

POLARITY EFFECT ON DICHLOROBENZENE SORPTION BY HEXADECYLTRIMETHYLAMMONIUM-EXCHANGED CLAYS

GUANGYAO SHENG AND STEPHEN A. BOYD

Department of Crop and Soil Sciences, Michigan State University, East Lansing, Michigan 48824, USA

Abstract—Sorptive properties of organoclays may be greatly influenced by the physicochemical properties of organic sorbates. Hexadecyltrimethylammonium(HDTMA) clays were prepared using a high-charge smectite (HDTMA-SAz-1), a low-charge smectite (HDTMA-SWy-2), and an illite (HDTMA-ILL). The resultant organoclays were used to sorb aqueous phase 1,2-dichlorobenzene (*o*-DCB), 1,3-dichlorobenzene (*m*-DCB), and 1,4-dichlorobenzene (*p*-DCB). Sorptive characteristics of these compounds were determined by their molecular polarities (*o*-DCB > *m*-DCB > *p*-DCB) and the HDTMA-clay interlayer distance. HDTMA-ILL was used for comparison to HDTMA-SAz-1 and HDTMA-SWy-2. All dichlorobenzene isomers were directly intercalated in the interlayers of HDTMA-SAz-1, causing interlayer expansion. *o*-DCB and *m*-DCB were not intercalated in the interlayers of HDTMA-SWy-2 at low concentrations, but intercalation occurred at higher concentrations, which caused interlayer expansion. The concentration needed to produce interlayer expansion depended on the solute molecular polarity, hence a higher concentration of *m*-DCB than *o*-DCB was required. *p*-DCB was sorbed primarily by the HDTMA phase on the external surfaces of HDTMA-SWy-2. In the presence of chlorobenzene (CB), *p*-DCB sorption by HDTMA-SWy-2 is greatly enhanced, owing to the interlayer expansion by CB and a cosolvent effect. Sorption of *o*-DCB resulted from both direct solvation-type interactions with HDTMA and partitioning into HDTMA. Such sorption results in double-sigmoid isotherms. *m*-DCB weakly solvates the HDTMA and partitions into the HDTMA, displaying either a double-sigmoid or a type-III isotherm depending on clay type. *p*-DCB lacks ability to solvate HDTMA and partitions into HDTMA as its sole mechanism, producing type-III isotherms. HDTMA-clays are potentially effective for treating dichlorobenzene-contaminated wastewater.

Key Words—CMS Clay SAz-1, CMS Clay SWy-2, Dichlorobenzene, HDTMA, Organoclay, Polarity, Sorption.

INTRODUCTION

The impressive sorptive capabilities of organoclays makes them potentially useful in a variety of environmental applications and technologies (Beall, 1985; Harper and Purnell, 1990; Boyd *et al.*, 1991; Brixie and Boyd, 1994; Smith and Jaffe, 1994; Wagner *et al.*, 1994; Gullick *et al.*, 1996; Li *et al.*, 1996; Xu *et al.*, 1997). Examples of applications include: as extenders for activated carbons for water treatment (Beall, 1985), as components of clay barriers to immobilize dissolved organic contaminants and to prevent hydraulic failure of the barrier when exposed to concentrated or pure organic liquids (Smith and Jaffe, 1994; Li *et al.*, 1996; Gullick *et al.*, 1996), and as adsorbents for airborne organic contaminants (Harper and Purnell, 1990). The high stability and sorptive capabilities of organoclays also suggest uses in management and remediation of contaminant plumes in the subsurface. Sorbent zones could be created *in situ* by injecting solutions of organic cations to convert aquifer clays to organoclays. With proper placement, these sorbent zones could intercept and immobilize advancing contaminant plumes (Boyd *et al.*, 1988a; Lee *et al.*, 1989a; Burris and Anth, 1992; Xu *et al.*, 1997; Sheng *et al.*, 1998; Rakhshandehroo *et al.*, 1998). Coupled with *in situ* biodegradation (Nye *et al.*, 1994; Crocker *et al.*, 1995) or recovery of trapped contaminants (Hayworth and Bur-

ris, 1997), this technology could ultimately remediate contaminated groundwaters.

