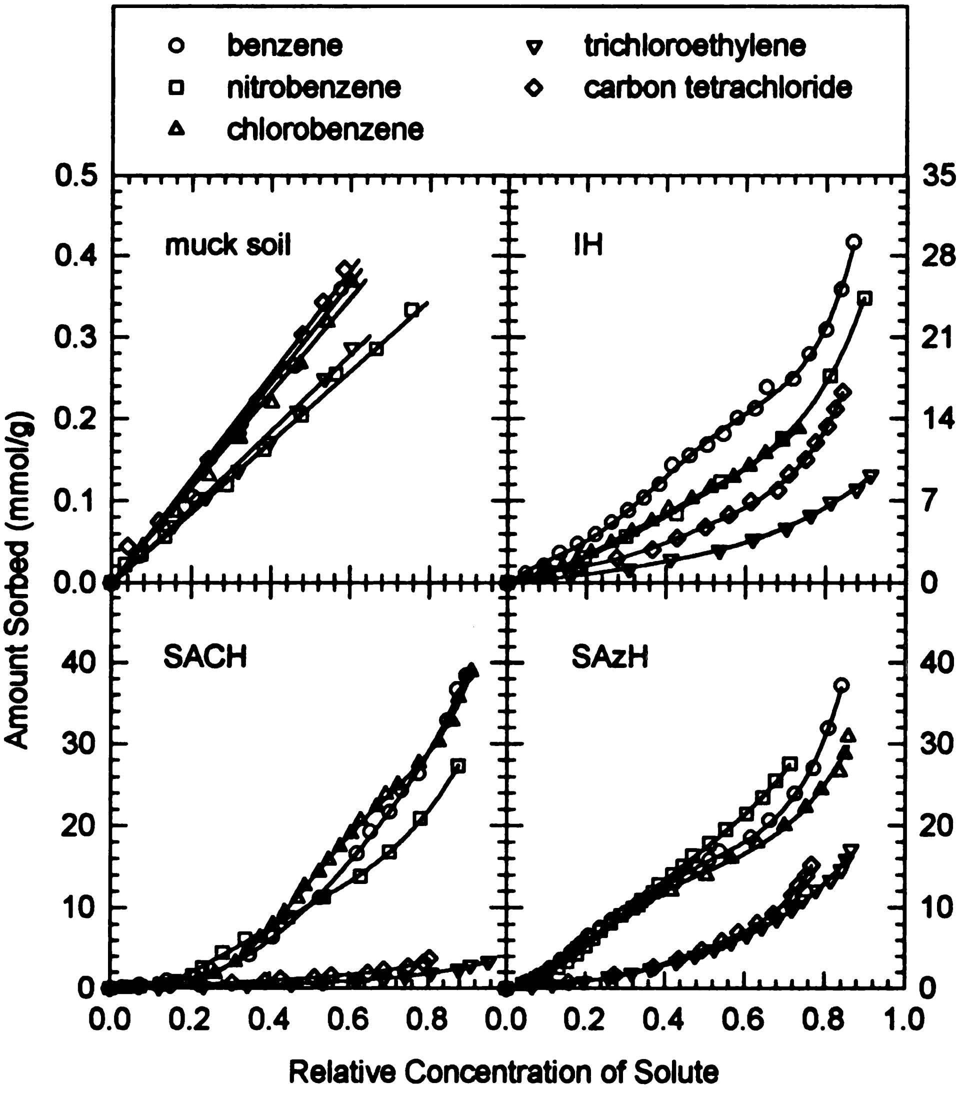

Figure 1.1 Sorption of aqueous phase organic solutes on a muck soil and hexadecyltrimethylammonium(HDTMA)-clays normalized to organic carbon content

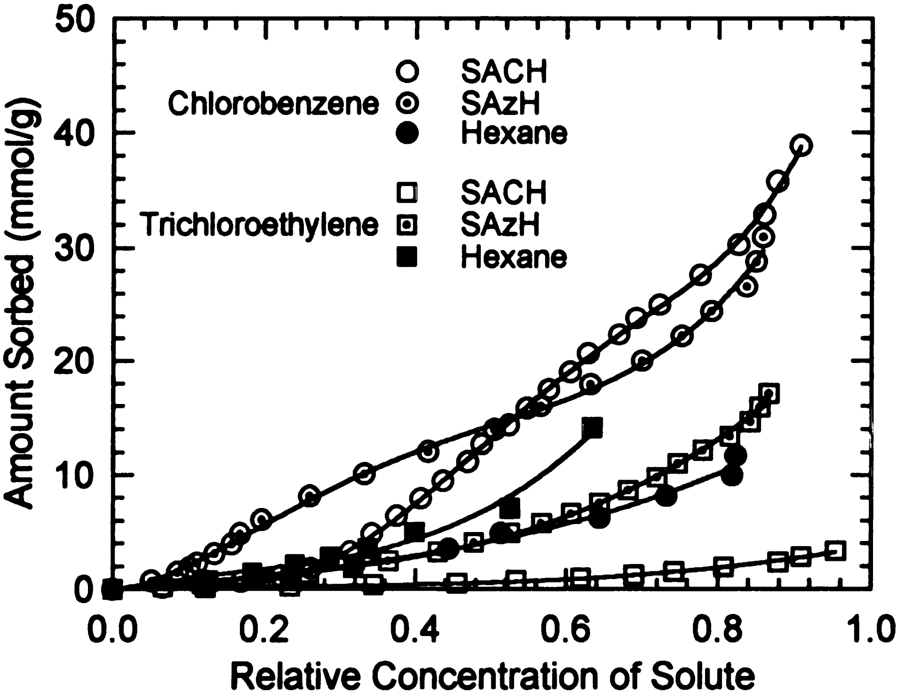

Figure 1.2 Comparison of organic carbon normalized sorption isotherms of SACH, SAzH, and hexane for chlorobenzene and trichloroethylene

trichloroethylene more effectively increases the solubility parameter of the HDTMA phase than carbon tetrachloride, resulting in a type III isotherm despite the comparatively low amount of trichloroethylene sorbed (small Q) on SACH.

Table 1.2. Organic carbon normalized distribution coefficients of organic compounds at a relative concentration of 0.4 and their solubility parameters (δ_2).

Organic Compound	Distribution Coefficient (l/kg)			δ_2* ($cal^{1/2}/cm^{3/2}$)	$\frac{d\delta}{d\phi_2}$ **
	IH	SAzH	SACH		
benzene	1035.8	1369.7	675.8	9.1	1.1
nitrobenzene	970.6	2119.0	1276.6	10.9	2.9
chlorobenzene	3541.7	6678.6	4174.8	9.6	1.6
trichloroethylene	563.5	863.6	133.8	9.3	1.3
carbon tetrachloride	1764.8	1551.4	506.1	8.7	0.7

* Barton, A.F.M. *Handbook of Solubility Parameters and Other Cohesion Parameters.* CRC Press: Boca Raton, FL, 1991. 739pp.

** This term represents the change in the solubility parameter of the HDTMA phase with solute content. ϕ_2 is the volume fraction of the solute. δ_{HDTMA} is not available and was substituted for by $\delta_{C_{16}H_{34}}$=8.0 $cal^{1/2}/cm^{3/2}$.

A comparison of trichloroethylene and carbon tetrachloride distribution coefficients (Table 1.2) on SACH, SAzH and IH (external organic phase only) shows that both molecules are intercalated in the interlamellar region of SAzH while they are only partitioned into the external HDTMA phase of SACH. This results in substantially lower organic carbon normalized distribution coefficients for SACH, and is apparently due to the smaller d-spacing of SACH than SAzH (Table 1.1). XRD shows no increase in the d-spacing of SACH, but a significant increase in the d-spacing of SAzH, accompanying sorption of trichloroethylene (Figure 1.3), confirming its intercalation by SAzH. Intercalation of these solutes by SAzH is

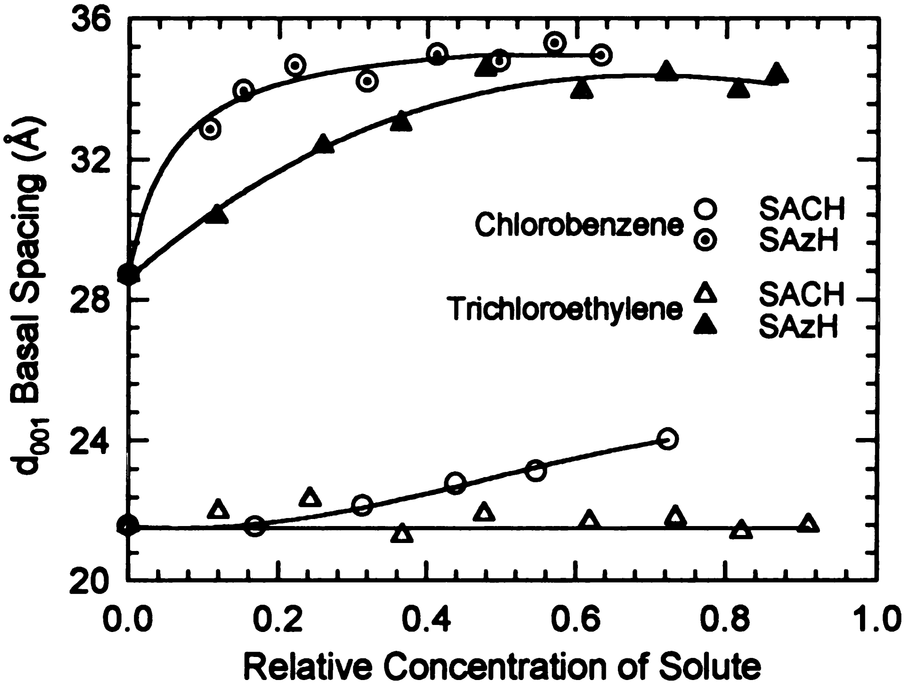

Figure 1.3 Sorption-dependent variation of the d-spacings of SACH and SAzH

allowed by its initially greater d-spacing of 28.7Å corresponding to a paraffin layer structure of HDTMA *(Xu et al., 1995)* as compared to a 21.6Å d-spacing in SACH corresponding to a flat-lying pseudotrimolecular layer arrangement of HDTMA.

We propose that multiple mechanisms are involved in the sorption of aromatic compounds (viz., benzene, chlorobenzene, nitrobenzene) by HDTMA-clays. Aromatic molecules, due to their planar shape and delocalized π-bonds, interact strongly with HDTMA, causing a reorientation of the alkyl chains. These solute molecules solvate the cationic ammonium centers and alkyl chains of HDTMA *(Slabaugh et al., 1968; Solomon et al., 1983)*, causing a transition from a parallel to more vertical position relative to the silicate sheets. Solute molecules are concomitantly adsorbed on the vacated mineral surfaces which are hydrophobic in nature *(Jaynes et al., 1991a)*. An increase in the d-spacing accompanied chlorobenzene but not trichloroethylene sorption by SACH (Figure 1.3). Solute partitioning into the HDTMA phase is also an important concurrent mechanism. The combination of solvation and partitioning produces substantially higher sorption of aromatic hydrocarbons than of aliphatic hydrocarbons.

The d-spacing of SACH is initially too small to effectively intercalate aromatic hydrocarbons, and hence they are sorbed to a similar extent as trichloroethylene and carbon tetrachloride. This can be inferred from the low degree of sorption (as compared to SAzH) at low relative solute concentrations (Figure 1.2). At a relative chlorobenzene concentration of about 0.2, however, the chemical potential is apparently sufficient to cause an interlayer expansion, which can be observed directly with XRD (Figure 1.3). Similar isotherms were observed for benzene and nitrobenzene, suggesting the same phenomena. Once the interlayers are open, solvation and solute partitioning together produce high sorption of aromatic molecules by SACH, similar to SAzH. The greater d-spacing of SAzH as compared to SACH provides immediate access of both aromatic and aliphatic solutes to the interlayer regions, resulting in swelling of SAzH (Figure 1.3). Partitioning of trichloroethylene and carbon tetrachloride increases the interlayer volume as well as the solvency of the HDTMA phase, resulting in a type III isotherm. For the aromatic molecules, the combination of this mechanism plus solvation of HDTMA and mineral surfaces leads to higher sorption and double-sigmoid isotherms.

In contrast to organoclays, sorption of NOCs by natural soil organic matter is characterized by highly linear sorption isotherms and similarity in the degree of uptake of aromatic and aliphatic molecules of similar water solubilities (Figure 1.1). Also, the presence of a cosolute caused differential effects on sorption by soil organic matter and organoclays. Sorption of trichloroethylene in binary solute systems containing chlorobenzene is shown in Figure 1.4. In the case of natural soil organic matter, the presence of chlorobenzene has absolutely no effect on the sorption of trichloroethylene, consistent with the concept of simple solute partitioning, and the comparatively low degree of chlorobenzene sorption. In contrast, the addition of chlorobenzene causes substantially increased uptake of trichloroethylene by SACH. Solvation of HDTMA by chlorobenzene separates the clay layers (as described above), rendering the interlayers accessible for trichloroethylene sorption. Chlorobenzene sorption by SACH also increases the solvency of the HDTMA phase for trichloroethylene, resulting in greater uptake. Similar effects have been observed in cosolute systems containing nitrobenzene *(Sheng et al., 1996)*.

The sorption mechanisms proposed here for organoclays are consistent with the partitioning results of chlorobenzene and trichloroethylene between hexane and water (Figure 1.2), the findingsof Slabaugh et. al. *(1968; Solomon et al., 1983)*, and previous statistical thermodynamic studies on the sorption of gases on polymers *(Pyda et al., 1982, 1983, 1993)*. The lack of solvation of hexane by chlorobenzene results in lower uptake of chlorobenzene from water by hexane than by HDTMA-clays where solvation of HDTMA by chlorobenzene and partitioning both occur. Conversely, partitioning of trichloroethylene into hexane, which

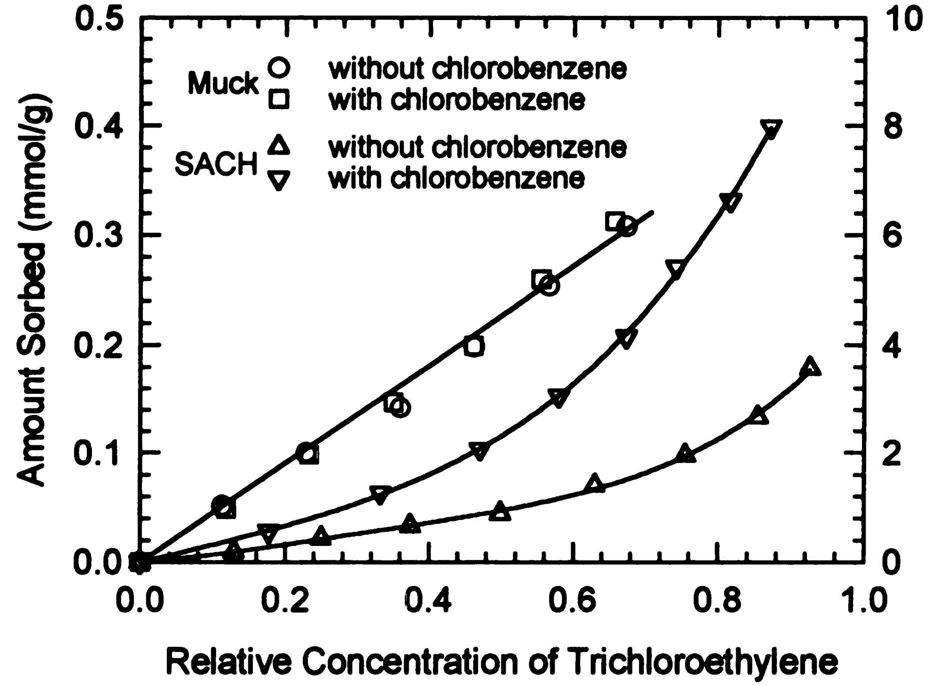

Figure 1.4 Sorption of trichloroethylene by a muck soil (left scale) and SACH (right scale) in the adsence and presence of chlorobenzene as a competing solute

is a free organic phase, is higher than the sorption of trichloroethylene by HDTMA-clays (Figure 1.2) in which the HDTMA derived organic phase is somewhat restricted. Swelling of HDTMA-clays with a low d-spacing requires the solvation of HDTMA and the vacated mineral surfaces *(Slabaugh et al., 1968; Solomon et al., 1983)*. Aromatic molecules (benzene, nitrobenzene, chlorobenzene) fulfill these requirements, whereas aliphatic molecules (trichloroethylene, carbon tetrachloride) are not able to adequately solvate HDTMA. It is proposed that aromatic molecules solvating the alkyl chains of HDTMA interact with each other indirectly, particularly at low concentrations, through the intra-chain conformational subsystem of the HDTMA chains *(Pyda et al., 1982, 1983, 1993)*, leading to a cooperative effect. Solvation of HDTMA chains by aromatic molecules also weakens the inter-chain interactions of HDTMA, resulting in a non-linear swelling effect. Both cooperative sorption and non-linear swelling generate a sigmoid isotherm. Combination of a sigmoid isotherm from solvation and a type III isotherm from solute partitioning produces the double sigmoid-shaped isotherms reported here.

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Chapter 2 Cosorption of Organic Contaminants from Water by Hexadecyltrimethylammonium-Exchanged Clays

Abstract

The characteristics of organoclays as sorbents for neutral organic contaminants (NOCs) in aqueous systems containing multiple solutes were evaluated by measuring the sorption of trichloroethylene on hexadecyltrimethylammonium (HDTMA) exchanged illite and smectite in the absence and presence of carbon tetrachloride, nitrobenzene and ethyl ether. Trichloroethylene partitioned into HDTMA-derived phases present on the external surfaces of the clay particles manifesting type III isotherms. Carbon tetrachloride functioned to increase the solvency of the external HDTMA phase, and hence enhanced sorption of trichloroethylene. Nitrobenzene solvated HDTMA resulting in a more vertical orientation of the C-16 alkyl chains and interlayer expansion. This rendered the interlamellar region of HDTMA-smectite accessible for trichloroethylene sorption, and nitrobenzene sorption simultaneously increased the solvency of HDTMA phase for trichloroethylene. Ethyl ether sorption suppressed the uptake of trichloroethylene by decreasing the solvency of HDTMA phase for trichloroethylene. Sorption of trichloroethylene also facilitated sorption of carbon tetrachloride and nitrobenzene. The results suggest that multiple organic compounds generally produce a synergistic effect on the uptake of NOCs from water by HDTMA-clays, and support multiple mechanisms controlling the sorption process.

Key Words - Cosorption, organic compound, organoclay, mechanism, solvency, solvation.

Introduction

The environment at the clay mineral surface is hydrophilic in nature due primarily to the hydration of inorganic cations on the exchange sites. As a result, clays are ineffective sorbents for neutral organic compounds (NOCs) in the presence of water. Organoclays can be formed by replacing natural inorganic cations on the surfaces of clay minerals with organic cations via simple ion exchange reactions (*Xu and Boyd, 1995*). The exchange reaction is favored by van der Waals interaction between organic cations and the reduced solvent shielding of the ions in the interlamellar environment. Organoclay surfaces are hydrophobic and effectively sorb a wide variety of organic compounds from water and air (*Barrer and Perry, 1961; Boyd et al., 1988a; Mortland et al., 1986*). This is due to the lesser tendency of organic cations to hydrate, and to their inherent organophilic nature.

Organoclays show several promising applications in pollution prevention and environmental remediation including the treatment of waste effluents, as extenders for activated carbon and as components of clay barriers, for example in clay slurry walls, hazardous waste landfills and petroleum tank farms (*Boyd et al., 1988b, 1993; Jaynes and Boyd, 1990, 1991a, 1991b; Lee et al., 1989a; McBride et al., 1977*). Recent studies have also investigated the concept of *in-situ* soil modification using quaternary ammonium cations such as HDTMA to enhance the sorptive capabilities of soils for aqueous phase organic contaminants (*Boyd et al., 1988c; Burris and Antworth, 1992; Lee et al., 1989b*). These studies demonstrated that HDTMA-derived organic matter in soils is 10-30 times more effective than natural soil organic matter for sorbing organic contaminants from water, and that soil modification greatly attenuates the mobility of organic contaminants in soils. Coupling contaminant immobilization with *in-situ* biodegradation would provide a comprehensive restoration technology to permanently eliminate target contaminants (*Burris and Antworth, 1992; Nye et al., 1994; Crocker et al., 1995*).

The mechanisms controlling sorption of organic compounds on organoclays are dependent on the type of organic cations forming organoclays (*Boyd et al., 1993*). We have used quaternary ammonium cations of the general form $[(CH_3)_3NR]^+$, where R is an aromatic or alkyl hydrocarbon group, to replace inorganic cations on smectite clays, and evaluated their sorptive properties for common organic contaminants (*Boyd et al., 1988a, 1988b, 1993; Jaynes and Boyd, 1990, 1991a, 1991b; Lee et al., 1989a; Mortland et al., 1986*). When R is a relatively small group (e.g., $R=-CH_3$, $-C_6H_5$) the organic cations in the interlamellar region of smectite are isolated from each other. Such organoclays have relatively high surface areas and display characteristics of surface adsorbents. For example, adsorption of organic compounds is often characterized by type I isotherms, strong competitive effects in multisolute systems, and molecular shape selectivity (*Boyd et al., 1988a; Jaynes and Boyd, 1990, 1991a; Lee et al., 1989a*). Alternatively, when R is a large alkyl group (e.g., hexadecyltrimethylammonium (HDTMA), $R=-C_{16}H_{33}$), the resultant organoclays have low surface areas and act as partitioning media in the sorption of organic contaminants from water (*Boyd et al., 1988b; Jaynes and Boyd, 1991b*). Sheng *et al.* (*1996*) recently proposed multiple mechanisms controlling sorption of organic contaminants by HDTMA-smectites. In addition to solute partitioning into the HDTMA-derived organic phase, solvation of HDTMA and the mineral surfaces may occur, manifesting complex double sigmoid shaped isotherms.