Organoclays are formed by the replacement of native inorganic exchangeable cations with organic cations of various forms. The most commonly used organic cations are quaternary ammonium cations (QACs) of the form $[(\text{CH}_3)_3\text{NR}]^+$ or $[(\text{CH}_3)_2\text{NR}_2]^+$, where R is either an alkyl or aromatic-hydrocarbon group. QACs are commercially available at reasonable costs, have high affinities for clay surfaces (selectivity coefficients up to 10^9), and the resultant organoclays are chemically stable (Xu and Boyd, 1995a, 1995b; Xu *et al.*, 1997). QACs also have much lower hydration energies compared to inorganic cations (Lee *et al.*, 1989b; Kukkadapu and Boyd, 1995). The high sorptive capability of organoclays is a manifestation of several mechanisms that may operate depending on the nature of the QAC and the clay. These mechanisms include solute interactions with the siloxane surfaces, which are revealed owing to the lack of cation hydration, and with the organic phases derived from the exchanged QACs (Boyd *et al.*, 1988b; Jaynes and Boyd, 1991a, 1991b; Sheng *et al.*, 1996a).

Slabaugh and Hiltner (1968) proposed a two-step mechanism in the swelling of alkylammonium-exchanged montmorillonites by sorbates possessing both polar and nonpolar moieties, or by mixtures of polar

Table 1. Properties of clays and derived HDTMA clays.

Clay	Mineralogy	CEC (cmol/kg)	HDTMA clay	
			HDTMA %	Basal spacing (Å)
SAz-1	high-charge montmorillonite	125	29.3	22.9
SWy-2	low-charge montmorillonite	90	20.9	18.5
ILL	illite	22.4	4.82	10.0

and nonpolar organics: adsorption of polar groups onto the silicate surfaces leading to displacement of the alkylammonium chains from the surfaces, and solvation of the alkyl chains by nonpolar species. In recent studies (Sheng *et al.*, 1996a, 1996b), we examined the sorption of the polar aromatic compounds chlorobenzene and nitrobenzene from water by hexadecyltrimethylammonium(HDTMA)-exchanged smectites. Based on supportive evidence, including sorption-dependent basal spacing variations and hexane-water partition behavior, we concluded that these solutes solvated the cationic centers leading to a more vertical orientation of the alkyl chains of HDTMA and an expansion of the interlayers; this may be accompanied by adsorption on the vacated mineral surfaces. Chlorobenzene and nitrobenzene molecules concurrently partitioned into the interlayer organic phases. The observed double-sigmoid isotherms resulted from a combination of the sigmoid isotherms owing to solvation-type interactions and the type-III isotherms owing to partitioning. In contrast, lack of HDTMA solvation by trichloroethylene or carbon tetrachloride was indicated by their inability to expand the interlayers of HDTMA-exchanged smectite. These solutes partitioned into the HDTMA-derived organic phase as a sole sorptive mechanism resulting in a type-III isotherm. Presence of trace quantities of nitrobenzene caused interlayer expansion of HDTMA-exchanged smectite, rendering the interlayers more accessible to trichloroethylene and producing greatly enhanced sorption.

In this study, we further examine the effect of solute polarity on sorption by utilizing the isomers of dichlorobenzene that display varying polarities depending on the positions of chlorine atoms on the aromatic ring. Sorption of 1,2-dichlorobenzene (*o*-DCB), 1,3-dichlorobenzene (*m*-DCB) and 1,4-dichlorobenzene (*p*-DCB) from water by HDTMA clays, and sorption-dependent basal spacing variations, were measured. Homoionic HDTMA clays derived from both high-charge and low-charge smectites, and illite, were examined to evaluate the effect of interlayer spacing on sorption.

EXPERIMENTAL

HDTMA clays

The clays used in this study are a low-charge smectite (SWy-2), a high-charge smectite (SAz-1), and an

Table 2. Structures and physicochemical properties of dichlorobenzene isomers.

Chemical	Water solubility ¹ (mg/L, 25°C)	log K_{ow} ¹	Dipole moment ² (Debye)
1,2-dichlorobenzene	156	3.43	2.27
1,3-dichlorobenzene	125	3.53	1.48
1,4-dichlorobenzene	76	3.44	0

¹ Howard and Meylan, 1997.

² Gould, 1959.

illite (ILL). Both SWy-2 and SAz-1 were obtained from the Source Clays Repository, The Clay Minerals Society, Columbia, Missouri, and ILL is from Fithia, Illinois. The <2- μ m clay fractions were obtained by wet sedimentation. HDTMA bromide (Aldrich Chemical Company, Milwaukee, Wisconsin) was dissolved in warm distilled water and was used to prepare HDTMA clays. Clay suspensions containing 25 g of clay were treated by adding HDTMA-bromide solution (0.03 mol/L) in an amount approximately equal to the cation-exchange capacity (CEC) of the clay (90 cmol/kg for SWy-2, 125 cmol/kg for SAz-1, and 22.4 cmol/kg for ILL). The mixtures were agitated overnight on a magnetic stirrer at room temperature. The HDTMA-clay suspensions were then washed with distilled water repeatedly until free of bromide ions as indicated by $AgNO_3$. These HDTMA clays were subsequently quick-frozen, freeze-dried, and stored in bottles for later use. Organic carbon (OC) contents of the HDTMA clays were determined using a Dohrmann DC-190 high temperature OC analyzer (Rosemount Analytical Inc., Santa Clara, California). The OC contents were subsequently converted to HDTMA contents by multiplying OC contents by a factor of 1.246 based on the molecular formula of HDTMA. Properties of clays and derived HDTMA clays are listed in Table 1.

Sorption isotherms

Chlorobenzene (CB), *o*-DCB, *m*-DCB, and *p*-DCB (purity >98%) were purchased from Aldrich Chemical Company and used without further purification. Physicochemical properties of *o*-DCB, *m*-DCB, and *p*-DCB are given in Table 2. Sorption of these chemicals by HDTMA clays was measured using a batch-equilibration technique. A weight of 0.1 g of HDTMA-exchanged SWy-2 (HDTMA-SWy-2), 0.1 g of HDTMA-exchanged SAz-1 (HDTMA-SAz-1), or 0.4 g of HDTMA-exchanged ILL (HDTMA-ILL) and 25 mL of distilled water were placed in Corex glass centrifuge tubes. Between 1–45 μ L of *o*-DCB or *m*-DCB were delivered directly into the tubes as the neat liquid using a Hamilton microsyringe to produce a range of initial and final concentrations. *p*-DCB was dissolved in acetone (226.6 mg/mL) and delivered into the tubes. No changes in $d(001)$ -values of organoclays were ob-

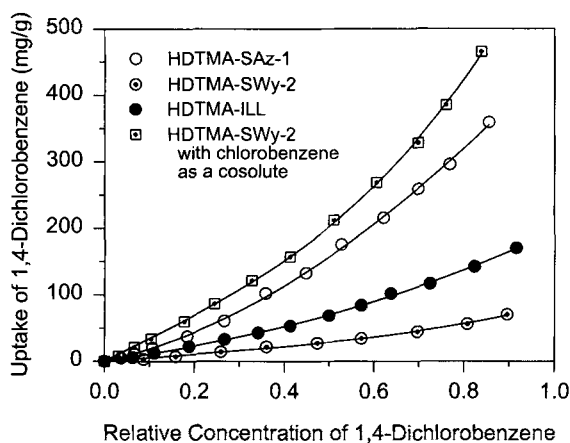


Figure 1. Sorption isotherms of 1,4-dichlorobenzene on HDTMA-saturated high-charge smectite (HDTMA-SAz-1), low-charge smectite (HDTMA-SWy-2), illite (HDTMA-ILL), and sorption isotherm of 1,4-dichlorobenzene on HDTMA-SWy-2 in the presence of chlorobenzene as a cosolute.

served when only acetone was delivered. The tubes were capped with teflon-backed septa immediately after solute delivery and placed on a rotator for 24 h at room temperature. Preliminary experiments showed that sorption reached equilibrium within 18 h. After equilibration, the tubes were centrifuged at 7649 g for 10 min to separate liquid and solid phases. A volume of 5 mL of supernatant was extracted with 5 mL of carbon disulfide in a glass vial.