In this paper, we investigate the sorption of trichloroethylene from water by HDTMA organoclays in the absence and presence of carbon tetrachloride, nitrobenzene and ethyl ether as cosolutes. The objective was to determine the sorptive characteristics of HDTMA organoclays in the presence of multiple organic contaminants, and elucidate how the interactions between sorbent and sorbate influence sorption effectiveness of the organoclays. Our results show that sorption of multiple organic compounds on HDTMA organoclays may produce a synergistic or antagonistic effect, and supported multiple mechanisms involved in the sorption process.

Experimental Section

The clays used in this study were illite from Fithia, Illinois and smectite (mostly low-charge montmorillonite) from Wyoming (American Colloid Company, Chicago, IL). The <2μm clay fractions were obtained by wet sedimentation and subsequently saturated with Ca^{2+} cations by washing the clay repeatedly with $CaCl_2$ solution (0.1 mol/l). HDTMA bromide (Aldrich Chemical Co.) was dissolved in warm distilled water and used to prepare HDTMA organoclays. A portion of clay suspensions containing 25 g of either illite or smectite was treated by adding HDTMA bromide solution (0.03 mol/l) in an amount just equal to the cation-exchange capacity of the clays (224 $mmol_c$/kg for illite and 900 $mmol_c$/kg for smectite). The mixtures were agitated overnight on a magnetic stirrer at room temperature. The HDTMA-illite and HDTMA-smectite suspensions were then washed with distilled water repeatedly until free of bromide ions as indicated by $AgNO_3$. These HDTMA organoclays were subsequently quick-frozen, freeze-dried, and stored in bottles for later use. Organic carbon contents of these HDTMA organoclays were determined using Dohrmann DC-190 high temperature TOC analyzer (Rosemount Analytical Inc., Santa Clara, CA). Some properties of these HDTMA organoclays are given in Table 2.1.

Table 2.1 Properties of HDTMA organoclays.

HDTMA-clay	illite	smectite
Source	Fithia, IL	Wyoming Bentonite^a
Charge (mol$_c$/unit cell)	1.44^b	0.64^c
Cation-exchange capacity (mmol$_c$/kg)	224	900
Organic carbon (%)	4.96	16.5
d-Spacing (Å)	10.1^b	21.6^b

a From American Colloid Co.
b measured.
c Laird *et al.* (*1989*).

Sorption of trichloroethylene (Aldrich Chemical Co.) on HDTMA organoclays was conducted using a batch equilibration technique. A weight of 0.8 g of HDTMA-illite or 0.2 g of HDTMA-smectite and 25 ml of distilled water were placed in Corex glass centrifuge tubes. Between 5 and 50 µl of trichloroethylene were delivered directly into the tubes as the neat liquid using a Hamilton microliter syringe, and the tubes were capped immediately with teflon-backed septa. The tubes were shaken for 24 hours on a rotator at room temperature. Preliminary experiments showed that sorption reached equilibrium within 18 hours. After equilibration, the tubes were centrifuged at 8000 rpm (RCF=4302 g) for 10 minutes to separate liquid and solid phases. A volume of 5 ml of supernatant was extracted with 10 ml of carbon disulfide in a glass vial.

Analysis of trichloroethylene in the carbon disulfide extracts was made by gas chromatography. A Hewlett-Packard 5890A gas chromatograph was used with flame ionization detector and a packed column (Alltech Co.) with N_2 as the carrier gas. Peak areas were recorded by a Hewlett-Packard 3392A integrator, and compared to external standards to determine the concentrations of trichloroethylene. The recovery of trichloroethylene in blanks not containing organoclays was about 90%. The amount of trichloroethylene sorbed on HDTMA organoclays was calculated from the differences between the amount of trichloroethylene added and that remaining in the final equilibrium solutions. Sorption isotherms were made by plotting the amount sorbed versus the equilibrium concentration in solution.

Sorption of trichloroethylene in the presence of a cosolute was performed by adding either carbon tetrachloride, nitrobenzene or ethyl ether (Aldrich Chemical Co.) into the tubes containing HDTMA organoclays, distilled water and trichloroethylene. For carbon tetrachloride, either 5 μl or 15 μl were added, corresponding to an initial relative concentration (the ratio of the calculated initial aqueous concentration (C) to the solubility (Cs) of carbon tetrachloride in water) of 0.40 or 1.20 , respectively. For nitrobenzene, either

10 µl or 50 µl were added, corresponding to an initial relative concentration of 0.25 or 1.25, respectively. For ethyl ether, a volume of 50 µl was added, corresponding to an initial relative concentration of 0.02. Immediately after addition of carbon tetrachloride, nitrobenzene or ethyl ether, the experiments were continued following the procedure described above. The aqueous phase equilibrium concentrations of carbon tetrachloride and nitrobenzene were analyzed by gas chromatography. We were unable to determine the concentration of ethyl ether by gas chromatography due to coelution of carbon disulfide and ethyl ether. The amounts of carbon tetrachloride and nitrobenzene sorbed on HDTMA organoclays were again calculated by difference between the amount added and that remaining in the equilibrium solutions.

Basal spacings of HDTMA organoclays and of HDTMA-smectite with trichloroethylene and carbon tetrachloride or nitrobenzene sorbed were determined by X-ray diffraction analysis. HDTMA clay suspensions were dropped on glass slides, and immediately covered by teflon tape to prevent vapor loss. X-ray diffraction patterns were recorded using CuKα radiator and a Philips APD3720 automated X-ray diffractometer using an APD3521 goniometer fit with a θ-compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator, from 2 to $10^{o}2\theta$, in steps of $0.03^{o}2\theta$, 1 sec/step.

Results

The isotherms for sorption of trichloroethylene by HDTMA-illite were type III (Figure 2.1A). In the presence of either carbon tetrachloride or nitrobenzene, sorption of trichloroethylene was enhanced while isotherms remained type III. The extent of sorption

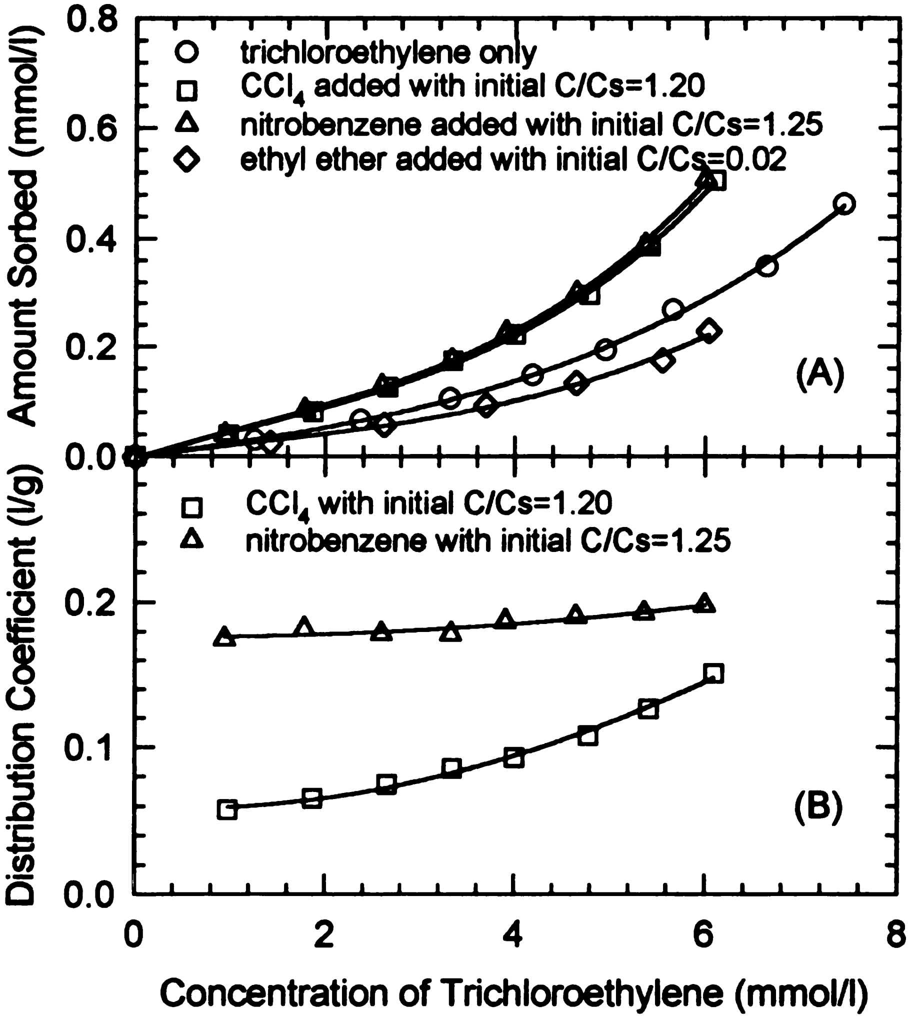

Figure 2.1 Sorption of trichloroethylene by HDTMA-illite in the absence and presence of carbon tetrachloride, nitrobenzene or ethyl ether as a competing solute.

(A): Isotherms of trichloroethylene;

(B): Dependence of sorption distribution coefficient of carbon tetrachloride and nitrobenzene on equilibrium concentration of trichloroethylene.

enhancement was significant; 63% in the presence of carbon tetrachloride and 70% in the presence of nitrobenzene, at a trichloroethylene equilibrium concentration of 5 mmol/l. Sorption of carbon tetrachloride and nitrobenzene occurred concomitantly with trichloroethylene sorption. Although the amount of carbon tetrachloride and nitrobenzene initially added into each tube was constant, the amount of carbon tetrachloride and nitrobenzene sorbed on the organoclay, and hence their distribution coefficients, increased with the equilibrium concentration of trichloroethylene (Figure 2.1B).

Sorption of trichloroethylene by HDTMA-illite was suppressed in the presence of ethyl ether as a cosolute while the isotherm remained type III (Figure 2.1A). The sorption of trichloroethylene by HDTMA-illite was decreased by 26% at the trichloroethylene equilibrium concentration of 5 mmol/l in the presence of ethyl ether having an initial relative concentration equal to 0.02.

The isotherms for sorption of trichloroethylene by HDTMA-smectite were type III (Figure 2.2A). The presence of carbon tetrachloride enhanced the sorption of trichloroethylene by HDTMA-smectite while the isotherms remained type III. The extent of enhancement increased with increasing concentration of carbon tetrachloride; 48% and 245% (calculated at a trichloroethylene equilibrium concentration of 5 mmol/l) in the presence of carbon tetrachloride having initial relative concentrations (C/Cs) equal to 0.4 and 1.2, respectively . As with HDTMA-illite, carbon tetrachloride was sorbed by HDTMA-smectite, and increased with increasing sorption of trichloroethylene (data not shown).

The presence of nitrobenzene dramatically enhanced the sorption of trichloroethylene by HDTMA-smectite while the isotherms remained type III (Figure 2.2B). The sorption of

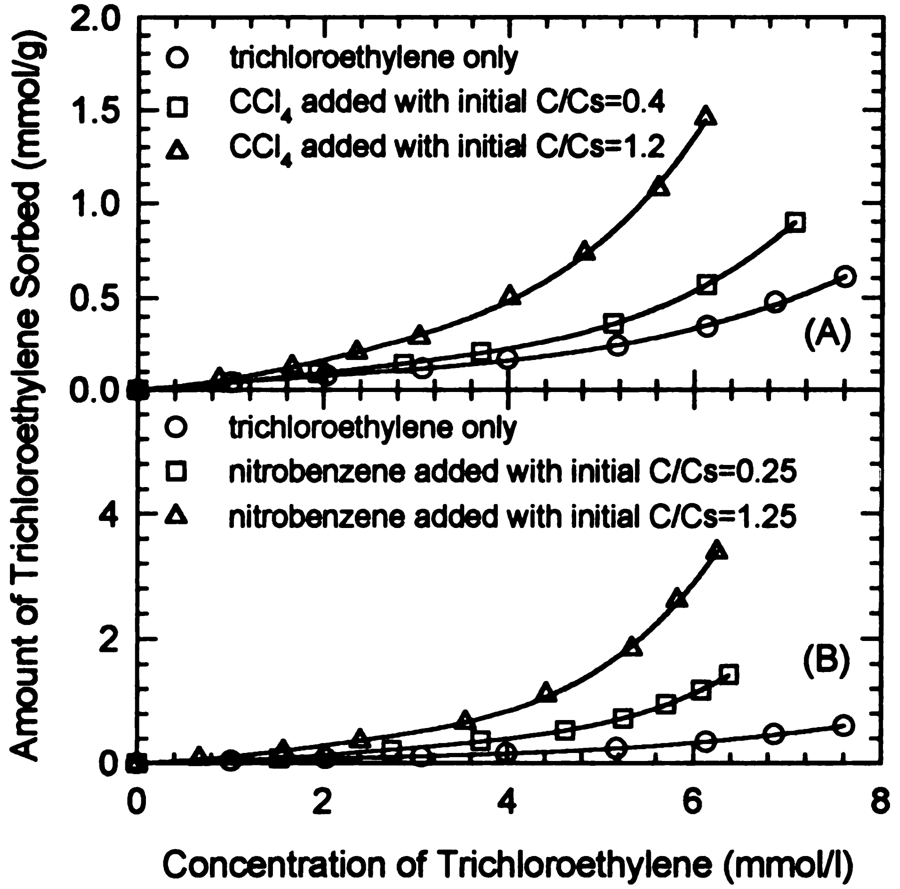

Figure 2.2 Sorption of trichloroethylene by HDTMA-smectite in the absence and presence of cosolute as a competing solute.
(A): Isotherms of trichloroethylene in the absence and presence of carbon tetrachloride;
(B): Isotherms of trichloroethylene in the absence and presence of nitrobenzene.

trichloroethylene was increased by 181% and 563% (calculated at a trichloroethylene equilibrium concentration of 5 mmol/l) in the presence of nitrobenzene having initial relative concentrations of 0.25 and 1.25, respectively. Compared to carbon tetrachloride, nitrobenzene was about twice as effective in enhancing the sorption of trichloroethylene on HDTMA-smectite.

To quantify the sorption enhancement, the sorption distribution coefficients of trichloroethylene in the absence and presence of carbon tetrachloride or nitrobenzene were calculated. The increase in the distribution coefficient ($K-K_{tce}$), where K is the distribution coefficient in the presence of carbon tetrachloride or nitrobenzene and K_{tce} the distribution coefficient in the absence of carbon tetrachloride or nitrobenzene, divided by the amount of carbon tetrachloride or nitrobenzene sorbed (Q) at the corresponding equilibrium concentration of trichloroethylene, was plotted versus the equilibrium concentration of trichloroethylene (Figure 2.3). Sorption enhancement of trichloroethylene by carbon tetrachloride or nitrobenzene increased steadily with the equilibrium concentration of trichloroethylene. The extent of trichloroethylene sorption enhancement per unit mass of carbon tetrachloride sorbed increased when the initial relative concentration of carbon tetrachloride increased from 0.4 to 1.2 (Figure 2.3A); conversely, it decreased when the initial relative concentration of nitrobenzene increased from 0.25 to 1.25 (Figure 2.3B).

Sorption-dependent variation of HDTMA-smectite basal spacing is represented in Figure 2.4. The basal spacing of HDTMA-smectite remained approximately 21.6Å with the sorption of trichloroethylene. Addition of carbon tetrachloride also did not change the basal spacing or the intensity of diffraction peak. In contrast, addition of nitrobenzene expanded

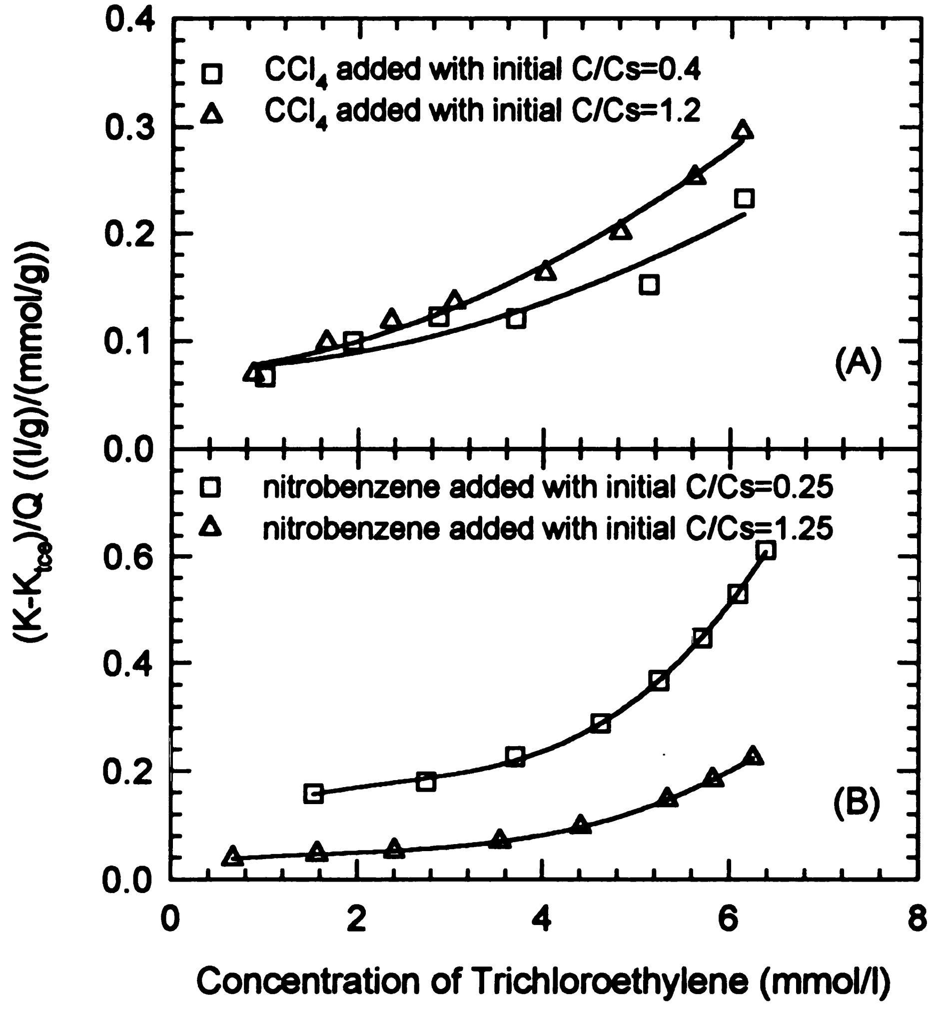

Figure 2.3 Increase in sorption distribution coefficient of trichloroethylene on HDTMA-smectite (K_{tce}) in the presence of carbon tetrachloride or nitrobenzene (K) with different concentrations normalized by respective amount of carbon tetrachloride or nitrobenzene sorbed (Q).
(A): Trichloroethylene - carbon tetrachloride system;
(B): Trichloroethylene - nitrobenzene system.

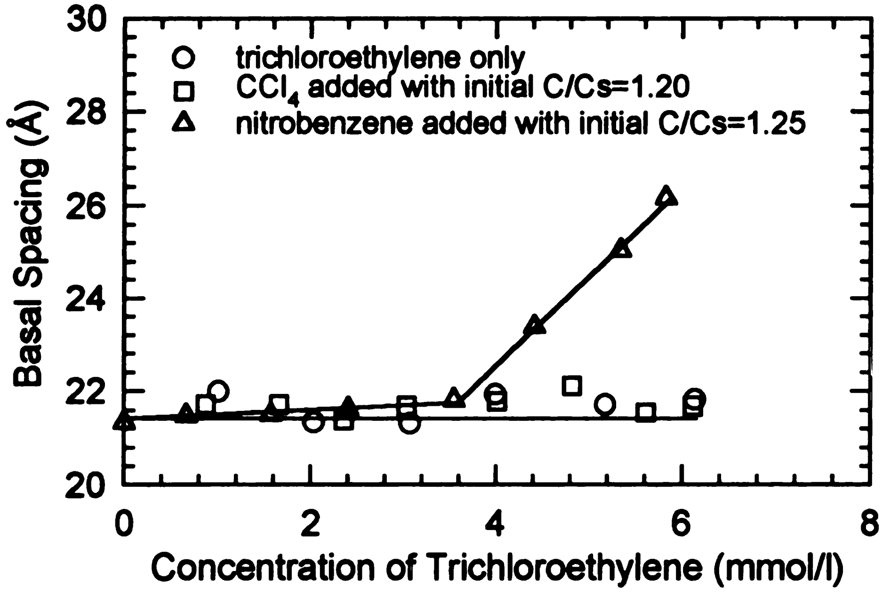

Figure 2.4 Sorption-dependent variation of basal spacing for HDTMA-smectite.

HDTMA-smectite little if any at low trichloroethylene concentrations and then more sharply at trichloroethylene concentrations > 4 mmol/l. It was also observed that the intensity of diffraction peak decreased with increasing the sorption of trichloroethylene in the presence of nitrobenzene. The diffraction peak disappeared at a trichloroethylene equilibrium concentration of about 6 mmol/l.

Discussion

Recently, we demonstrated that sorption of aromatic molecules (viz. benzene, chlorobenzene, nitrobenzene) by HDTMA-smectites produced complex double sigmoid shaped isotherms. This was attributed to the occurrence of multiple mechanisms (*Sheng et al., 1996*) including solvation of HDTMA, and solute partitioning into the HDTMA-derived organic phases present in both the interlamellar regions and on the external surfaces. Apparently, aromatic compounds, due to their delocalized π-bond system, interact strongly with the cationic ammonium centers and alkyl chains of HDTMA, causing a reorientation of the alkyl chains to a more vertical position, which may allow solute interaction with the revealed mineral surfaces. This process results in interlayer expansion of HDTMA-smectites, making the interlamellar regions accessible and hence promoting solute partitioning into the expanded phase. In contrast, aliphatic compounds such as trichloroethylene and carbon tetrachloride are apparently not able to adequately solvate HDTMA. For such compounds, the singular sorptive mechanism is solute partitioning into the HDTMA-derived organic phase.