Analysis of *o*-DCB, *m*-DCB, and *p*-DCB in the carbon-disulfide extracts was conducted using 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 and compared to external standards to determine the solute concentrations. Solute recovery in blanks not containing organoclays was >98%. The amount of solute sorbed was calculated from the difference between the amount added and that remaining in the equilibrium solution.

Sorption of *p*-DCB in the presence of CB was performed by adding 20 μ L of neat CB into the tubes containing 0.1 g of HDTMA-SWy-2 and 25 mL of distilled water. Immediately after addition of CB, *p*-DCB was delivered into the tubes and the experiments were continued following the procedure described above. The aqueous-phase equilibrium concentrations of both CB and *p*-DCB were analyzed by gas chromatography.

X-ray diffraction (XRD)

Basal spacings of HDTMA clays were determined by XRD analysis. For HDTMA-SWy-2 and HDTMA-SAz-1 with *o*-DCB or *p*-DCB sorbed, and HDTMA-SWy-2 with *p*-DCB sorbed in the presence of CB,

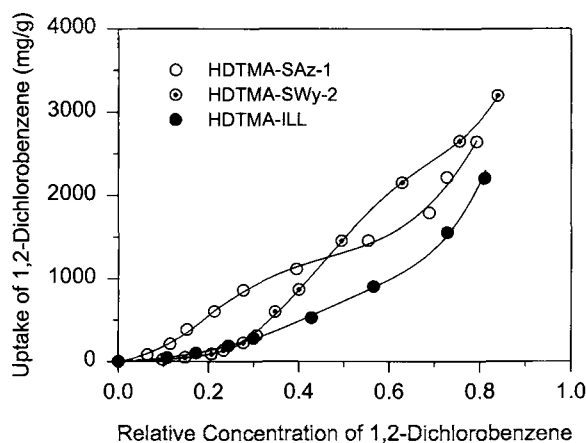


Figure 2. Sorption isotherms of 1,2-dichlorobenzene on HDTMA-saturated high-charge smectite (HDTMA-SAz-1), low-charge smectite (HDTMA-SWy-2), and illite (HDTMA-ILL).

HDTMA-clay suspensions were dropped on glass slides and immediately covered by teflon tape to prevent solute loss through vaporization. XRD patterns were recorded using $CuK\alpha$ radiation and a Philips APD3720 automated X-ray diffractometer (Mahwah, New Jersey) with an APD3521 goniometer equipped with a θ -compensating slit, a 0.2-mm receiving slit, and a diffracted-beam graphite monochromator, from 2 to 12 $^{\circ}2\theta$, in steps of 0.02 $^{\circ}2\theta$, 2 s/step.

RESULTS

SAz-1 has a higher cation-exchange capacity (CEC) than SWy-2 (Table 1), which resulted in a higher HDTMA content and a larger basal spacing in HDTMA-SAz-1 than in HDTMA-SWy-2. Owing to the collapsed interlayers of ILL, the basal spacing remained unchanged (10.0 \AA) following HDTMA treatment, and the HDTMA content of HDTMA-ILL was much lower than that of either of the HDTMA-exchange smectites. In this organoclay, HDTMA was not intercalated but instead confined to the external surfaces of the clay. Calculations based on the HDTMA contents showed that nearly 100% of the CEC sites in these clays were occupied by HDTMA.

Sorption isotherms of *p*-DCB, *o*-DCB, and *m*-DCB by HDTMA-SAz-1, HDTMA-SWy-2, and HDTMA-ILL are shown in Figures 1–3. To permit direct comparison, uptake of these solutes was normalized to the HDTMA content of the corresponding organoclay (mg/g HDTMA), and the equilibrium concentration is expressed in relative concentration (C_e/S_w , where C_e is the equilibrium concentration and S_w is the solute-water solubility). Generally, sorption of dichlorobenzene isomers by the same HDTMA clay increases in the order *p*-DCB < *m*-DCB < *o*-DCB.