The results obtained here further substantiate the mechanisms summarized above. Sorption of trichloroethylene on HDTMA organoclays is due to partitioning into the organic phase formed by HDTMA in organoclays. The type III isotherms observed, which are convex to the abscissa commencing at the origin, are due to an increase in HDTMA phase solvency for trichloroethylene as its content in the HDTMA phase increases (*Chiou et al., 1992*). Similar type III isotherms are observed for the partitioning of trichloroethylene between water and hexane (Figure 2.5).

The change in solvency of HDTMA-derived organic phase resulting from trichloroethylene uptake can be described using the solubility parameters (*Hildebrand et al.,*

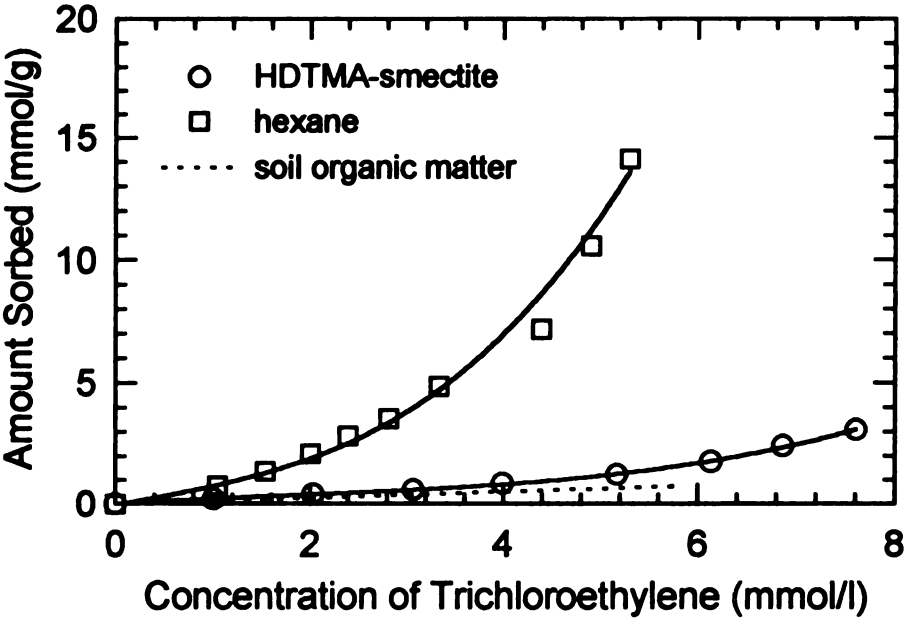

Figure 2.5 Comparison of HDTMA phase, hexane and soil organic matter as partition media for trichloroethylene. (Data normalized to organic carbon content. Data for hexane from Sheng *et al.*, *1996*; Linear line for soil organic matter calculated by K_{oc} from Garbarini and Lion, *1986*.)

1970) of pure HDTMA (δ_{HDTMA}) and trichloroethylene (δ_2) according to the following equation:

$$\delta = (1 - \phi_2)\delta_{HDTMA} + \phi_2\delta_2 \tag{2.1}$$

where ϕ_2 is the volume fraction of trichloroethylene (*Barton, 1991; Hildebrand et al., 1970*). The change in solubility parameter with trichloroethylene content in the HDTMA phase is:

$$\frac{d\delta}{d\phi_2} = \delta_2 - \delta_{HDTMA} \tag{2.2}$$

The value of $\frac{d\delta}{d\phi_2}$ is the measure of the ability of trichloroethylene to increase the solvency of the HDTMA phase for trichloroethylene, and is directly related to the difference in the solubility parameters of the two mixing phases. The solvency increase of the HDTMA phase is thus dependent on ($\frac{d\delta}{d\phi_2} \times Q \times f$) where Q is the amount of trichloroethylene sorbed and f the conversion factor to convert Q in mmol/g to the volume fraction. The value of $\frac{d\delta}{d\phi_2}$ for trichloroethylene (=1.3 cal$^{1/2}$/cm$^{3/2}$) is greater than zero because δ_2 is greater than δ_{HDTMA} (Table 2.2). Obviously, the value of ($\frac{d\delta}{d\phi_2} \times Q \times f$) increases with increasing the sorption of trichloroethylene, resulting in a type III isotherm (Figure 2.1, Figure 2.2).

Table 2.2 Solubility parameters (δ) of organic compounds.

organic compound	solubility parameter* (cal$^{1/2}$/cm$^{3/2}$)	$\frac{d\delta}{d\phi_2}(\frac{\partial\delta}{\partial\phi_2}, \frac{\partial\delta}{\partial\phi_3})$**
trichloroethylene	9.3	1.3
carbon tetrachloride	8.7	0.7
nitrobenzene	10.9	2.9
ethyl ether	7.7	-0.3
HDTMA	8.0	0.0

* Barton A.F.M. (*1991*).

** This term represents the change in the solubility parameter of the HDTMA phase with solute content. ϕ_2 and ϕ_3 are the volume fractions of the solute and cosolute, respectively. δ_{HDTMA} is not available and was substituted for by $\delta_{C_{16}H_{34}}$=8.0 cal$^{1/2}$/cm$^{3/2}$.

The effect of nitrobenzene and carbon tetrachloride on trichloroethylene sorption by organoclays depends in part on the swelling properties of the clay. Because illite is a non-swelling clay, interlayer expansion of HDTMA-illite due to HDTMA solvation by nitrobenzene does not occur, and hence the effect of solvation on trichloroethylene sorption is minimal. As a result, carbon tetrachloride and nitrobenzene both function primarily to change the solvency of the HDTMA phase of HDTMA-illite for trichloroethylene. Here, the solubility parameter of the HDTMA phase with trichloroethylene and either carbon tetrachloride or nitrobenzene sorption follows the equation:

$$\delta = (1 - \phi_2 - \phi_3)\delta_{HDTMA} + \phi_2\delta_2 + \phi_3\delta_3 \qquad (2.3)$$

where ϕ_3 is the volume fraction of either carbon tetrachloride or nitrobenzene, and δ_3 is the solubility parameter of the corresponding compound. The change in the solubility parameter of the HDTMA phase with cosorption of trichloroethylene and either carbon tetrachloride or nitrobenzene is:

$$\frac{\partial \delta}{\partial \phi_2} = \delta_2 - \delta_{HDTMA} \qquad (2.2)$$

$$\frac{\partial \delta}{\partial \phi_3} = \delta_3 - \delta_{HDTMA} \qquad (2.4)$$

Table 2.2 shows the values of $\frac{\partial \delta}{\partial \phi_2}$ for trichloroethylene calculated by equation (2.2) and $\frac{\partial \delta}{\partial \phi_3}$ for carbon tetrachloride and nitrobenzene calculated by equation (2.4). The value of $\frac{\partial \delta}{\partial \phi_3}$ being greater than zero indicates that sorption of carbon tetrachloride and nitrobenzene increases the solubility parameter of the HDTMA phase towards trichloroethylene. The increased sorption of trichloroethylene shown in Figure 2.1 is therefore the result of this solvency increase of the HDTMA phase by either carbon tetrachloride or nitrobenzene sorption and additional trichloroethylene sorption. Similarly, the sorption of trichloroethylene also increases the solvency of the HDTMA phase for carbon tetrachloride and nitrobenzene due to the fact that the solubility parameters of all three compounds are greater than that of the HDTMA phase (Table 2.2). As a result, sorption of one compound produces a synergistic effect on the sorption of the other, and hence the sorption coefficient of nitrobenzene and carbon tetrachloride increases with the amount of trichloroethylene sorbed (Figure 2.1B).

That trichloroethylene is sorbed primarily on external HDTMA phase of HDTMA-smectite in the absence of cosolutes is supported by the fact that the organic carbon normalized trichloroethylene uptake is much smaller for HDTMA-smectite than for hexane (*Sheng et al., 1996*), yielding a log K_{oc} value of 2.1 (at Ce/Cs of 0.4) which is similar to the log K_{oc} value of 2.0 reported for soil organic matter (*Garbarini and Lion, 1986*) (Figure 2.5). If the interlayer regions of HDTMA-smectite were fully accessible to trichloroethylene, the trichloroethylene sorption isotherm and log K_{oc} values should resemble those of hexane due to the compositional similarity of the two phases as partition media, and furthermore, should be substantially higher than soil organic matter which is a poorer partition phase for NOCs due to its more polar nature. In addition, we previously observed that trichloroethylene sorption into the interlayers of a higher charge HDTMA-smectite was accompanied by interlayer expansion (*Sheng et al., 1996*). The basal spacing of the lower charge HDTMA-smectite described here did not increase upon sorption of trichloroethylene, as reflected by the constant basal spacing of ~21.6Å (Figure 2.4). As in the case of HDTMA-illite, the type III isotherms for trichloroethylene sorption resulted from the solvency increase of the external HDTMA phase. Addition of carbon tetrachloride as a cosolute with trichloroethylene did not increase the basal spacing of HDTMA-smectite indicating that it was not intercalated. This is because carbon tetrachloride interacts only weakly with the HDTMA phase and the molecular size of carbon tetrachloride is larger than that of trichloroethylene. Carbon tetrachloride increases the uptake of trichloroethylene by increasing the solvency of the external HDTMA phase of HDTMA-smectite, and this effect is more pronounced with higher initial levels of carbon tetrachloride which manifest higher amounts of sorbed carbon tetrachloride (positive $\frac{\partial \delta}{\partial \phi_3}$, Table 2.2). Because only the external HDTMA phases of both HDTMA-illite and HDTMA-smectite are available for trichloroethylene sorption in the absence and presence of carbon tetrachloride, the increase in sorption distribution coefficient of trichloroethylene on both organoclays by carbon tetrachloride was within the same range (0.06-0.30 (l/g)/(mmol/g)).

The addition of nitrobenzene as a cosolute with trichloroethylene causes an increase in the basal spacing of HDTMA-smectite (Figure 2.4). Random interstratification of nitrobenzene in the interlayers of HDTMA-smectite seems to occur, based on the diminution of the original diffraction peak (at 21.6 Å) and the eventual increase in basal spacing. Apparently, nitrobenzene solvates both cationic ammonium centers and alkyl chains of HDTMA, causing a more vertical reorientation of the alkyl chains and interlayer expansion. Similar results have been obtained with the aromatic molecules such as benzene and chlorobenzene (*Sheng et al., 1996*). Interlayer expansion by nitrobenzene renders the interlamellar space of HDTMA-smectite accessible to trichloroethylene. The nitrobenzene activated HDTMA-smectite is thus able to intercalate trichloroethylene with swelling of the organoclay and the formation of layer complexes in a bimolecular layered arrangement (*Solomon and Hawthorne, 1983*), causing the intensity of the diffraction peak to decrease and the apparent d_{001} spacing to increase. The d_{001} spacing of HDTMA-smectite in a bimolecular layered arrangement is not able to be determined because it is over the lower angle limit of the X-ray diffractometer used in this study. Nitrobenzene simultaneously functions to increase the solvency of both external and interlamellar HDTMA phases for trichloroethylene, resulting in enhanced uptake.

In an attempt to separate the solvation and solvency effect of nitrobenzene on trichloroethylene sorption by HDTMA-smectite, we have plotted the increase in trichloroethylene sorption coefficient per unit mass of nitrobenzene sorbed (Figure 2.3B). This plot reveals that the lower level of nitrobenzene addition is more effective than the higher level, in direct contrast to the effect of carbon tetrachloride (Figure 2.3A) which only influences solvency. This suggests that the major role of nitrobenzene when added at the lower level is to solvate the HDTMA. This causes an expansion of the interlayers, rendering the interlamellar regions available for sorption of trichloroethylene. Apparently, additional nitrobenzene functions primarily to enhance the solvency of the HDTMA phase for trichloroethylene sorption which continues to increase (Figure 2.2B) since the interlayers are already sufficiently expanded. As a result, the effectiveness of nitrobenzene on a unit mass basis is diminished.

In accordance to the above discussion, sorption of ethyl ether, with a solubility parameter of 7.7 $\mathrm{cal}^{1/2}/\mathrm{cm}^{3/2}$ and $\frac{\partial \delta}{\partial \phi_3}$ of -0.3 (Table 2.2), should decrease the solvency of the HDTMA phase for trichloroethylene. In fact, we observed experimentally a decrease in trichloroethylene sorption by HDTMA-illite in the presence of ethyl ether as a cosolute (Figure 2.1A).

Most of the common organic contaminants (>95 %) have higher solubility parameters than that of the HDTMA phase. Sorption of such contaminants by organophilic organoclays like HDTMA-smectite should produce a synergistic, rather than antagonistic (or competitive), effect on contaminant removal from water. This represents an advantage of organoclays over conventional adsorbents such as activated carbon or shale where sorption is depressed in the presence of cosolutes due to competitive effects.

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Chapter 3 Surface Heterogeneity of Trimethylphenylammonium-Smectite as Revealed by Adsorption of Aromatic Hydrocarbons from Water

Abstract

Adsorption studies of aromatic hydrocarbons of various molecular sizes on organoclays in aqueous solution were carried out for characterizing the surface heterogeneity of organoclays. Benzene, toluene, p-xylene, ethyl-benzene and n-propylbenzene adsorption by a smectite with five different exchange degrees of trimethylphenylammonium (TMPA) cations for Ca^{2+} was measured. The Langmuir isotherm equation did not adequately describe the experimental data, especially for small molecules, whereas the Dubinin-Radushkevich (DR) equation combined with a gamma-type adsorption energy distribution function described all experimental data well, suggesting the surface and structural heterogeneity of TMPA-smectites. The calculated adsorption energy distributions indicated that the apparent heterogeneity depends on the molecular size of adsorbates. Small adsorbate molecules such as benzene explore a highly heterogeneous surface of TMPA-smectites while large molecules such as n-propylbenzene detect a relatively homogeneous surface. The surface fractal dimension was dependent on the extent of TMPA exchange for Ca^{2+}. When TMPA content is less than 75 percent of the cation-exchange capacity of the smectite, the heterogeneity decreases as TMPA content increases; it increases with TMPA content thereafter. These results are related to the micropore size distributions of TMPA-smectites. The micropores in TMPA-smectites are defined by the two semi-infinite aluminosilicate sheets and the interlayer cations. The micropore size distributions and hence heterogeneity are created in part by the inhomogeneity of the charge density of clay surfaces and the tendency for cation segregation in these systems.

Key Words - adsorption, aromatic hydrocarbons, organoclays, heterogeneity, DR equation, adsorption energy distribution, fractal dimension, micropore size distribution.

Introduction

Organoclays are formed when inorganic cations such as Ca^{2+} and Na^{+} in natural clay minerals are replaced by organic cations. Such organoclays are effective sorbents for a variety of aqueous organic compounds including many common groundwater contaminants *(Boyd et al., 1988a,b, 1991; Jaynes and Boyd, 1991a; Sheng et al., 1996; Xu et al., 199_)*. When relatively small organic cations, e.g. trimethylphenylammonium (TMPA) cations, are employed, the organoclays behave with the adsorptive properties, resulting in Langmuir-type adsorption isotherms *(Jaynes and Boyd, 1990, 1991b)*. Thus, the Langmuir adsorption equation is often used to represent this type of experimental data.

Langmuir adsorption theory *(Langmuir, 1918)* has been extensively used in various monolayer adsorption systems because of its simplicity of form and directness of derivation. In most cases, however, difficulties arise in applying the Langmuir equation to describe practical adsorption systems *(Rudzinski and Wojciechowski, 1993)*. One of the major assumptions underlying the Langmuir adsorption equation is that the solid surface is energetically homogeneous *(Langmuir, 1918)*, which is often not true, especially for naturally occuring solids such as clays. It is now well known that geometric and energetic heterogeneity is a fundamental feature of many solid surfaces *(Rudzinski and Wojciechowski, 1993)*. The main sources of heterogeneity are the complexity of crystallographical and geometrical structure of solids and their complex chemical compositions.

Understanding the surface heterogeneity of adsorbents is important because it may directly affect their adsorptive properties. Even though various modern techniques such as electron microscopy, IR spectroscopy, electron spectroscopy, small-angle X-ray scattering, NMR, etc. have been widely used to provide molecular scale information about the heterogeneity of solid surfaces *(Jaroniec and Brauer, 1986)*, macromolecular measurements of adsorption and desorption on solid surfaces are still very useful for characterizing heterogeneous adsorbents *(Lee et al., 1989, 1990; Janes and Boyd, 1991b)*.

Adsorption energy distribution of solid surfaces, and pore-size distribution and fractal dimension of fractally porous solids are among the most important quantities for characterizing the heterogeneity of solids *(Jaroniec and Madey, 1988)*. Adsorption energy distribution, which characterizes the overall energetic heterogeneity of solid surfaces, has been extensively studied on microporous activated carbons *(Dubbin, 1975; Jaroniec and Madey, 1989; Rudzinski and Wojciechowski, 1993)*. Pore-size distribution of porous solids is usually calculated from the low-temperature nitrogen adsorption-desorption isotherm using the Kelvin equation. Empirical relationships between pore size and characteristic adsorption energy of activated carbons have been established *(Stoeckli et al., 1989; Dubinin, 1988)*. Fractal dimension depends on the microporosity of solids, and has recently been used to characterize surface irregularity. Pfeifer et al. *(1983)* and Avnir et al. *(1983, 1984)* were the first to introduce and apply Mandelbrot's non-Euclidean fractal geometry to characterize adsorption systems. By using adsorbates of varying molecular cross section, they showed that most solid surfaces are fractals, and that the fractal dimension measures the irregularity of the surface accessible to molecules during adsorption processes, and is also useful to study the porous structure of solids, the surface phase structure, and the adsorbent-adsorbent interactions. Linear relationships between the monolayer adsorption and the molecular size of adsorbates have been established to determine fractal dimension of a given solid surface based on the adsorption experiments.

Most of the work on the heterogeneity of solid surfaces has been focused on activated carbons and other inorganic adsorbents and catalysts *(Jaroniec and Madey, 1988)*. Comparatively little work on the heterogeneity of clay minerals *(Barrow et al., 1993; Lagaly, 1979, 1981, 1982)* and none on organoclays has been done. In this study, the adsorption of toluene, p-xylene, and n-propylbenzene in aqueous solutions by Ca-smectite partially and fully exchanged with trimethylphenylammonium (TMPA) cations was measured. The resulting isotherms were analyzed by several adsorption equations to characterize the heterogeneity of such organo-smectites. In these systems, individual pores are defined by two semi-infinite parallel silicate sheets which have permanent negative charge, and by adsorbed interlayer Ca^{2+} and TMPA cations which neutralize this charge. The interlayer cations act as pillars to separate silicate sheets, and to define the dimensions of the micropores. As such, the size and structure of micropores in organo-smectites are largely dependent on the nature of the exchange cations (e.g. Ca^{2+} and TMPA), and the proportion of the cation-exchange capacity (CEC) they occupy.

The objectives of this study were to evaluate the applicabilities of different adsorption equations (the Langmuir equation, the DA equation and the DR equation) for describing the uptake of aromatic hydrocarbons from water by mixed Ca/TMPA- and TMPA-smectites, and to characterize these organo-smectites as heterogeneous adsorbents through an analysis of adsorption energy distribution, fractal dimension and micropore size distribution.

Background and Theory

Based on the Polanyi potential theory of adsorption *(Goldman and Polanyi, 1928; Polanyi and Welke, 1928)*, and extensive gas and vapor adsorption studies, Dubinin and Astakhov *(Dubinin, 1975)* developed a theory for the volume filling of micropores, expressed semiempirically by the following equation (DA equation):

$$\theta(A) = \exp[-(\frac{A}{\beta E_0})^n] \qquad (3.1)$$

with

$$A = RT\ln\frac{p_0}{p} \qquad (3.1a)$$

where θ is the degree of volume filling, expressed as the ratio of the amount adsorbed in the micropores at temperature T and relative pressure p/p_0 to the maximum adsorption amount. R is the gas constant, A is the Polanyi adsorption potential, and E_0 is the characteristic adsorption energy of a reference adsorbate, and depends only on the adsorbate. The similarity (affinity) coefficient β is a shifting factor, and is a measure of the similarities between the characteristic vapor adsorption for the adsorbate being studied and that of a reference adsorbate. β depends only on the adsorbate and can be defined as the ratio of the characteristic adsorption energy of any adsorbate, E, to the characteristic adsorption energy of a reference adsorbate, E_0, i.e., $\beta=E/E_0$. By convention, benzene is selected as the reference adsorbate, as Dubinin *(1975)* suggested (i.e., $\beta_{C_6H_6}=1$). The exponent n varies between 1 and 3, depending on the nature of adsorbent used. The value of n approaches 3 for adsorbents with homogeneous micropores, whereas n approaches 1 for adsorbents with highly heterogeneous micropores. When n=2, for average adsorbents, Equation 3.1 becomes:

$$\theta(A) = \exp[-(\frac{A}{\beta E_0})^2] \tag{3.2}$$

This equation is referred to as Dubinin-Radushkevich equation (DR equation) *(Dubinin, 1975)*. The DR equation is a good mathematical description of both vapor adsorption and adsorption in dilute liquid/solid systems *(Jaroniec and Derylo, 1981)*. In liquid/solid systems, the DR equation is written as

$$\theta(A) = \exp[-(\frac{A}{\beta E_0^*})^2] \tag{3.3}$$

with

$$A = RT\ln\frac{C_0}{C} \tag{3.3a}$$

where C and C_0 are the respective equilibrium liquid phase concentration and the liquid solubility, and E_0^* is the characteristic adsorption energy of a reference adsorbate (C_6H_6) in such adsorption systems.

Choma *et al. (1993)* introduced an "interfacial" similarity (affinity) coefficient β^* to relate the characteristic energies E_0 and E_0^*:

$$\beta^* = \frac{E_0^*}{E_0} \tag{3.4}$$

They examined β^* value for benzene by using eight different activated carbons of different sources. The resulting β^* value was 0.052±0.004 and did not depend on the heterogeneity of the activated carbons used, illustrating the usefulness of β^* as a measure of the similarity between the characteristic adsorption curves of any adsorbate in the gas/solid and liquid/solid systems. Thus, the DR equation in the dilute liquid/solid adsorption systems can be rewritten as:

$$\theta(A) = \exp[-(\frac{A}{\beta\beta^{*}E_0})^2] \qquad (3.5)$$

It should be emphasized that β defines the similarities between gas/solid adsorptions for an adsorbate compound and a reference compound, while β*, which is equal to 0.52 for benzene, defines the similarities between liquid/solid and gas/solid adsorptions for an adsorbate.

Recent studies *(Stoeckli, 1989; Stoeckli et al., 1990; Innes et al., 1989)* have shown that the DR equation satisfactorily describes adsorption only in uniform and weakly heterogeneous micropores. Stoeckli *et al. (Stoeckli, 1977; Dubinin and Stoeckli, 1980)* suggested an integral equation combined with an adsorption energy distribution function to describe adsorption in heterogeneous micropores. The DR equation is rewritten as:

$$\theta(A) = \exp[-\frac{\pi}{4}(\frac{A}{\bar{A}})^2] \qquad (3.6)$$

where $\bar{A}=(\pi^{1/2}/2)\beta\beta^{*}E_0$ is the average adsorption potential. Letting $z=1/\bar{A}$, adsorption in heterogeneous micropores can be expressed as:

$$\theta(A) = \int_0^{\infty}\exp(-\frac{\pi}{4}A^2z^2)G(z)dz \qquad (3.7)$$

where G(z) is the distribution function of z correlated to the characteristic adsorption energy E_0. Dubinin *et al. (1987)* assumed a Gaussian distribution for representing the adsorption energy distribution function. However, because the Gaussian distribution has a non-zero value at zero point argument and the resulting adsorption isotherm equation contains the error function of the adsorption potential, Jaroniec and Madey *(1989)* proposed a gamma-type distribution function for representing adsorption energy distribution function, which is physically and mathematically meaningful and leads to a simple adsorption isotherm equation . The following distribution function was obtained:

$$G(z) = \frac{2q^{v/2}}{\Gamma(v/2)} z^{v-1} \exp(-qz^2); \quad q>0 \text{ and } v>-1 \tag{3.8}$$

with

$$\int_0^\infty G(z)dz = 1 \tag{3.8a}$$

where $\Gamma(v/2)$ is the gamma function, q and v are parameters associated with the dispersion σ_z of the distribution and mean $\bar{z}$.

Integration of Equation 3.7 with the substitution of G(z) leads to the following adsorption isotherm equation:

$$\theta(A) = \left[\frac{q}{q+(\pi/4)A^2}\right]^{v/2} \tag{3.9}$$

Equation 3.9 does not contain the coefficient β^*, and it can be used for adsorptions in both gas/solid and liquid/solid systems.

Equations 3.8 and 3.9 are good mathematical representations of adsorptions in gas/solid and dilute liquid/solid systems. The simplicity of these equations allows one to properly characterize adsorption with only the parameters q, v, β^*, and β which can be calculated from experimental adsorption data.

Experimental Section

Smectite from a Wyoming bentonite (SAC) with a cation-exchange capacity (CEC) of 90 cmol_c/kg was obtained from the American Colloid Company (Chicago, IL). The <2μm clay fractions were obtained by wet sedimentation and subsequently saturated with Ca^{2+} cations by washing the clay repeatedly with $CaCl_2$ solution (0.1 mol/l).

Trimethylphenylammonium (TMPA) bromide (Aldrich Chemical Co.) was dissolved in distilled water and used to prepare TMPA organo-smectites (SAC-TMPA). Clay suspensions containing 25 g of Ca-clay were treated by adding different amounts of TMPA bromide solution (0.03 mol/l) to form either mixed Ca/TMPA-clays or fully saturated TMPA-clay (SAC-TMPA). The amounts of TMPA added relative to the CEC were about 0.2, 0.4, 0.65, 0.75 and 1.0. The mixtures were agitated overnight on a magnetic stirrer at room temperature. The organo-clay suspensions were then washed with distilled water repeatedly until free of bromide ions as indicated by $AgNO_3$, and stored in bottles for later use. Organic carbon contents of clays were determined using Dohrmann DC-190 high temperature TOC analyzer (Rosemount Analytical Inc., Santa Clara, CA), and were used to calculate the exact percent of CEC occupied by TMPA cations. These organo-clays are referred to as SAC-TMPA.17, SAC-TMPA.38, SAC-TMPA.65, SAC-TMPA.75, and SAC-TMPA1.0, respectively, in which the numerical value represents the fraction of the CEC occupied by TMPA. The properties of these SAC-TMPAs are given in Table 3.1.

Adsorption of benzene, toluene, ethylbenzene, p-xylene and n-propylbenzene by the organoclays was conducted using a batch equilibration technique. A weight of 100 mg of organoclay and 25 ml of distilled water were placed in Corex glass centrifuge tubes. Organic solutes were added neat using a Hamilton microliter syringe to produce a range of initial and final concentrations. The tubes were capped immediately with teflon-backed septa. The tubes were shaken for 24 hours on a rotator at room temperature. Preliminary experiments showed that sorption reached equilibrium within 18 hours. After equilibration, the tubes were centrifuged at 8000 rpm (RCF=4302 g) for 10 minutes to separate liquid and solid phases.

Table 3.1 Properties of TMPA-smectites

clay	sample name	OC%	% of CEC occupied by TMPA	d_{001} (Å)
1	SAC-TMPA.17*	1.66	17	14.42, 18.89
2	SAC-TMPA.38	3.57	38	14.12, 18.97
3	SAC-TMPA.65	5.88	65	14.16
4	SAC-TMPA.75	6.75	75	14.95
5	SAC-TMPA1.0	8.84	100	14.38

* SAC stands for the smectite clay from American Colloid Company; TMPA.XX and TMPA1.0 represent that SAC is treated with TMPA and the degree of the CEC occupied by TMPA is .XX and 1.0, respectively.

A volume of 5 ml of supernatant was extracted with 10 ml of carbon disulfide in a glass vial.

Analysis of organic solutes in the carbon disulfide extracts was made by gas chromatography. A Hewlett-Packard 5890A gas chromatograph fitted with a flame ionization detector and a packed column (Alltech Co.) was used; N_2 was the carrier gas. Peak areas were recorded by a Hewlett-Packard 3392A integrator, and compared to external standards to determine the concentrations of organic solutes. The recovery of organic solutes in blanks not containing organoclays was >90%. The amount of organic solutes sorbed was calculated from the differences between the amount of organic solutes added and that remaining in the final equilibrium solutions. Sorption isotherms were made by plotting the amount sorbed versus the equilibrium concentration in solution.

Basal spacings (d_{001}) of SAC-TMPA organoclays with organic solutes sorbed were determined by XRD analysis. Organoclay suspensions were dropped on glass slides, and immediately covered by teflon tape to prevent vapor loss. X-ray diffraction patterns were recorded using CuKα radiator and a Philip APD3720 automated X-ray diffractometer using an APD3521 goniometer fit with a θ-compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator, from 2 to $10^{0}2\theta$, in steps of $0.03^{0}2\theta$, 1 sec/step.

Pore size distributions of the organoclays were determined by QuantaChrome Co. (Romeoville, IL). The organoclays were outgassed for 16 hrs at 70^{0}C. N_2 sorption measurements were analyzed using the Brunauer-Emmett-Teller (BET) equation *(Brunauer et al., 1938)* and the Horvath-Kawazoe (H-K) method *(Horvath and Kawazoe, 1983)*.

Results and Discussion

The adsorption isotherms of benzene, toluene, p-xylene, ethylbenzene and propylbenzene are shown in Figure 3.1. All isotherms are type I, indicating that the adsorption occurs on the surfaces and in the micropores of SAC-TMPAs. Benzene shows the highest uptake by the organoclays; progressively lower uptake occurs for larger molecules in the order of benzene > toluene > p-xylene ≈ ethylbenzene > n-propylbenzene. At Ce/Cs (equilibrium concentration in water / aqueous solubility) =0.5, the sorbed concentration on SAC-TMPA.65 is about 78 mg/g for benzene, 51 for toluene, 41 for p-xylene and ethylbenzene, and 36 for n-propylbenzene. X-ray analysis showed that SAC-TMPAs do not undergo interlayer expansion after adsorption of the test compounds over the experimental concentration range used, indicating that the microstructures of SAC-TMPAs were not

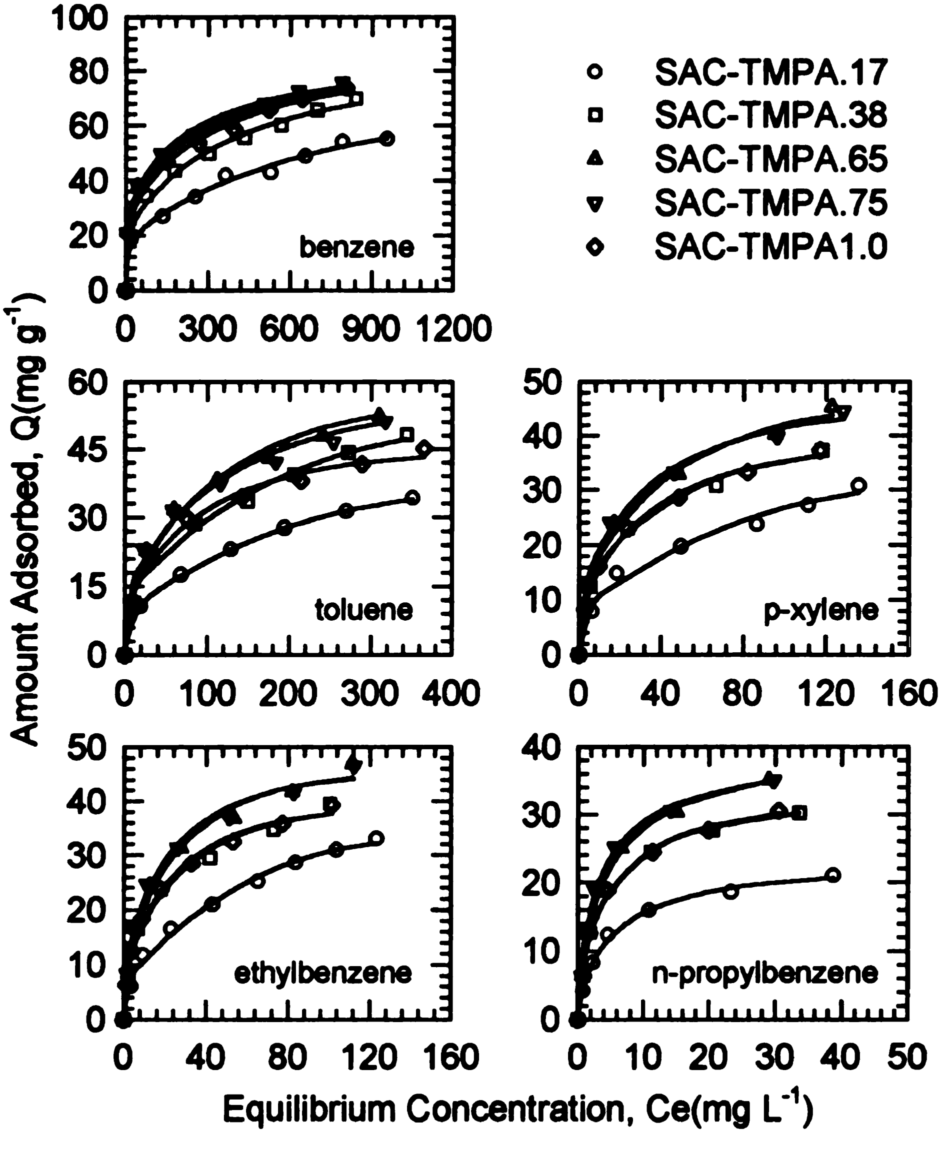

Figure 3.1 Adsorption isotherms of benzene and alkylbenzenes by mixed Ca/TMPA- and TMPA-smectites

altered.

Choice of the adsorption isotherm equation. All adsorption isotherms were fit to the Langmuir isotherm equation and the Dubinin-Astakhov isotherm equation with n=2 and n=3. Typical fitting results are represented in Figure 3.2. For small adsorbates such as benzene, the Langmuir equation overestimates adsorption at low concentrations and underestimates adsorption at high concentrations (Figure 3.2). For larger molecules like n-propylbenzene, the Langmuir equation gives a better fit, but it still deviates slightly from the experimental data (Figure 3.2).

The DA equation with n=3 provides a good description of adsorption of gases and aqueous compounds on activated carbons that contain uniform micropores *(Stoeckli, 1989; Stoeckli et al., 1990; Innes et al., 1989)*. When combined with the gamma-type adsorption energy distribution function, it also describes adsorption on heterogeneous activated carbons. However, it does not give a good fit to our experimental data in water/SAC-TMPA systems. The DR equation, which is suitable for weakly heterogeneous activated carbons *(Stoeckli, 1989; Innes et al., 1989; Kraehenbuehl et al., 1986)*, combined with the gamma-type adsorption energy distribution, does provide an excellent fit of our experimental data over the whole concentration range used (Figure 3.2).

The DR equation is a fundamental mathematical description of gas adsorption on porous and microporous solids. It is also very useful for describing gas adsorption on mesoporous, macroporous, and non-porous solids, although there is no theoretical basis for the equation *(Hobson, 1961; Cerofolini, 1974)*. Our results suggest that the DR equation may be extended to clay/organoclay systems, and in the following discussion it will be used to

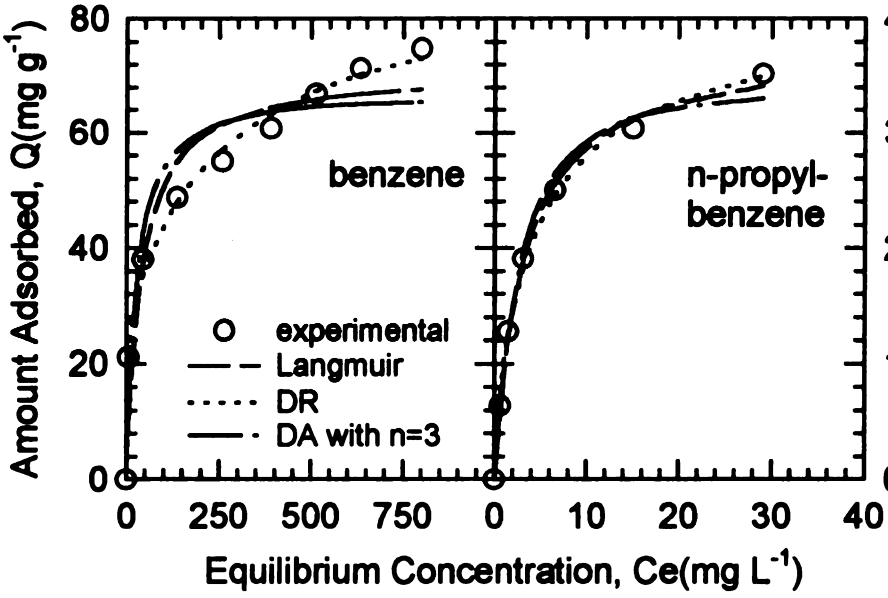

Figure 3.2 Adsorption isotherms of benzene and n-propylbenzene fitted to the Langmuir equation, the DA equation and the DR equation

characterize the aqueous organoclay adsorption systems presented here.

Adsorption energy distribution function. Adsorption energy distribution functions are dependent on the heterogeneity parameters q and v (Equation 3.8). In order to obtain q and v for calculating the adsorption energy distribution functions for SAC-TMPAs, all isotherms were fit to Equation 3.9. The resulting values of q and v, together with the maximum adsorption amount Q_m, are listed in Table 3.2.

Table 3.2 Parameters Q_m, v, q for adsorption of aromatic hydrocarbons in water/TMPA-smectite systems

SAC-TMPA		.17	.38	.65	.75	1.0
benzene	Q_m(mg/g)	60.61	73.24	77.84	78.51	77.36
	v	1.095	1.588	1.482	1.589	1.508
	q(kJ/mol)^2	1.031x10^4	2.594x10^4	3.411x10^4	4.238x10^4	3.033x10^4
toluene	Q_m(mg/g)	35.50	49.65	55.30	53.22	43.90
	v	1.328	1.219	1.979	1.598	2.466
	q(kJ/mol)^2	9.955x10^3	9.493x10^3	2.485x10^4	2.028x10^4	4.281x10^4
p-xylene	Q_m(mg/g)	30.87	38.00	45.51	44.16	37.63
	v	1.219	2.109	2.170	2.356	2.977
	q(kJ/mol)^2	8.368x10^3	3.224x10^4	3.023x10^4	4.144x10^4	5.199x10^4
ethyl-benzene	Q_m(mg/g)	32.72	38.62	44.98	44.64	38.48
	v	1.353	2.696	3.400	3.065	3.466
	q(kJ/mol)^2	8.520x10^3	4.545x10^4	5.978x10^4	6.140x10^4	6.574x10^4
n-propyl-benzene	Q_m(mg/g)	21.31	31.54	37.16	36.97	31.88
	v	33.42	65.39	86.98	56.33	75.79
	q(kJ/mol)^2	9.801x10^5	2.152x10^6	2.848x10^6	2.125x10^6	2.430x10^6

The adsorption energy distribution functions versus the inverse value of the average adsorption potential, z, calculated from Equation 3.8, are shown in Figure 3.3. All are asymmetrical gamma-type distributions with a broadening toward lower energies. To better describe those adsorption energy distributions, the z_{max} values (at which adsorption energy

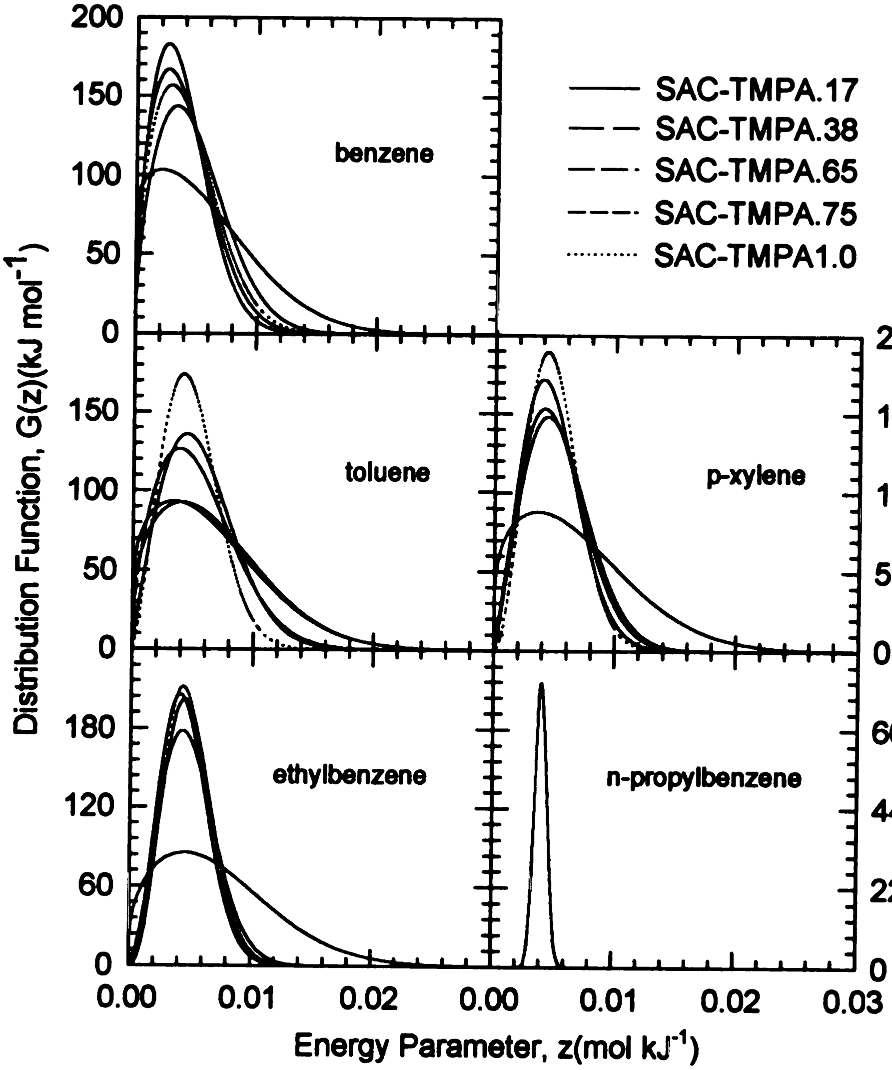

Figure 3.3 Adsorption energy distributions of mixed Ca/TMPA- and TMPA-smectites

distributions reach a maximum), the average $\bar{z}$ values, and the dispersion σ_z values were calculated according to the following equations *(Jaroniec and Madey, 1989)*:

$$z_{max} = \sqrt{\frac{\nu-1}{2q}} \qquad (3.10)$$

$$\bar{z} = \int_0^\infty zG(z)dz = \frac{\Gamma(\frac{\nu+1}{2})}{\Gamma(\frac{\nu}{2})} \frac{1}{\sqrt{q}} \qquad (3.11)$$

$$\sigma_z = \sqrt{\int_0^\infty z^2G(z)dz - \bar{z}^2} = \sqrt{\frac{\nu}{2} - \frac{\Gamma^2(\frac{\nu+1}{2})}{\Gamma^2(\frac{\nu}{2})}} \frac{1}{\sqrt{q}} \qquad (3.12)$$

The results are listed in Table 3.3. For all SAC-TMPAs, the energy distributions of benzene reach a maximum at higher adsorption energies compared to alkylbenzene studied, with an average z_{max} value of 0.0028 mol/kJ. By comparison, z_{max} values for toluene, p-xylene, ethylbenzene and n-propylbenzene were all about 0.0040 mol/kJ. As indicated by σ_z, the energy distributions of toluene are broader than that of benzene, and then progressively narrower for larger molecules in the sequence: benzene < toluene > p-xylene ≈ ethylbenzene > n-propylbenzene. For n-propylbenzene, the adsorption energy distributions are very sharp and nearly symmetrical. For the adsorption of the same adsorbate on different SAC-TMPAs, SAC-TMPA.17 gives the broadest distributions. The adsorption energy distributions for the other four SAC-TMPAs are similar to each other, particularly in the case of larger molecules such as ethylbenzene, but remarkably different from SAC-TMPA.17, the general trend in width being SAC-TMPA.38 ≈ SAC-TMPA1.0 > SAC-TMPA.65 ≈ SAC-TMPA.75. In the case of n-propylbenzene, they actually overlap, and only one curve is shown in Figure 3.3 for n-propylbenzene.

Table 3.3 The characteristics of adsorption energy distribution

SAC-TMPA		.17	.38	.65	.75	1.0	average
benzene	z_{max}(mol/kJ)	0.0029	0.0034	0.0026	0.0026	0.0029	0.0028
	$\bar{z}$(mol/kJ)	0.0059	0.0048	0.0040	0.0037	0.0043	
	σ_z(mol/kJ)	0.0043	0.0028	0.0024	0.0022	0.0026	
toluene	z_{max}(mol/kJ)	0.0041	0.0035	0.0044	0.0038	0.0041	0.0041
	$\bar{z}$(mol/kJ)	0.0068	0.0066	0.0056	0.0054	0.0049	
	σ_z(mol/kJ)	0.0045	0.0045	0.0029	0.0032	0.0023	
p-xylene	z_{max}(mol/kJ)	0.0036	0.0041	0.0044	0.0040	0.0044	0.0040
	$\bar{z}$(mol/kJ)	0.0071	0.0051	0.0054	0.0048	0.0049	
	σ_z(mol/kJ)	0.0048	0.0026	0.0027	0.0023	0.0021	
ethylbenzene	z_{max}(mol/kJ)	0.0046	0.0043	0.0045	0.0041	0.0043	0.0044
	$\bar{z}$(mol/kJ)	0.0075	0.0050	0.0050	0.0046	0.0048	
	σ_z(mol/kJ)	0.0048	0.0022	0.0020	0.0019	0.0019	
n-propylbenzene	z_{max}(mol/kJ)	0.0041	0.0039	0.0039	0.0036	0.0039	0.0039
	$\bar{z}$(mol/kJ)	0.0041	0.0039	0.0039	0.0036	0.0039	
	σ_z(mol/kJ)	0.0005	0.0005	0.0005	0.0005	0.0005	

As a probe for the heterogeneity of adsorbents, adsorbate molecules only detect those sites that interact with the probe molecules during the adsorption process. Therefore, the adsorption experiments provide information concerning the "relative" heterogeneity. It is apparent from the adsorption energy distributions summarized above that there is a steric effect involved in adsorption. Benzene molecules, due to their small sizes, are adsorbed on the sites of (relatively) high energies, whereas toluene and larger molecules can only be adsorbed on sites of lower energies. Stoeckli *et al. (1989)* have shown that the characteristic adsorption energy and micropore size of activated carbons have an inverse relationship. A similar relationship correlating the characteristic adsorption energy and micropore sizes may exist in TMPA organo-smectites. This suggests the existence of fine micropores of high adsorption energies in SAC-TMPAs which are accessible for benzene molecules but sterically exclude toluene and larger molecules. Such molecules can only be adsorbed in larger micropores, and on mesoporous, macroporous and flat surfaces which have the sites of lower energies, as indicated by the shift of z_{max} values for these molecules. These results also suggest that sites of benzene adsorption have micropore diameters larger than the length of the benzene molecules (5.6 Å) but smaller than the length of toluene molecule (7.1 Å). Molecular planes of the adsorbates must be parallel to the basal plane of the clay as indicated previously by Jaynes and Boyd *(1991b)*. If adsorbed molecules were oriented vertically to the clay surfaces, all five adsorbates used in this study would fill micropores since they have the same widths of 4.8 Å.

The above discussion is supported by the measured pore size distributions of SAC-TMPAs shown in Figure 3.4. All pores are in the micropore region. A significant portion of the micropores have pore diameters about 6.5 Å, larger than the length of the benzene molecule and smaller than the length of toluene.

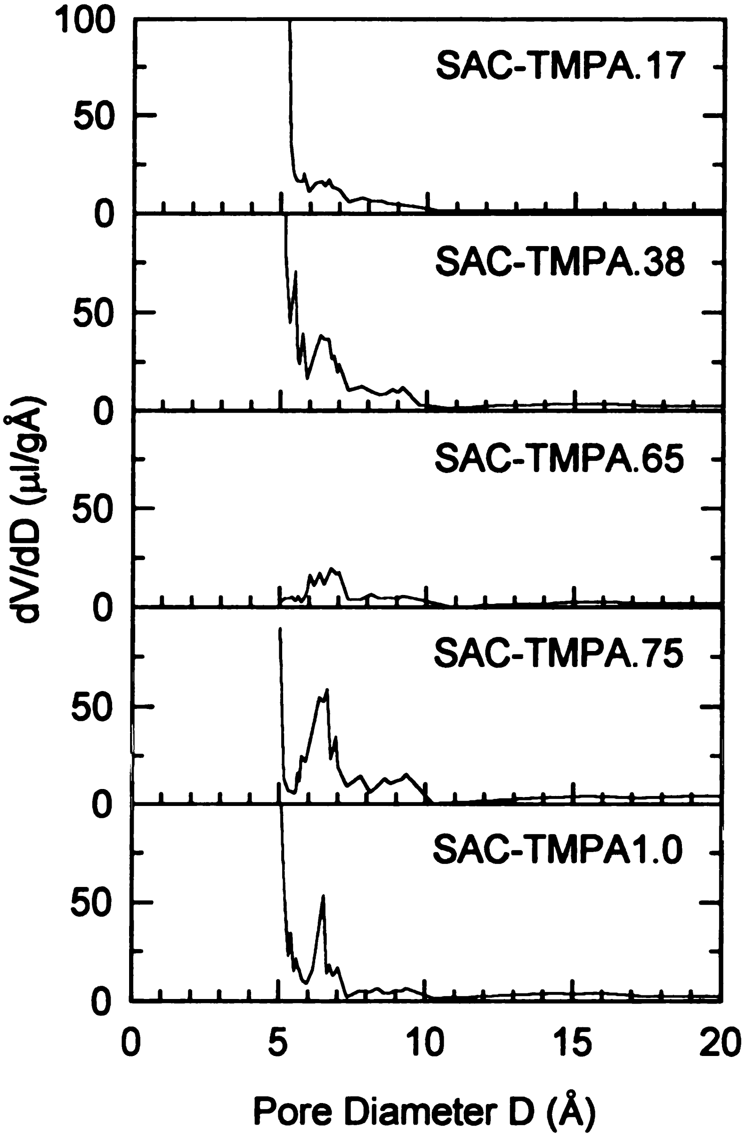

Figure 3.4 Micropore size distributions of mixed Ca/TMPA- and TMPA-smectites

Although benzene molecules can fill the fine micropores, toluene, p-xylene, ethylbenzene, and n-propylbenzene are adsorbed in larger micropores and on surfaces. The smaller toluene molecules explore more sites of different energies on the clay surfaces than the larger alkylbenzenes. As a result, toluene detects a more heterogeneous surface and gives broader adsorption energy distributions. The adsorption energy distribution narrows and the heterogeneity is concealed gradually as the adsorbate molecular size increases. In the case of n-propylbenzene, the heterogeneity is concealed completely so that the adsorption isotherms can be fit to Langmuir equation (Figure 3.2).

Cation segregation, especially at low TMPA content, may lead to a broadening of the energy distribution profile. McBride and Mortland *(1973)* observed the segregation of different cations in a smectite when ethylammonium was partially exchanged by tetrapropylammonium up to about 55 percent of the CEC. Faver and Lagaly *(1991)* reported that large quaternary ammonium cations (e.g. hexadecyltrimethylammonium) are preferentially adsorbed on low charge density clay surfaces while small organic cations such as TMPA prefer to be adsorbed on surfaces of high charge density. We have also observed that Ca^{2+} and TMPA cations are partially segregated in SAC-TMPAs, resulting in the formation of Ca^{2+}-rich and TMPA-rich patches. This is due to self-interaction of TMPA cations and the inhomogeneity of layer charge density *(Sheng, 1996)*. This type of topographical heterogeneity is especially significant for SAC-TMPA.17, producing the broad adsorption energy distributions. As the TMPA content increases in these clays, Ca^{2+} and TMPA distribution becomes more random and hence the surfaces more homogeneous. This is indicated by the progressively narrower adsorption energy distributions of SAC-TMPA.38, SAC-TMPA.65, and SAC-TMPA.75. Once the CEC is fully saturated by TMPA (in SAC-TMPA1.0), the adsorption energy distribution is slightly broader. This may be related to the formation of more fine micropores due to the high TMPA density on the surfaces.

Surface fractal dimension and micropore size distribution. Surface fractal dimension has a promising application for characterizing heterogeneous adsorbents. For a serial of spherical molecules, Pfeifer *et al. (1983)* and Avnir *et al. (1983, 1984)* derived the following relationship which relates the monolayer amount adsorbed (Q_m) to the spherical radius of the adsorbate molecule (r) and the surface fractal dimension (D) which is between 2 and 3:

$$Q_m \propto r^{-D} \tag{3.13}$$

However, the adsorbate molecules need not be spherical, provided they are adsorbed flat on the adsorbent surface and belong to a homologous series for which the ratio of the square of the linear extent (i.e., largest distance, r, between any two points on the probe) to the effective cross sectional area is the same for all members *(Pfeifer et al., 1983)*. For the sorption data presented here, a plot of logarithm Q_m versus logarithm r yields a straight line (Figure 3.5), indicating that these requirements are satisfied. Values of fractal dimension (D) are obtained from the slopes of these plots and listed in Table 3.4 together with the lengths of the aromatic molecules (r) which were used to estimate the fractal dimensions. Correlation coefficients (R^2) in Table 3.4 verify the highly linear relationship between log Q_m and log r. The high D value for SAC-TMPA.17 suggests a comparatively high degree of heterogeneity for SAC-TMPA.17. This high heterogeneity can be attributed to the formation of TMPA-rich patches in regions of higher charge density and the associated formation of numerous fine

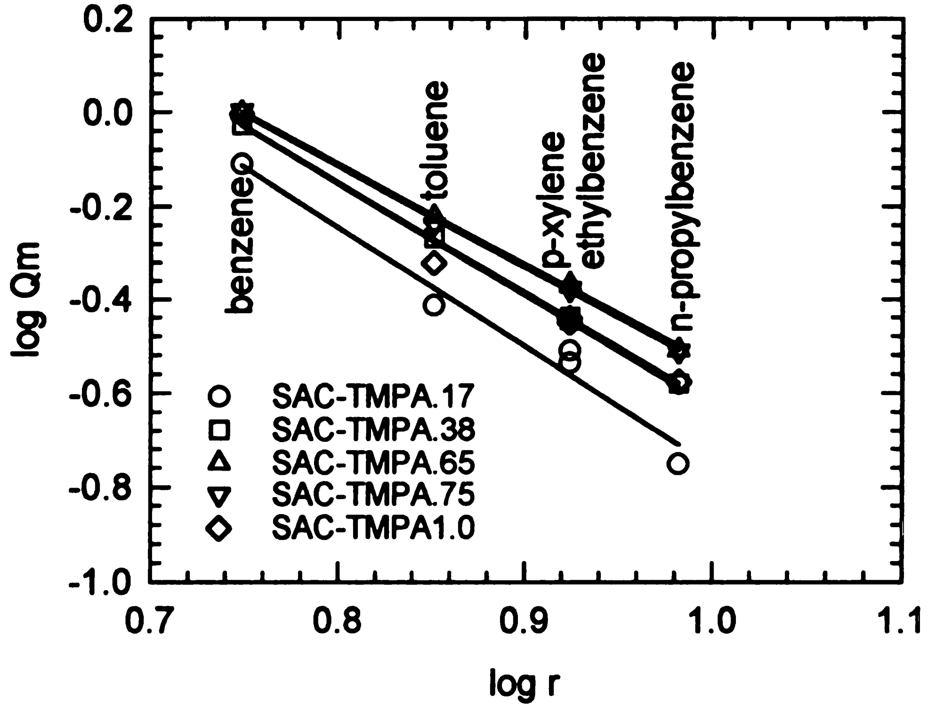

Figure 3.5 Dependence of monolayer adsorption on molecular size

micropores due to the high TMPA density. The D value decreases from 2.550 for SAC-TMPA.17 to 2.153 as the TMPA content increases to about 0.65CEC, indicating that TMPA-smectite becomes less heterogeneous. This can be attributed to the adsorption of TMPA on the layers of lower charge density, and the resultant formation of larger pores which lowers the fractal dimension. The D value increases again to 2.397 for SAC-TMPA1.0 as the TMPA content increases to 1.0CEC due to the formation of additional micropores. The analysis of fractal dimension results is consistent with the previous analysis of adsorption energy distributions.

Table 3.4 Molecular lengths of adsorbates and fractal dimensions of SAC-TMPAs

adsorbate	benzene	toluene	p-xylene	ethylbenzene	n-propylbenzene
length (Å)	5.6	7.1	8.4	8.4	9.6
SAC-TMPA	.17	.38	.65	.75	1.0
D	2.550	2.360	2.153	2.164	2.397
R^2	0.9704	0.9998	0.9989	0.9984	0.9842

These results are also consistent with the measured pore size distributions of SAC-TMPAs shown in Figure 3.4. The volume fraction of the portion of the micropores with pore diameters of about 6.5 Å increases (as the D value decreases) in the order: SAC-TMPA.17 < SAC-TMPA.38 < SAC-TMPA.65, decreases thereafter (as the D value increases) in the order: SAC-TMPA.65 > SAC-TMPA.75 > SAC-TMPA1.0.

Theoretically, as long as the relationship between the adsorption energy parameter z and pore size x is known, the adsorption energy distributions (G(z)) can be transformed into micropore size distributions (J(x)) according to the following relationship *(Jaroniec et al., 1990)*:

$$J(x) = G(z)\left(\frac{dz}{dx}\right) \qquad (3.14)$$

Stoeckli *et al. (1989)* have shown that, in activated carbons which are believed to have slit-like micropores, the adsorption energy parameter (z) (and hence the characteristic adsorption energy E_0) is simply related to the size of the micropores (x). Although several complex relationships between z and x have been proposed *(Stoeckli et al., 1989; Dubinin, 1988)*, the following simple inverse relationship has been successfully used on activated carbons *(Stoeckli et al., 1989; Dubinin, 1988)*:

$$xE_0 = k \text{ (nm.kJ/mol)} \tag{3.15}$$

where k is a constant in the micropore region between 9 and 13 nm·kJ/mol for activated carbons, and x is the size of the micropores (in nanometers), corresponding to the half-width in the case of slit-like micropores in activated carbons. With the molecular probes of various sizes, x is the half-width of the micropores accessible to probe molecules. A similar relationship may be applicable to organoclays which also have slit-like micropores. However, the constant k would likely be different, and is unknown, which makes it impossible to directly transform the adsorption energy distributions into micropore-size distributions in this study.

Based on the theory of adsorption on fractally porous solids, Avnir *et al. (1983)* have developed the following theoretical proportionality relationship between pore-size distribution J(x) and fractal dimension:

$$J(x) \propto x^{2-D} \tag{3.16}$$

In the micropore region, Jaroniec *et al. (1990)* derived the following equation:

$$J(x) = \frac{3-D}{x_{max}^{3-D} - x_{min}^{3-D}} x^{2-D} \tag{3.17}$$

where x_{max} is the upper limit of micropore size, and x_{min} is the lower limit of micropore size. Plotting fractal dimension against mean pore size, shown in Figure 3.6, gives the following

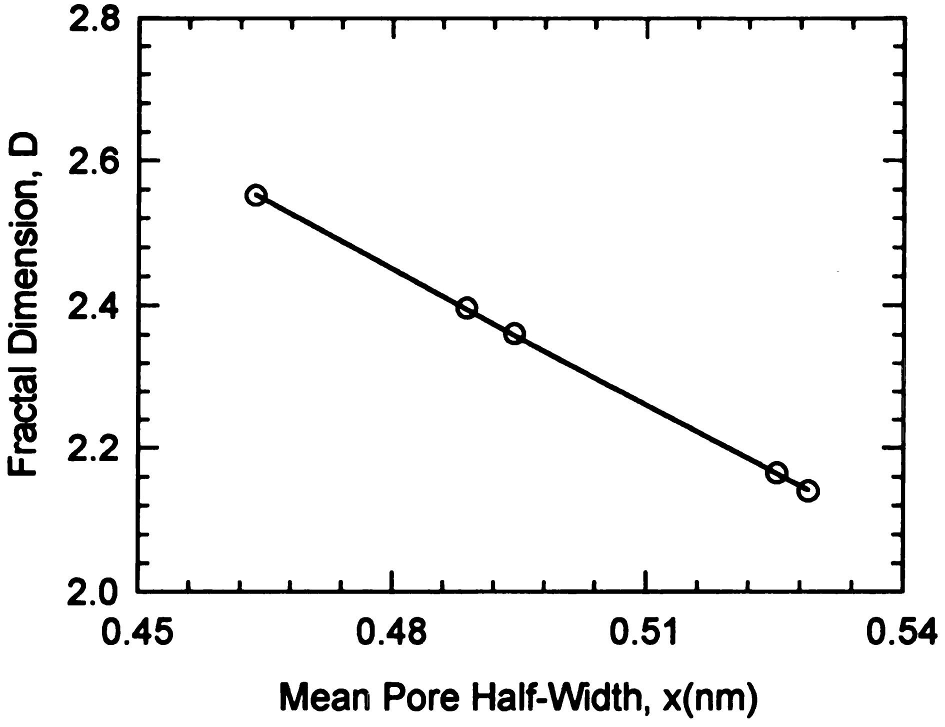

Figure 3.6 Dependence of fractal dimension on mean pore size of mixed Ca/TMPA- and TMPA-smectites

linear relationship:

$$D = 5.478 - 6.308\,\bar{x} \qquad R^2=1.000 \qquad (3.18)$$

This type of linear relationship was also obtained for activated carbons and consistent with the theoretical analysis *(Jaroniec et al., 1993)*. This relationship could be used to estimate the fractal dimension from experimental micropore size distribution of TMPA-smectites. In the above relationship, the mean pore size is calculated via the following expression using

x_{max}=1.0 nm and x_{min}=0.1 nm:

$$\bar{x} = \frac{\int_{x_{min}}^{x_{max}} xJ(x)dx}{\int_{x_{min}}^{x_{max}} J(x)dx} \tag{3.19}$$

Our experimental results of micropore size distribution and the theoretical linear relationship between D and $\bar{x}$ illustrate that D is simply correlated to the microporosity of SAC-TMPAs and reflects the fact that the surface irregularities of SAC-TMPAs are largely generated by their microporosity.

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Chapter 4 Function of Trimethylphenylammonium Cations in Smectite for Adsorption of Aqueous Organic Compounds

Abstract

Several organoclays were formed by exchanging Ca^{2+} in a Ca^{2+}-saturated smectite partially or fully with trimethylphenylammonium (TMPA) cations. The functions of TMPA cations in these organoclays as adsorbents for organic compounds in aqueous solutions were then examined. TMPA cations were found to take a partially random distribution in the interlayers of mixed Ca/TMPA-smectites. The presence of TMPA and its partially random distribution result in far less water associated with the clay surfaces and interlayers. In these clays, water molecules are held by Ca^{2+} ions only via coordination and electrostatic attraction, composing about two hydration shells around each Ca^{2+}. The interspersing of TMPA and Ca^{2+} ions prohibits the formation of a network of larger hydration shells around Ca^{2+}. Calculations showed that water molecules held in any other fashion, e.g. via weak hydrogen bonding to the siloxane surface, are completely removed during the adsorption of organic compounds. These results demonstrate that the amount of water associated with the clay surfaces and interlayers depends on the nature of the exchange cation, and not on the amount of available siloxane surface area *per se*. In TMPA-smectites, the TMPA cations function as non-hydrated pillars, and sorption of organic solutes occurs predominantly on the adjacent siloxane surfaces, which are hydrophobic in nature. The hydration shell around Ca^{2+} in mixed Ca/TMPA-smectites obscures some of the siloxane surfaces. This diminishes sorption capacity because organic solutes cannot displace the water of hydration.

Key Words - Adsorption, Organoclay, Smectite, TMPA.

Introduction

Due to the isomorphous substitution in the aluminosilicate layers, natural clay minerals usually have a net negative charge which is balanced by alkali-metal and alkaline-earth-metal cations such as Na^+ and Ca^{2+}. The strong hydration of these inorganic cations makes the mineral surfaces hydrophilic. Early studies (*Stark, 1948; Hanson and Nex, 1953; Call, 1957; Spencer et al., 1969; Spencer and Cliath, 1970*) on vapor phase sorption by soils and clays demonstrated that pesticides and other relatively non-polar organic compounds are not strongly adsorbed on such mineral surfaces.

The surface properties of clay minerals can be dramatically changed by simple ion-exchange of inorganic cations with a variety of organic cations such as quaternary ammonium cations of the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NRR']^+$. Previous studies have shown (*Mortland et al., 1986; Boyd et al., 1988a,b,c; 1991*) that the organoclays can be used to effectively sorb organic compounds from water.

The sorptive properties of the organoclays formed with quaternary ammonium cations depend largely on the size of R- group (*Boyd et al., 1991*). Mortland *et al.* (*1986*) and Boyd *et al.* (*1988c*) found that when R is a large alkyl group such as hexadecyl, the organoclays formed from smectite were effective sorbents for phenol and chlorophenols compared to unmodified smectite. A recent study (*Sheng et al., 1996*) showed that clays modified with hexadecyltrimethylammonium cationic surfactant (HDTMA) effectively sorb neutral organic contaminants via multiple mechanisms. For aliphatic compounds such as trichloroethylene and carbon tetrachloride, partitioning into the organic phase derived from the conglomeration of HDTMA is the singular sorption mechanism by HDTMA-clays, consistent with previous observations and with the concept of solute partitioning into soil organic matter (*Chiou et al., 1979, 1983*). The sorption isotherms generally display type III (convex to the abscissa commencing at the origin) compared to the linear isotherms for soil organic matter. This is due to the much higher degree of sorption into the HDTMA phase, as compared to soil organic matter, which substantially changes the composition of HDTMA phase and causes the solvency of HDTMA phase for solutes to increase. Multiple mechanisms are involved in the sorption of aromatic compounds by HDTMA-clays. Aromatic molecules solvate the cationic ammonium centers and alkyl chains of HDTMA, and are concomitantly adsorbed on the vacated mineral surfaces. Solvation leads to a cooperative adsorption and yields a sigmoid isotherm. The combination of solvation (a sigmoid isotherm) and partitioning (a type III isotherm) produces a double-sigmoid isotherm for aromatic solute sorption by HDTMA-clays.

In contrast to the solvation and partitioning behavior of organoclays exchanged with large organic cations such as HDTMA, the organoclays formed with small organic cations display adsorptive properties. Due to their small size, organic cations such as tetramethylammonium (TMA) or trimethylphenylammonium (TMPA) do not form a continuous organic phase on the clay surfaces and in the interlayers. Rather, they are physically isolated, leaving unobscured (free) siloxane mineral surfaces between the ammonium pillars. Lee *et al.* (*1989, 1990*) studied the adsorption of benzene and substituted benzenes by TMA-smectite. Sorption of organic compounds as vapors by the dry clay and as solutes from water was examined. Sorption by the dry clay manifested type II isotherms and was not strongly dependent on sorbate size. However, shape-selective adsorption of aromatic molecules from water by TMA-smectite was evidenced by high uptake of benzene and progressively lower uptake of larger aromatic molecules. This phenomenon was ascribed to the shrinkage of interlamellar cavities by water.

Jaynes and Boyd (*1990*) reported that trimethylphenylammonium (TMPA)-smectite was also an effective adsorbent of water soluble aromatic hydrocarbons including benzene, toluene, ethylbenzene, p-xylene, butylbenzene, and naphthalene, and did not show strong shape-selective adsorption characteristics of TMA-smectite. It was suggested that the water hydration of TMPA as compared to TMA accounted for the different adsorption characteristics of the corresponding organoclays. In a subsequent study (*1991*), the charge density of smectite was reduced first, resulting in different TMPA contents in the organoclays. Adsorption was found to increase as layer charge and TMPA content decreased. They concluded that the siloxane surface of smectite is hydrophobic, and aromatic molecules were mainly adsorbed on the hydrophobic siloxane surfaces. TMPA cations had little direct effect on adsorption, and functioned as non-hydrated "pillars" to keep the smectite interlayers open for adsorption.

Considering the important effects of charge reduction on the adsorption of aromatic hydrocarbons by TMPA-smectites, it was of interest to evaluate the adsorptive properties of mixed Ca/TMPA-smectites. Differences would be expected between charge-reduced TMPA smectite and mixed Ca/TMPA-smectite because charge reduction leaves the hydrophobic siloxane surfaces available for the adsorption of organic compounds while Ca^{2+} in mixed Ca/TMPA-smectite will occupy the surfaces and may be hydrated. Furthermore, differences in the adsorptive properties would be expected between TMA/Ca-smectite, which does not contain an aromatic moiety, and Ca/TMPA-smectite which does. In the latter case, aromatic rings of TMPA may interact directly with the π electron system of aromatic adsorbate molecules. The overall objective of the current work is to evaluate the function of TMPA and Ca^{2+} cations in the adsorption of organic compounds on mixed Ca/TMPA-smectites.

Experimental Section

Smectite from a Wyoming bentonite (designated SAC), which has Na as the primary exchangeable cation and a cation-exchange capacity (CEC) of ~90 $cmol_c/kg$ was obtained from the American Colloid Company (Chicago, IL). The <2μm clay fractions were obtained by the wet sedimentation method, and subsequently Ca-saturated. Trimethylphenylammonium (TMPA) bromide (Aldrich Chemical Co., Milwaukee, WI) was used to prepare organoclays. To obtain mixed Ca/TMPA clay, aqueous TMPA solutions were added to 2 liters of smectite suspensions containing 25 grams of Ca-saturated smectite in amounts less than the CEC of the clay. To fully saturate the smectite with TMPA, the total amount of TMPA added was equal to 3 times the CEC of the smectite. The mixtures of the smectite suspensions and TMPA solution were stirred overnight at room temperature (~23°C). The clay suspensions were then washed with distilled water repeatedly until free of bromide ions (as indicated by $AgNO_3$ test), and subsequently quick-frozen, freeze-dried. Organic carbon (OC) contents were determined using Dohrmann DC-190 high temperature TOC analyzer (Rosemount

Analytical Inc., Santa Clara, CA), and used to calculate the percent of CEC occupied by TMPA cations (Table 4.1).

The batch equilibration technique was used to quantitate TMPA adsorption and Ca^{2+} release. Ca^{2+} saturated smectite (0.1g) was weighed into a series of 25-ml Corex glass centrifuge tubes containing different volumes of aqueous TMPA bromide solutions (3.6 cmol/L), corresponding to 0.16, 0.32, 0.4, 0.6, 0.8, 0.96, 1.2, 1.6, 2.4, 4.0, 6.0, 8.0 times CEC of the smectite, followed by adding distilled water to bring the total volume to 20 ml. The tubes were shaken on a reciprocating shaker at room temperature for 4 days. After centrifugation at 6000 rpm (RCF=4302 g) for 10 min, a portion of each supernatant was taken and diluted to the proper concentration. TMPA concentrations were measured using an ultraviolet absorption spectrophotometer (Hewlett-Packard 8452A, Diode Array, Germany) at 254 nm. Ca^{2+} concentrations were measured using an atomic absorption spectrophotometer (Perkin-Elmer 1100B, Norwalk, CT). The amounts of TMPA adsorbed were calculated by the differences between the initial and equilibrium concentrations. Adsorption of TMPA cations and release of Ca^{2+} were plotted against the equilibrium TMPA concentration.

Basal spacings were determined by X-ray diffraction analysis. TMPA-smectites with different exchange degrees were analyzed by dropping aqueous suspensions on glass slides which were subsequently covered by teflon tape to prevent them from drying. X-ray diffraction patterns were recorded using CuKα radiator and a Philips APD3720 automated X-ray diffractometer using an APD3521 goniometer fit with a θ-compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator, from 2 to $10^{0}2\theta$, in steps of

0.02°2θ, 1 sec/step.

Table 4.1 Properties of TMPA-smectites

clay	sample name	OC%	% of CEC occupied by TMPA	d_{001} (Å)
1	SAC-TMPA.17	1.66	17	14.42, 18.89
2	SAC-TMPA.38	3.57	38	14.12, 18.97
3	SAC-TMPA.65	5.88	65	14.16
4	SAC-TMPA.75	6.75	75	14.95
5	SAC-TMPA1.0	8.84	100	14.38

Adsorption isotherms of neutral organic compounds on TMPA-smectites were obtained using batch equilibration technique. Benzene, o-xylene, ethylbenzene, n-butylbenzene, and trichloroethylene (HPLC-grade) were obtained commercially (Aldrich Chemical Co., Milwaukee, WI), and used without further purification. TMPA-smectites (0.2g) were weighed into 25-ml Corex glass centrifuge tubes, followed by adding 25 ml of distilled water. Different amounts of each organic compound were delivered directly into the tubes as the pure liquid using a microliter syringe. The maximum amount of each compound added corresponded to a final equilibrium concentration of ~50 % of its water solubility. The tubes were capped immediately with teflon-backed septa and shaken for 24 hours on a reciprocating shaker at room temperature. Preliminary experiments showed that the adsorption process reached equilibrium within 18 hours. After equilibration, the tubes were centrifuged at 8000 rpm (RCF=4302 g) for 10 minutes. 5 ml of supernatant was extracted with 10 ml of carbon disulfide in a glass vial.

Analysis of the organic compounds in the CS_2 extracts was by gas chromatography. A Hewlett-Packard 5890A gas chromatograph was used with flame ionization detector and a packed column with N_2 as the carrier gas. Peak areas were recorded by a Hewlett-Packard 3392A integrator. Concentrations were calculated from the measured peak areas using a series of external standards. Recoveries were ~90%. Amounts adsorbed were calculated from differences between the amount of organic compounds added and that remaining in the final equilibrium solutions. Isotherms were made by plotting the amounts adsorbed against the equilibrium concentrations in solution.

Results

The adsorption of TMPA cations by, and the release of Ca^{2+} from, a Ca^{2+}-saturated smectite is shown in Figure 4.1. The curves relating TMPA uptake and Ca^{2+} release to the equilibrium concentration of TMPA are initially superimposable forming a unique S-shaped isotherm. At a TMPA content of about 80 cmol/kg, corresponding to about 90% of CEC, the curves begin to diverge. After this, the amount of TMPA cations bound to smectite exceeds the amount of Ca^{2+} released, which plateaus at about 90 cmol/kg. The amount of TMPA cations bound to smectite increases steadily beyond the CEC of smectite; at an aqueous TMPA concentration of 2.3 cmol/L, the amount of TMPA cations bound to smectite was twice the CEC. At this point the amount of TMPA added was 8 times the CEC of the clay. The lowest equilibrium concentration of TMPA cations in solution appears in the intermediate

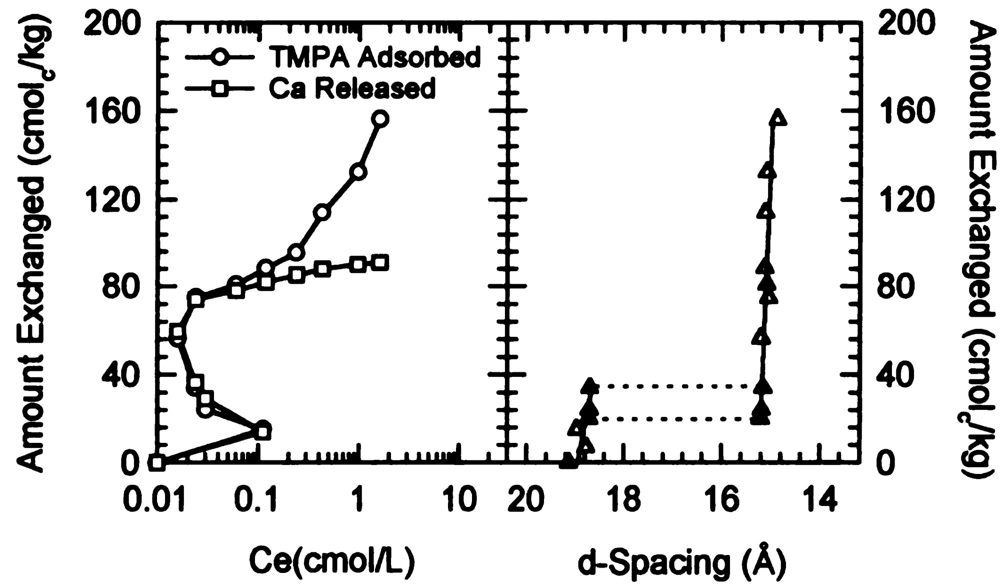

Figure 4.1 Adsorption of TMPA cations by and release of Ca^{2+} from Ca^{2+}-smectite (left), and corresponding basal spacings (right)

exchange degree of Ca^{2+} with TMPA cations.

Changes in basal spacings with the degree of TMPA exchange was observed (Figure 4.1). At TMPA levels up to about 16 cmol/kg, a single spacing of ~19Å was observed. Between 16 and 38 cmol/kg of TMPA level, two spacings of about 19Å and 15Å were present. The intensity of 15Å peak increased and the intensity of 19Å peak decreased as the TMPA level increased over this range. At TMPA levels above 38 cmol/kg, a single spacing of ~15Å was present.

Figure 4.2 shows the adsorption isotherms for benzene, o-xylene, ethylbenzene, n-

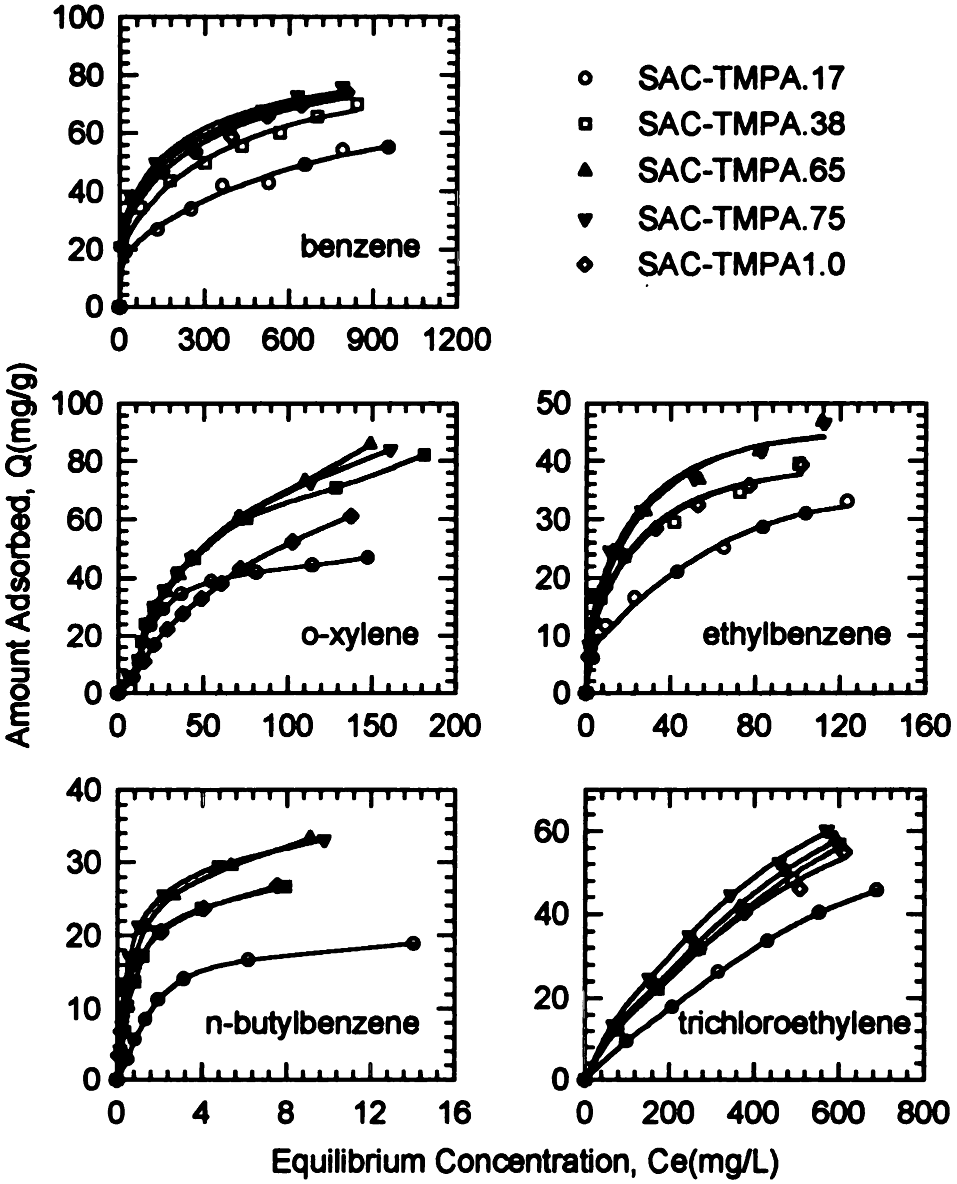

Figure 4.2 Adsorption of organic compounds by TMPA-smectites from aqueous solutions

butylbenzene and trichloroethylene. All the organoclays (mixed Ca/TMPA-smectites and TMPA-smectite) were effective adsorbents manifesting type I isotherms for all solutes except o-xylene. The occurrence of type I isotherms indicates that adsorption occurred in the interlayer pores and on the surfaces of the organoclays. The extent of the adsorbate-adsorbent interaction was different for the different adsorbate molecules, as evidenced by the curvature of the isotherms. The isotherms of trichloroethylene were less curvilinear than those of the alkylbenzenes, indicating a comparatively weaker interaction between trichloroethylene and the organoclays than between the alkylbenzenes and the organoclays. The isotherms of o-xylene were type V, indicating a weaker interaction between o-xylene and the organoclays than between o-xylene molecules themselves.

The degree of exchange of Ca^{2+} with TMPA cations also affected solute uptake. The adsorptive ability of the TMPA-smectites increased continually as the TMPA content increased from 0.17CEC (17% of the CEC) to 0.65CEC. TMPA contents of higher than 0.75CEC, however, caused a decrease in the adsorptive ability of the clay. As indicated in Figure 4.2, the adsorptive ability of SAC-TMPA1.0 is lower than that of SAC-TMPA.65/SAC-TMPA.75.

Discussion

The distribution and interaction of organic cations in the interlayers of smectite have a pronounced effect on the adsorption of organic compounds. The exchange reaction of TMPA cations on smectite and the release of Ca^{2+} from smectite in this study provided useful information about the distribution and interaction of TMPA cations in the interlayers of smectite. In this study, the unique S-shaped adsorption isotherm of TMPA, and the extra adsorption of TMPA over the CEC indicate strong lateral interaction between the adsorbed TMPA cations. Xu and Boyd (*1994, 1995*) observed a similar S-shaped isotherm for the exchange of Na^+ but not Ca^{2+} by HDTMA in smectite. In the case of Ca-smectite, the face to face aggregation of clay sheets limited access of HDTMA to the interlayers. This promoted lateral interactions among adsorbed HDTMA even at very low loadings. For Na-smectite, the clay sheets are fully expanded. This manifested a more random distribution of HDTMA at low loadings, and minimized lateral interactions. As the loading increased, lateral interactions commenced, causing a decrease in the equilibrium concentration of HDTMA, and hence the S-shaped isotherm. In the case of TMPA exchange onto Ca-smectite, lateral interactions manifest a collapse of the clay layers. As a result, TMPA cations on opposing clay surfaces are brought in close proximity to each other, perhaps producing strong π-π interaction between the phenyl groups. This result agrees with the findings of Jaynes and Boyd (*1991*) who proposed that TMPA cations on opposing clay surfaces interact through π-π interactions, producing a more stable arrangement for the organic cations, and also creating larger areas of the siloxane surface between ammonium ions for the adsorption of organic compounds. Washing with distilled water removes the excess of TMPA cations from smectite over the CEC, as indicated by OC content measurements in Table 4.1.

The S-shaped isotherm of TMPA adsorption also strongly suggests that Ca^{2+} and TMPA cations are not segregated in the different interlayers of smectite, although segregation of organic cations in smectite is commonly observed (*McBride and Mortland, 1973*). As alluded to above, segregation of HDTMA cations exchanged onto Ca^{2+}- smectite and vermiculite (*Xu and Boyd, 1994, 1995*) occurred due to the limited expansion of the clay layers and large size of HDTMA cations. The random distribution of TMPA and Ca^{2+} cations in Ca^{2+}-smectite may occur due to the smaller size of TMPA (compared to HDTMA) and hence greater access to the interlayer exchange sites. The random distribution is evidenced by the two distinct basal spacings at low and high TMPA levels. This random distribution was also observed for mixed Ca/TMA-smectite based on the surface area measurements (*Lee et al., 1989*).

The smectite surface itself is inhomogeneous, containing a spectrum of charge densities. This is indicated by changes in basal spacings as a function of TMPA level. TMPA cations, owing to their small size, are preferentially adsorbed on the surfaces of high charge density (*Faver and Lagaly, 1991*), and successively on surfaces of lower charge density. TMPA-smectite collapses over a range, albeit a narrow one, of TMPA levels. This indicates that although Ca^{2+} and TMPA cations are distributed randomly on surfaces with similar charge densities, they may segregate to some extent in smectite as a whole. Overall, TMPA cations are neither completely segregated nor randomly distributed. Rather, the distribution of TMPA cations in the interlayers of smectite could be described as partially random distribution.

Our results show that partial replacement of Ca^{2+} in smectite with TMPA cations significantly increases the adsorptive ability of smectite even though part of siloxane surface of smectite is still covered by Ca^{2+} ions. To illustrate this, our results are compared to those for reduced charge TMPA-smectites having no exchangeable Ca^{2+} reported by Jaynes and Boyd (*1991*). Although adsorption isotherms on TMPA-smectites are better described by the

Dubinin-Radushkevich (DR) equation (*Sheng et al., 1996*), the data were still fit to the Langmuir equation to allow comparison to the data reported by Jaynes and Boyd (*1991*). The monolayer adsorption capacities Q_m of benzene, ethylbenzene, n-butylbenzene and trichloroethylene on the mixed Ca/TMPA-smectites and TMPA-smectite described here and on the reduced charge TMPA-smectites of Jaynes and Boyd (*1991*) are summarized in Table 4.2. The monolayer adsorption capacities of these organic compounds versus organic carbon (from TMPA) content are presented in Figure 4.3. The steep initial rise of the curves is additional evidence that Ca^{2+} and TMPA cations are not completely segregated, but rather that some TMPA cations occur in patches. Otherwise, the monolayer adsorption capacity would be linearly correlated to TMPA content (OC content) in smectite (dashed line in Figure 4.3).

In order to determine the function of TMPA cations in the adsorption of organic compounds, SAC-TMPA.75 in our study and SAz-0.6Li-250-TMPA (indicates a high-charge smectite from Arizona, SAz, with lithium added in an amount of 60% of the CEC to reduce charge at 250°C) from Jaynes and Boyd (*1991*) compared because these two smectites have similar TMPA contents (6.75% and 6.70% OC contents, respectively) and the interlayers in SAz-0.6Li-250-TMPA are not collapsed. The monolayer adsorption capacities of SAC-TMPA.75 are lower than those of SAz-0.6Li-250-TMPA by ~20% (17.6% for benzene, 17.7% for ethylbenzene, and 23.2% for n-butylbenzene). This is near to but slightly less than the 25% of the CEC occupied by Ca^{2+}. This implies that the siloxane surface of TMPA-smectites is only partially covered by hydrated Ca^{2+} ions, the extent of which roughly corresponds to the percent of the CEC occupied by Ca^{2+}. Hydration of TMPA or the siloxane surface around TMPA cations is not indicated because this would significantly depress their adsorptive ability of the mixed Ca/TMPA-smectites for neutral organic compounds because the hydrophobic surface would be no longer available for adsorption.

Table 4.2 Monolayer adsorption capacities of organic compounds on TMPA-smectites

organo-clay type	O.C.%	monolayer adsorption capacity (mg/g)			
		benzene	ethyl-benzene	n-butyl-benzene	trichloro-ethylene
Ca/TMPA-smectite					
SAC-TMPA.17	1.66	61.38	38.26	22.40	100.80
SAC-TMPA.38	3.57	74.38	42.66	30.74	126.47
SAC-TMPA.65	5.88	77.29	50.45	36.83	128.49
SAC-TMPA.75	6.75	78.17	48.83	35.54	135.91
SAC-TMPA1.0	8.84	76.95	42.09	28.59	112.70
Reduced charge TMPA-smectite*					
SAz-1.0Li-250-TMPA	1.33	64.60	43.51		
SAz-0.8Li-250-TMPA	3.42	87.66	40.93	41.67	
SAz-0.6Li-250-TMPA	6.70	94.79	59.31	46.28	
SAz-0.3Li-250-TMPA	9.33	71.92	28.58	25.35	

* Data from Jaynes and Boyd (*1991*).

To further illustrate this, SAC-TMPA.75 is again chosen to calculate the area covered by dehydrated Ca^{2+} cations. A crystal radius of 0.99Å for Ca^{2+} is used in the calculation. In

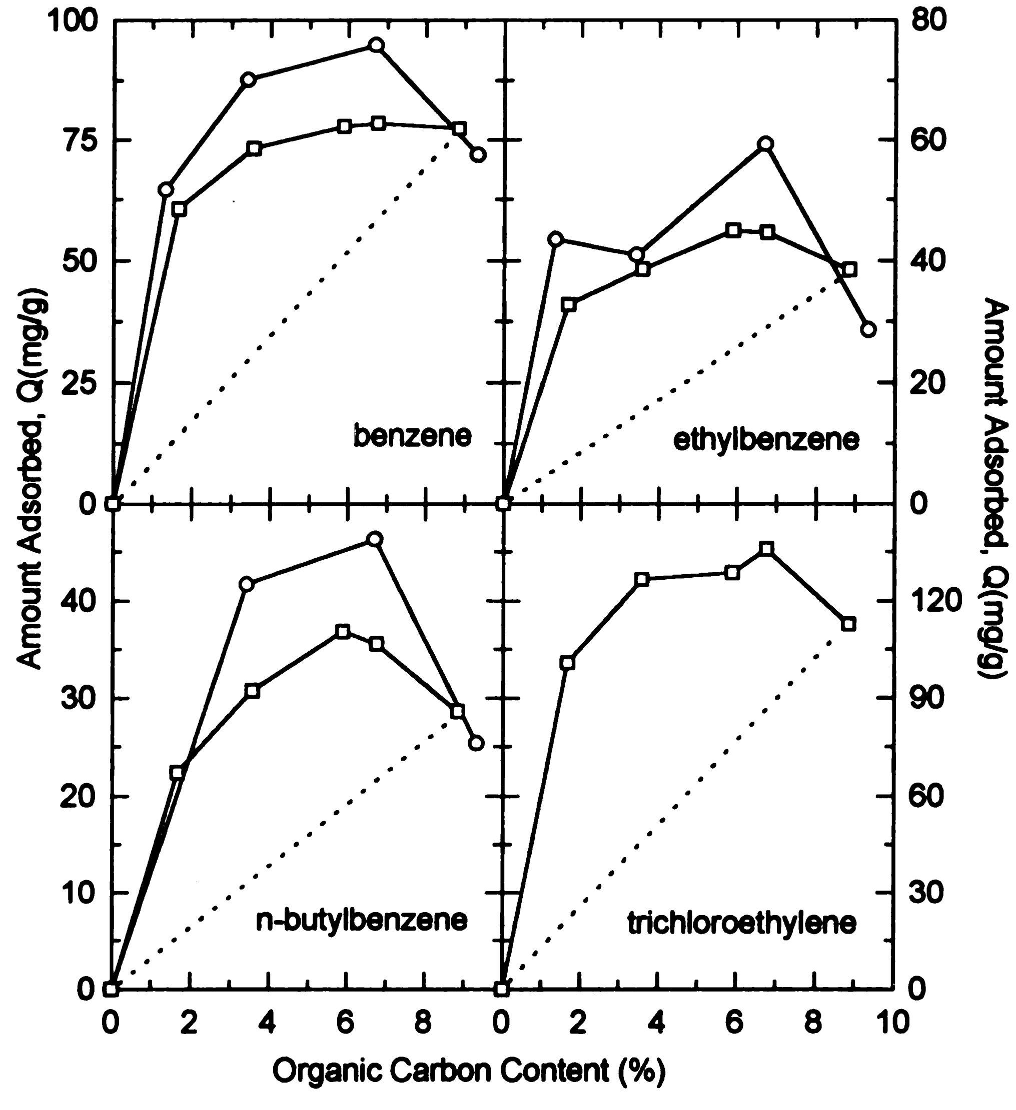

Figure 4.3 Dependence of monolayer adsorption capacity on organic carbon content on Ca/TMPA-smectites (square) and reduced charge TMPA-smectites from Jaynes and Boyd (*1991*) (circle) for benzene, ethylbenzene, n-butylbenzene and trichloroethylene

SAC-TMPA.75 in which 25% of CEC is occupied by Ca^{2+} ions, the area covered by dehydrated Ca^{2+} would be 2.09 m^2/g. Jaynes and Boyd (*1991*) reported a surface area of 239.6 m^2/g for SAz-0.6Li-250-TMPA. If it is supposed that the surface areas of SAC-TMPA.75 without Ca^{2+} ions and of SAz-0.6Li-250-TMPA are the same or very close, and the 20% difference of adsorption capacities between SAC-TMPA.75 and SAz-0.6Li-250-TMPA is produced via covering the siloxane surface by Ca^{2+} and water molecules, then the area covered by water molecules is approximately 45.83 m^2/g ($239.6\times20\%-2.09$). Then, the total number of monolayer water molecules on the surface is ca. 7.66×10^{20} /g (using the radius of water molecule equal to 1.38 Å (*Hunt, 1965*)). Thus, the ratio of the number of water molecules to that of Ca^{2+} ions in SAC-TMPA.75 is 11.3. If the surface in SAC-TMPA.75 was completely covered by Ca^{2+} and water (2.09 m^2/g by Ca^{2+}, and 237.5 m^2/g by water), then the ratio of H_2O/Ca^{2+} would be 58.8. Similarly, if the water vapor isotherm on the same Ca^{2+}-smectite reported by Boyd *et al.* (*1988b*) is used to calculate the ratio of H_2O/Ca^{2+} in the smectite, the limiting adsorption amount of water vapor on smectite obtained is ~224 mg/g by extrapolating the linear portion of the isotherm to $p/p_0=1$. This adsorption amount gives the ratio of H_2O/Ca^{2+} 54.5 at $p/p_0=1$. This number is very close to that in SAC-TMPA.75 with the monolayer coverage by water. Thus, the amount of water on the surface of SAC-TMPA.75 is much less than the monolayer amount, demonstrating that a large part of the siloxane surface is not covered by water and therefore for the adsorption of organic compounds. Furthermore, these calculations indicate that the presence of TMPA cations in the mixed Ca/TMPA-smectites subsequently reduces the amount of water associated with each Ca^{2+} ion, and with the surfaces as a whole. Thus, the nature of the exchange cation, not the amount of siloxane surface area *per se*, dictates the degree to which water is associated with the clay surfaces.

It appears that upon replacement of Ca^{2+} by TMPA cations, the overall interaction between water molecules and Ca^{2+} ions weakens. The partially random distribution of TMPA and Ca^{2+} cations increases the percentage of the surfaces which are covered by the weakly held water film. As the neutral organic molecules are introduced into the interlayers of smectite, they are able to displace weakly bound water molecules from the siloxane surfaces of smectite. However, those water molecules close to Ca^{2+} ions (in inner region) are still strongly held by coordination bonds and electrostatic forces. The ratio of H_2O/Ca^{2+} of 11.3 suggests that most of the water molecules present in SAC-TMPA.75 are associated with two hydration shells around Ca^{2+} since the coordination number for Ca^{2+} with H_2O is equal to 6.

In general, the replacement of Ca^{2+} by TMPA enhances the adsorptive ability of the resultant clay for neutral organic compounds. However, TMPA cations may also have a negative effect on the adsorption of neutral organic compounds at high TMPA levels. At low TMPA levels, TMPA cations are separated too far to interact with each other. They function only to make the hydrophobic siloxane surface available for adsorption. The higher the content of TMPA is, the more surface is available for the adsorption of organic compounds. However, when the amount of TMPA cations in smectite is high enough, i.e. over 75% of CEC, the size of the adsorptive regions between neighboring ammonium ions diminishes sufficiently so that some of this surface cannot accommodate the adsorbate molecule. As a result, the adsorption amount is lower at high levels of TMPA cations than at intermediate levels.

Lee *et al.* (*1989*) showed that water molecules shrink the interlamellar cavities in TMA-smectite, resulting in a strong selective adsorption of aromatic compounds. This presumably results from the hydration of TMA cations which have an appreciable hydration energy of ~32 kcal/mol. TMPA-smectites do not show this water induced shape selectivity, indicating that TMPA is less strongly hydrated. This maintains the size of the adsorptive regions between TMPA ions, even in the presence of water. However, adsorbates of sufficient size may still be sterically excluded. In TMPA-smectites, all alkylbenzenes with the same width except o-xylene showed high affinity for the surface. However, the presence of adjacent substituents in o-xylene molecules increases the size of the molecule in two dimensions and this creates steric hindrance which leads to the weak adsorbent-adsorbate interaction.

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Chapter 5 Conclusions and Significance

Sorption of neutral organic contaminants by organoclays

Naturally occurring aluminosilicates (e.g. smectites and vermiculites) do not sorb significant amounts of hydrophobic organic contaminants (HOCs) in presence of water due to the preferential adsorption of water around the metallic exchangeable cations (*Prost, 1975*). The sorptive characteristics of soils and clays for neutral organic compounds (NOCs) are dramatically improved when the inorganic exchangeable cations are replaced by organic cations such as quaternary ammonium cations (QACs) (*Lee et al., 1989a; 1990; Boyd et al., 1988 a, b; 1991; Jaynes and Boyd, 1991a*). For example, as shown in Figure 5.1, sorption coefficients for several common organic groundwater contaminants (e.g. benzene, toluene, xylene) are increased by over 2 orders of magnitude by hexadecyltrimethylammonium (HDTMA) modification of a subsoil containing vermiculite and illite as major clay minerals (*Boyd et al., 1988a; Lee et al., 1989a*). The large increase in sorptive capability of modified soil is partially due to increase in organic carbon content resulting from HDTMA adsorption, and partially due to the fact that HDTMA-derived organic matter is 10-30 times more effective than natural organic matter for sorbing NOCs (*Lee et al., 1989a*).

The sorption properties of a given modified clay or soil depend in part on the nature of the organic modifiers. Replacing the inorganic exchangeable cations with small organic cations such as tetramethylammonium (TMA), trimethylphenylammonium (TMPA) and tetramethylphosphonium (TMP) increases the sorption of NOCs (*Lee et al., 1990; Jaynes and*

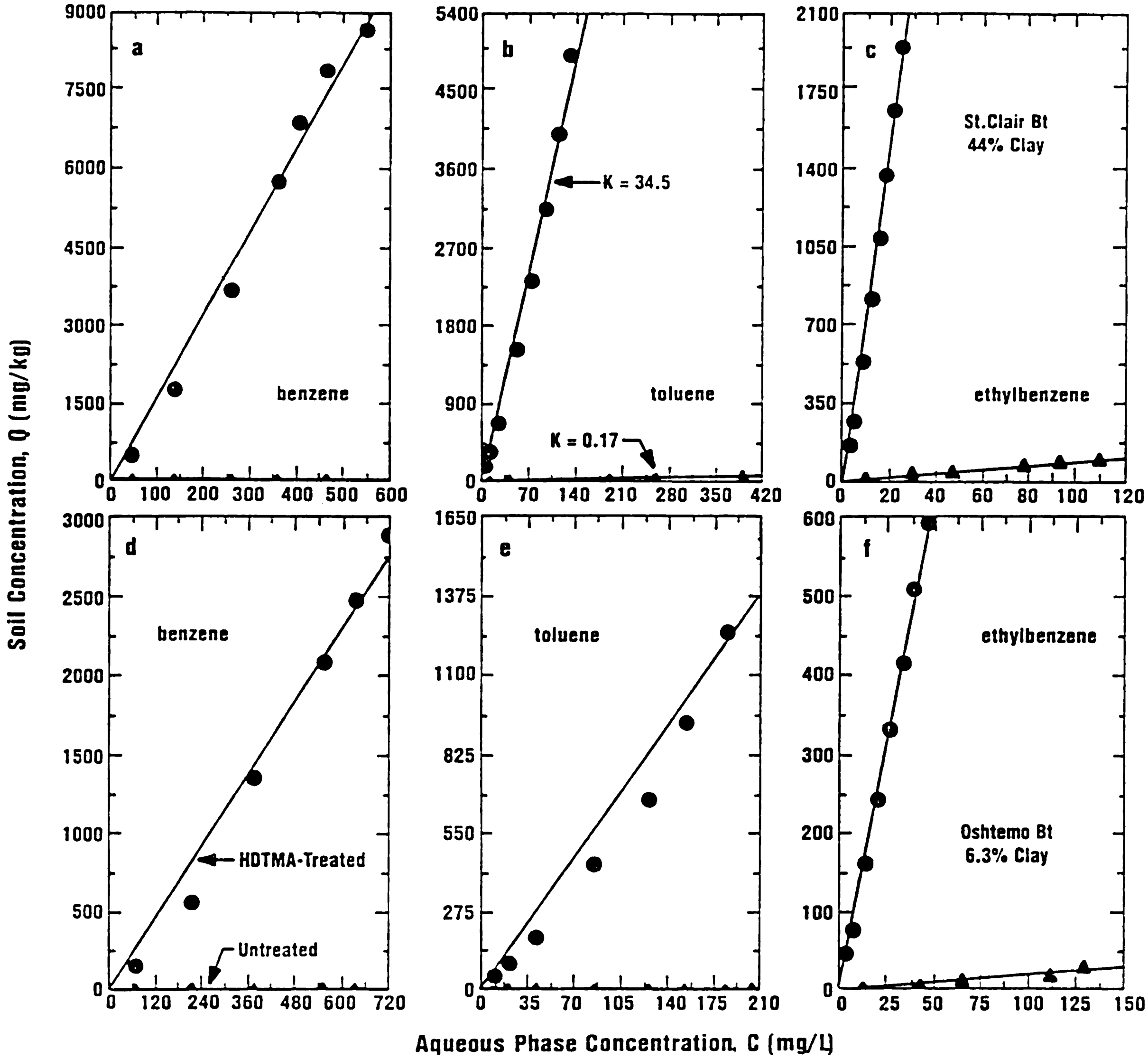


Figure 5.1 Enhanced sorption of common groundwater contaminants following treatment of soil with hexadecyltrimethylammonium. Sorption isotherms of benzene, toluene, and ethylbenzene from water by untreated and treated St. Clair (a-c) and Oshtemo (d-f) Bt horizon soils are shown. Reproduced from Lee *et al.* (*1989a*).

Boyd, 1990, 1991b; Kukkadapu and Boyd, 1995). The sorption is characterized by Langmuir-type isotherms, indicating surface adsorption as the primary retention mechanism (*Jaynes and Boyd, 1991b*). These clays are commonly referred to as "adsorptive organoclays" (*Boyd et al., 1991*). The fact that the amount of NOC adsorbed by TMPA-smectite was directly proportional to the surface area of the organoclay but inversely proportional to the layer charge of the clay or its organic carbon content (*Lee et al., 1990; Jaynes and Boyd, 1991b*) demonstrates that either direct interaction of sorbed NOCs with the exchangeable TMPA cations does not occur, or, additional mechanism(s) occur simultaneously (*Jaynes and Boyd, 1991b*). Jaynes and Boyd (*1991b*) proposed that in the presence of bulk water the primary adsorptive sites for aromatic hydrocarbons are the uncharged siloxane oxygens, and that small organic cations such as TMPA function primarily as pillars to prop open interlayers and satisfy the cation exchange capacity. The above interpretation is consistent with the arguments presented by others that uncharged siloxane surfaces in montmorillonites are hydrophobic, and that the hydrophilicity of untreated montmorillonites is mainly due to the strong hydration of exchangeable metal cations (*Prost, 1975; Sposito and Prost, 1982*). The neutral surfaces of natural clays are apparently obscured by water which hydrates the metal exchangeable cations. Replacing these highly hydrated metal cations with much less hydrated organic cations exposes the neutral surface between the organic exchange cations, leading to the adsorption of NOCs (*Jaynes and Boyd, 1991b*). In this model, the adsorptive organoclays are viewed as a porous adsorbent. The dimension of those micropores is fixed by the size of the QACs, the charge density of the clays and by the distribution of the QACs in the interlayer regions. This is important because the size of the micropores may impose certain steric constraints on organic contaminant adsorption (*Lee et al., 1989b, 1990*).

For short chain QACs, cation exchange is the singular adsorption mechanism. The distribution of the short chain QACs in the interlayers should correspond closely to the distribution of negatively-charged sites. Due to the heterogeneity of layer charge distribution, the distribution of QACs such as TMPA in interlayers of smectite will be heterogeneous. This manifests different pore sizes within a given adsorptive organosmectite (*Sheng et al., 199_*). The heterogeneity of pore sizes influences the sorption of organic contaminants of different molecular dimensions. For example, among benzene and several alkylbenzenes, benzene can be adsorbed inside both small and large micropores of TMPA-smectite, manifesting the largest sorption capacity among the solutes and the most heterogeneous distribution of adsorption energies. In contrast, larger molecules like propylbenzene can be adsorbed only in the larger pores. As a result, the sorption capacity of organosmectite for propylbenzene is only 23% of that for benzene (*Sheng et al., 199_*). In addition, the sterically restricted adsorption of propylbenzene resulted in a more narrow distribution of adsorption energies. This explains the observation that the adsorption isotherm of benzene does not exactly fit the Langmuir equation, which assumes a uniform adsorption energy, while that of propylbenzene does.

The above discussion has focused on organoclays in which the clay is completely saturated with short chain QACs. There may be instances where the clay is only partially saturated with QACs because the last 10-20% of the exchange sites on layer silicates such as montmorillonite have comparatively low affinities for QACs (*Xu and Boyd, 1995a*). It has been demonstrated that adsorption capacity of TMPA-smectite for benzene, alkylbenzenes and TCE increases dramatically with the fraction of exchange sites occupied by TMPA until loading reaches 65%-75% of the CEC (*Sheng, 1996*). Further increases of TMPA loading beyond this level actually decreases the adsorption capacity of the organoclays.

Replacing the inorganic exchangeable cations of clays with long chain organic cations such as HDTMA results in an organoclay with fundamentally different sorptive properties than adsorptive organoclays (*Boyd et al., 1988 a,b, 1991; Jaynes and Boyd, 1991a; Lee et al., 1989a*). Sorption of NOCs from water by these organoclays manifests type III (concave) or double-sigmoid isotherms (Figure 5.2), suggesting different mechanisms may be responsible for sorption of NOCs. These organoclays are commonly referred to as organophilic clays. In organophilic clays, the large organic moieties (e.g. C-16 alkyl moieties of HDTMA) fixed on the mineral surface interact to form an organic phase. For HDTMA modified clay, the micropolarity sensed by a fluorescent probe, pyrene, decreased as HDTMA loading increased, suggesting that modification resulted in the formation of an organic phase much less polar than the untreated clay surface (*Brahimi et al., 1992; Kalyanasundaram and Thomas, 1977*).

The hydrophobic phase of such clays functions as a powerful partition medium for NOC sorption. Compared to linear isotherms for natural soil organic matter (Figure 5.2), Type III isotherms result from the high sorption ability of the hydrophobic phase for NOCs. In these organoclays, the weight of the sorbed compound, e.g. chlorobenzene, may exceed that of the HDTMA phase itself (Figure 5.2). The presence of such high amounts of a sorbed NOC increases the solvency of the hydrophobic phase for the NOC, which in turn manifests a Type III isotherm.

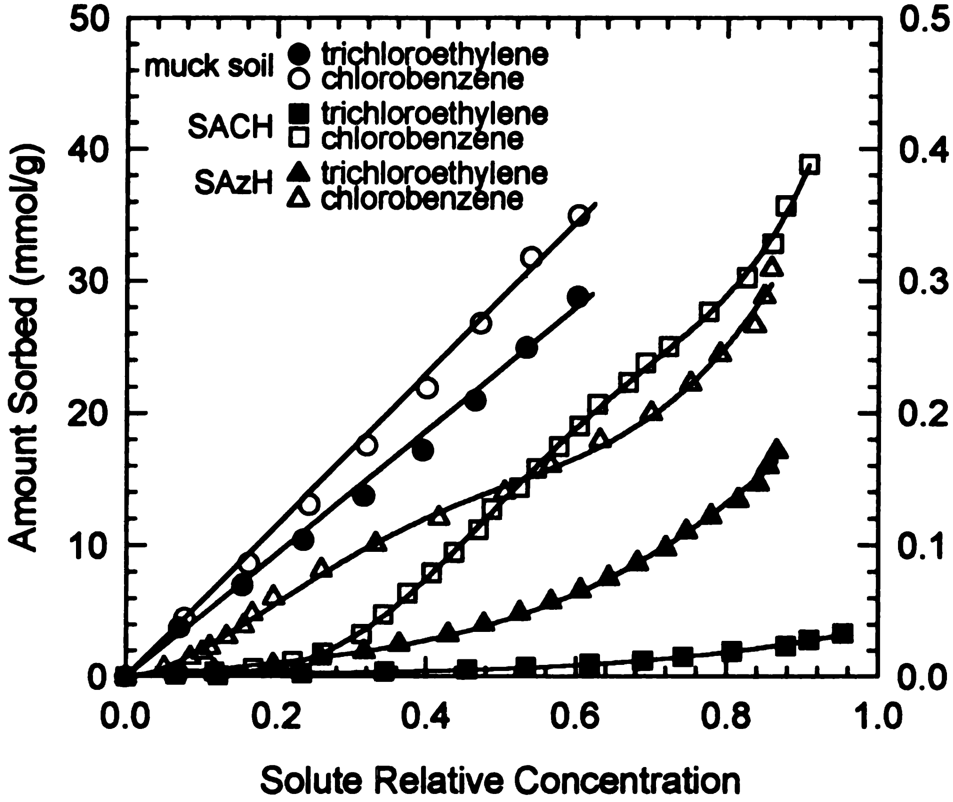
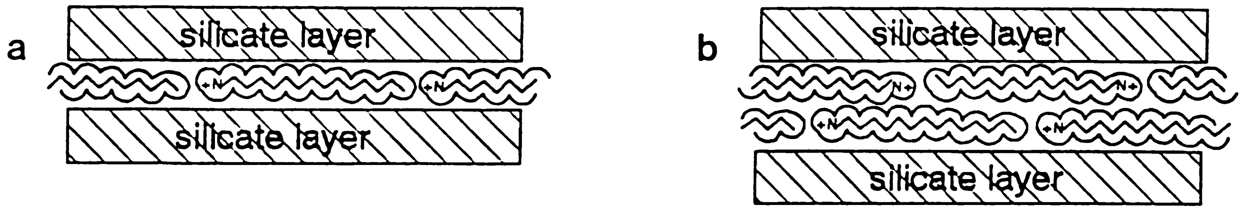


Figure 5.2 Type III isotherms for trichloroethylene and double-sigmoid isotherms for chlorobenzene sorption by low-charge hexadecyltrimethylammonium (HDTMA)-smectite (SACH) and high-charge HDTMA-smectite (SAzH), compared to the linear isotherms for trichloroethylene and chlorobenzene sorption by a muck soil. Data from Sheng *et al.* (1996a)

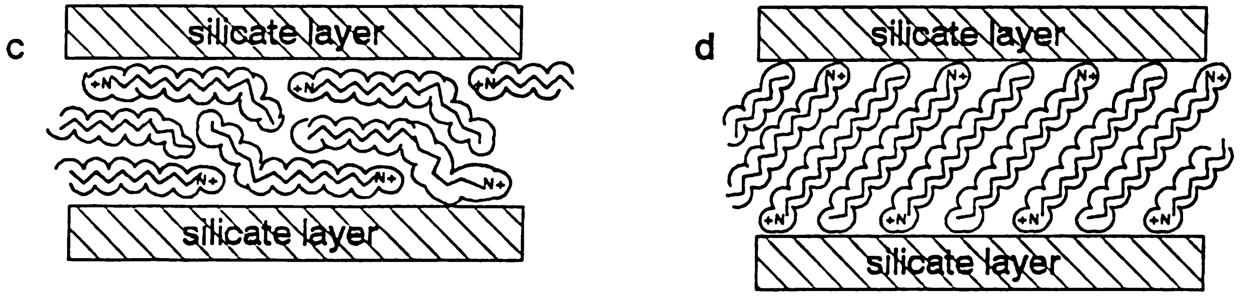
The function of the hydrophobic phase also depends on the arrangement of organic cations in the interlayers of clay, which in turn, depends on the charge density of the clay. For vermiculite, long chain QACs such as HDTMA adopt a vertical arrangement as illustrated in

Figure 5.3 (paraffin type). The tails of adsorbed HDTMA are highly flexible and the hydrophobic phase functions as a solubilizing medium for NOCs analogous to a bulk organic solvent. Solute partitioning has been suggested as a major HOC sorption mechanism for this type of organophilic clays, based on the observation of linear sorption isotherms. Our careful study using organoclay synthesized from both non-swelling and swelling 2:1 clay minerals with different layer charges demonstrates that double sigmoid adsorption isotherms are commonly observed for organophilic clays (Figure 5.2). The double sigmoid isotherms can be explained by combination of two sorption mechanisms, which are related to the arrangement of QACs in the interlayer region (*Sheng et al., 1996a*). In low charge smectites, HDTMA forms a flat-lying bilayer in the interlayers. The tails of the adsorbed HDTMA interact strongly with the mineral surfaces and with each other. The hydrophobic phases are relatively rigid and differ in this regard from a free solvent phase. As a result, NOC sorption at low relative solute concentrations (aqueous concentration/water solubility) is mainly due to the solvation of the adsorbed HDTMA and the mineral surfaces. Inserting organic contaminants between the hydrophobic "tails" of adsorbed HDTMA and the mineral surfaces is enhanced as solution concentrations increase. Ultimately, this results in detachment of the tails from surfaces and increases the d-spacing of the organoclay. As tails become more flexible, a more continuous solvent-like hydrophobic phase forms in the interlayer, and partitioning becomes a predominant sorption mechanism. The solvation and swelling is more easily achieved in high-charge smectite (e.g. SAz-1), in which the HDTMA tails adopt a pseudotrimolecular arrangement, manifesting weaker surface-tail interactions. Thus, the NOC sorption isotherm for HDTMA-SAz-1 is more linear at low relative concentration than that



Monolayer
Δ ~ 4.1 Å

Bilayer
Δ ~ 8.1 Å



Pseudotrimolectular Layer
Δ ~ 12.1 Å

Paraffin Complex
Δ > 12.4 Å

Figure 5.3 Possible interlayer arrangements of hexadecyltrimethylammonium and corresponding interlayer spacings (Δ). Reproduced from Jaynes and Boyd (*1991a*).

for HDTMA-SWy-1.

The sorptive characteristics of organoclays in single organic solute systems may be different from those in multi-solute systems, the latter being more representative of actual contaminated sites. These differences may arise, for example, if sorption of one solute causes interlayer expansion, or a change in the solvency of organic phase in the interlayers. We found the sorption of one contaminant may have synergistic or antagonistic effect on the sorption of another, depending on the nature of the co-solute (*Sheng et al., 1996b*). For example, the sorption of trichloroethylene (TCE) by HDTMA-modified smectites is much lower in a single solute system than that in the presence of other solutes such as nitrobenzene and carbon tetrachloride. Similarly, the presence of TCE increased the sorption of nitrobenzeneand carbon tetrachloride. In contrast, the presence of ethyl ether decreased the sorption of TCE by HDTMA-smectites. The synergistic effects occur because the cosolute caused interlayer expansion and/or increased solvency of the sorptive phase for the primary solute. Depending on the nature of the cosolute, the solvency of the sorptive phase may also decrease, as in the case of ethyl ether, causing an antagonistic effect. However, sorption of most common NOCs should cause an increase in the solvency of the sorptive phase of organophilic clays (e.g. HDTMA-smectite) and hence produce a synergistic, rather than antagonistic, effect on contaminant removal from water.

Application of organoclays to pollution abatement

Based on the thorough understanding of the sorptive properties, organoclays may be effectively used in pollution abatement.

Formation of organoclays involves the use of surfactants. Cationic surfactants such as QACs are combined with layer aluminosilicate clay minerals to form organoclay. The resultant organoclays have greatly enhanced sorptive capabilities for a variety of organic contaminants and are able to immobilize hydrophobic organic contaminants dissolved in water. In a similar application, anion surfactants such as sodium dodecyl sulfate (SDS) are used to replace the native exchangeable anions on iron and aluminum oxides (*Park and Jaffé, 1993, 1995*). SDS adsorbed on oxide surfaces forms hemimicelles (*Fuerstenau, 1970*) that substantially enhance the capability of oxides to sorb hydrophobic organic compounds from water via partitioning into the hemimicelles. The primary application of such modified oxides is water treatment. An interesting point is that some iron oxides (e.g. magnetite and maghemite) are magnetic and thus SDS-treated iron oxides can be separated from water or soil suspension with magnets (*Park and Jaffé, 1995*).

Different organic cations such as quaternary ammonium- (*Boyd et al. 1988b, 1991*), phosphonium- (*Kukkadapu and Boyd, 1995*), and alkylpyridinium- (*Wagner et al., 1994*) compounds may be used to produce organoclays. The resultant organoclays can have vastly improved and unique sorptive properties towards organic contaminants, depending on the nature of both organic cations and the types of layer silicates used. Importantly, organoclays have potential of being used both *ex-situ* and *in-situ*. For example, organoclays can be used in place of or in conjunction with activated carbon for water purification (*Beall, 1985*).

Contaminant transport in soils is usually dependent on the extent of contaminant sorption and the hydraulic conductivity of the soil. The hydraulic conductivity may, however, be sufficiently low in landfill barriers such as clay liners and bentonite slurry walls, that molecular diffusion of contaminants becomes a dominant transport mechanism. Addition of organoclays to landfill barriers will retard the mobility of contaminants through landfill barriers by greatly enhancing the extent of contaminant sorption. The inclusion of Na-bentonite in such barriers is needed because they form highly dispensed particles in water. These small particles fill voids in the liner material (e.g. soil) and effectively reduce hydraulic conductivity.

Gullick *et al.* (*1995*) used the following one-dimensional contaminant transport model under steady-state, uniform flow with equilibrium sorption in saturated, homogeneous, isotropic landfill barriers (*Weber et al., 1991*) to predict the effect of TMPA-bentonite addition to landfill barriers on contaminant transport:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \rho_s \frac{(1-\epsilon)}{\epsilon} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} \qquad [5.1]$$

where: C = contaminant concentration;

D_h = coefficient of hydrodynamic dispersion;

v_x = average linear groundwater velocity;

ρ_s = density of landfill barriers;

q = sorbed concentration;

ϵ = porosity of landfill barriers;

x = distance in the x direction;

and t = time.

The third term on the right side of the above equation describes the effect of sorption on contaminant transport in landfill barriers. Figure 5.4 shows the model predictions, under given

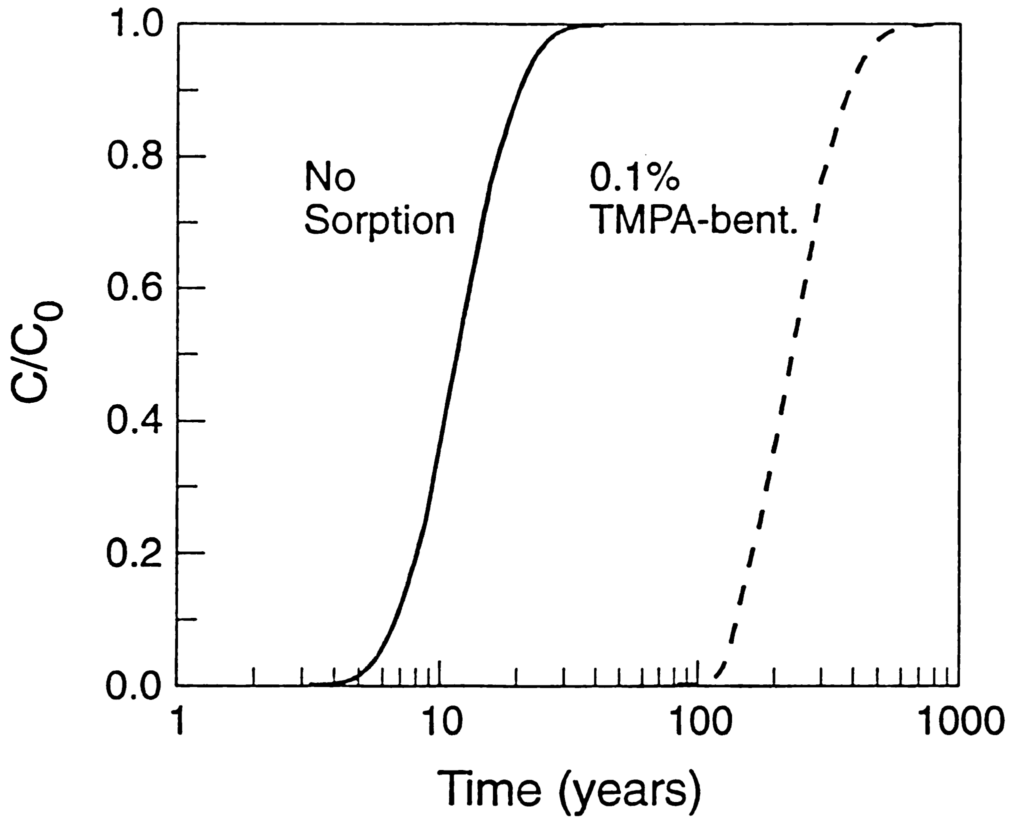


Figure 5.4 Simulated transport of 1,2,4-trichlorobenzene through bentonite liners with and without 0.1% trimethylphenyl (TMPA)-bentonite added. Conditions: $K_c = 10^{-7}$ cm/sec, dh/dl = 1, $D_e = 2.26 \times 10^{-6}$ cm^2/sec, $\epsilon = 0.40$, $\rho_b = 1.60$ g/cm^3, x = 1m, $C_0 = 5000$ µg/l, Freundlich adsorption parameters $K_f = 22.67$ and n = 0.808. Reproduced from Gullick *et al.* (*1995*).

conditions, of transport of 1,2,4-trichlorobenzene through landfill barriers with and without addition of TMPA-bentonite. The addition of 0.1% TMPA-bentonite to landfill barriers reduces 1,2,4-trichlorobenzene transport by tens of times. Smith and Jaffé(*1994*) evaluated benzene transport through landfill liners containing organo-bentonites. In this study, Ottawa sand (88%) was amended with untreated Wyoming bentonite (8%) (primarily Na-bentonite) and either 4% untreated bentonite or 4% organobentonite. The mixtures were compacted to simulate sand-bentonite landfill liners. Hydraulic conductivities of the organobentonite composite liners were low, all on the order of 10^{-8} cm/sec. A one-dimensional solute transport model was used to simulate benzene transport in conventional sand-bentonite liners and in liners containing two sorptive organo-bentonites, namely HDTMA-bentonite and benzyltrimethylammonium (BTMA)-bentonite. The addition of the organobentonites substantially delayed maximum benzene breakthrough from about four years in the conventional liner to about 275 years in the organo-bentonite amended liners (Figure 5.5).

Perhaps the most unique feature and important advantage of this chemistry is that it can be applied *in-situ*. Subsoils and aquifer materials contain negatively charged clay minerals and hence possess a cation exchange capacity (CEC). In earlier research, Boyd *et al.* demonstrated that sorption of common organic groundwater contaminants by aquifer materials or soils can be increased by at least two orders of magnitude by using cationic surfactants to convert soil clays into sorptive organoclays (*Boyd et al., 1988a, 1991; Lee et al., 1989*). These results suggested the possibility that aquifer materials or subsoils could be modified *in-situ* via injections of cationic surfactant solutions, and the modified soil materials could function as "sorptive zones." Such sorptive zones, if properly placed, could intercept

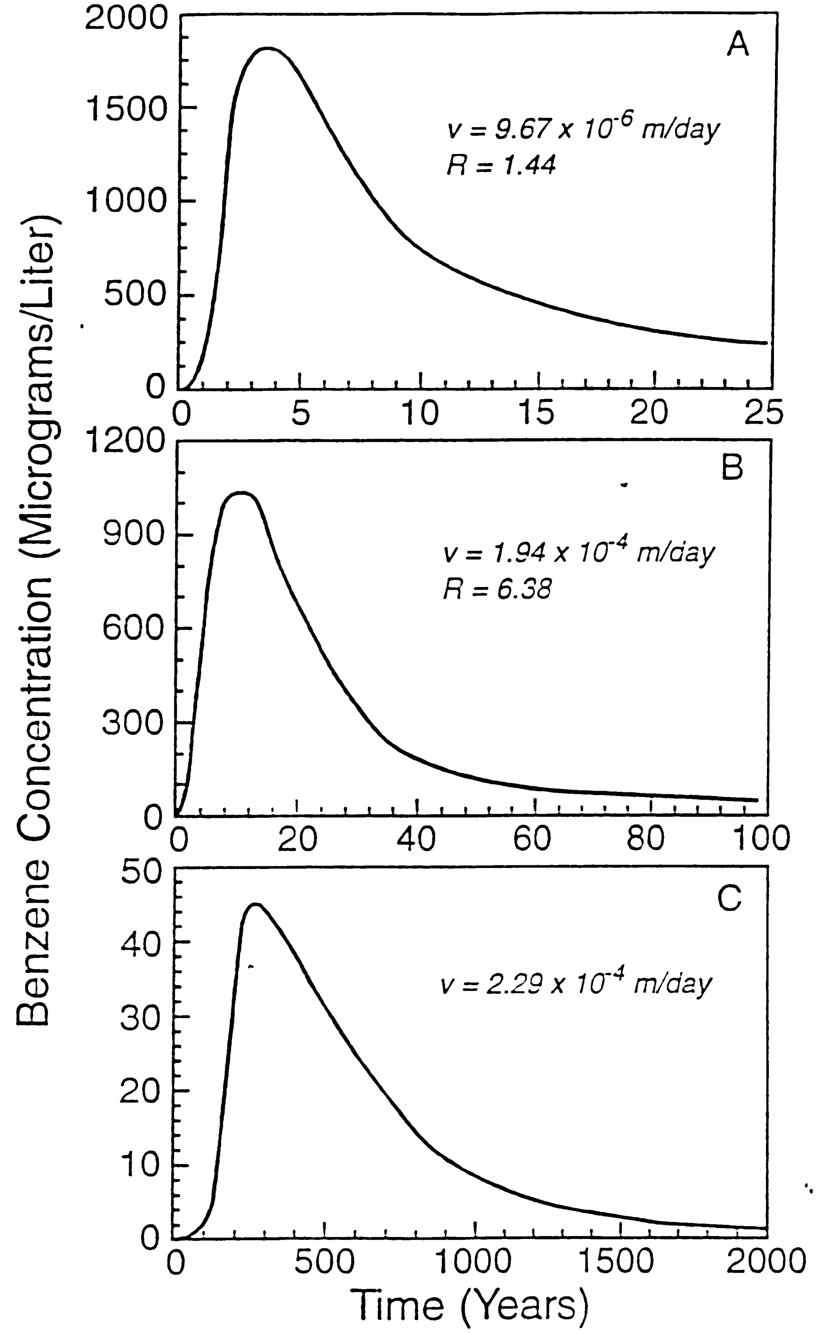


Figure 5.5 Benzene transport through landfill liners containing organophilic bentonite: (A) 88% sand and 12% Na-bentonite; (B) 88% sand, 8% Na-bentonite and 4% hexadecyltrimethyl-ammonium-bentonite; and (C) 88% sand, 8% Na-bentonite and 4% benzyltrimethylammonium-bentonite. R is the retardation factor, v is the linear velocity. Reproduced from Smith and Jaffé (*1994*).

and immobilize contaminant plumes containing dissolved organic chemicals as shown schematically in Figure 5.6. The immobilized contaminants could then be detoxified by various chemical or biological means, as for example through bioremediation using native microbial populations or introduced organisms. Containing contaminant migration in this fashion has the important advantages of preventing further downgradient aquifer contamination, and of concentrating contaminants in a defined zone that can be managed to enhance remediation. For example, in the case of bioremediation, nutrients and/or oxygen could be added to stimulate microbial activity.

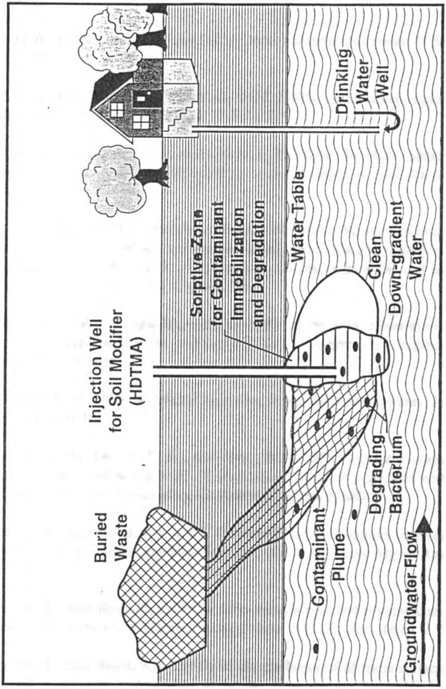


Figure 5.6 Proposed *in-situ* modification of aquifer material to create contaminant sorption zone, and coupled sorption and biodegradation of organic contaminants for groundwater cleanup.

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