Sorption of *p*-DCB by the HDTMA clays was characterized by type-III isotherms, which are convex to

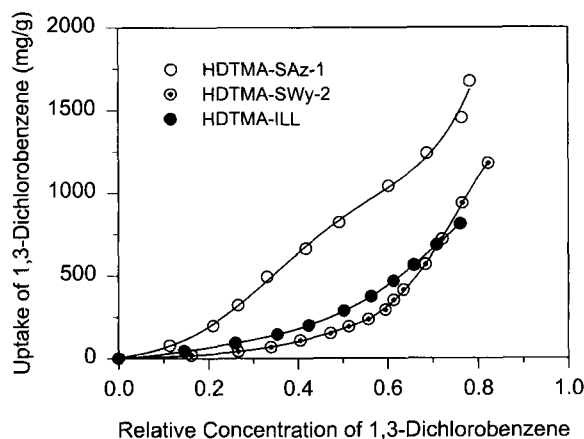


Figure 3. Sorption isotherms of 1,3-dichlorobenzene on HDTMA-saturated high-charge smectite (HDTMA-SAZ-1), low-charge smectite (HDTMA-SWy-2), and illite (HDTMA-ILL).

the abscissa commencing at the origin (Figure 1). *p*-DCB showed much higher sorption by HDTMA-SAZ-1 than by HDTMA-ILL, whereas its sorption by HDTMA-SWy-2 was somewhat lower than that by HDTMA-ILL. Linear regression for the low concentration portion of the isotherms ($C_e/S_w < 0.21$) showed that the log of the HDTMA-water distribution coefficient of *p*-DCB was 2.75 for HDTMA-SWy-2 and 3.18 for HDTMA-ILL. *p*-DCB sorption by HDTMA-SWy-2 was greatly enhanced by the presence of CB as a cosolute (Figure 1). With CB added, sorption of *p*-DCB by HDTMA-SWy-2 was higher than that by HDTMA-SAZ-1 in a system not containing CB.

Sorption of *o*-DCB by HDTMA clays displayed double-sigmoid isotherms (Figure 2), although the extent to which the double-sigmoid shape appeared for HDTMA-ILL was much less pronounced than for HDTMA-smectites. Sorption of *o*-DCB (per unit mass of HDTMA) by HDTMA-SAZ-1 was much higher than that by HDTMA-ILL over the entire range of concentrations. Sorption of *o*-DCB by HDTMA-SWy-2 at low concentrations was slightly lower than that by HDTMA-ILL. Linear regression for the low concentration portion of isotherms ($C_e/S_w < 0.21$) showed that the log value of the HDTMA-water distribution coefficient of *o*-DCB was 3.38 for HDTMA-SWy-2 compared to 3.54 for HDTMA-ILL. Sorption increased sharply at *o*-DCB relative concentrations of ~ 0.25 and above.

Sorption of *m*-DCB by HDTMA-SAZ-1 was characterized by a double-sigmoid isotherm (Figure 3). The amount of *m*-DCB sorbed (per unit mass of HDTMA) by HDTMA-SAZ-1 was higher than that by HDTMA-ILL over the entire range of concentrations. Sorption of *m*-DCB by HDTMA-ILL did not display a double-sigmoid isotherm, but instead displayed a type-III isotherm. Similarly, sorption of *m*-DCB by

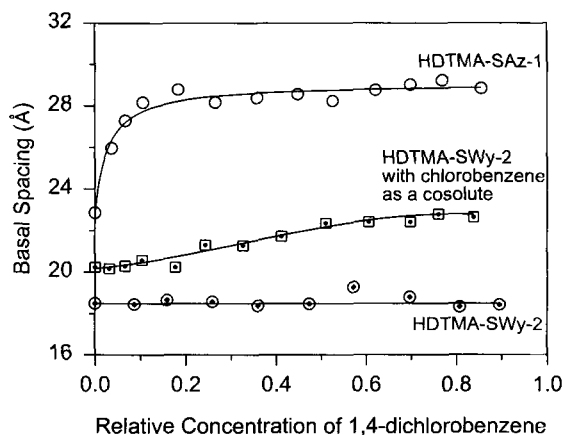


Figure 4. Basal-spacing variations in homoionic HDTMA high-charge smectite (HDTMA-SAZ-1) and low-charge smectite (HDTMA-SWy-2) owing to 1,4-dichlorobenzene sorption in the absence and presence of chlorobenzene as a cosolute.

HDTMA-SWy-2 initially displayed a type-III isotherm. Sorption of *m*-DCB increased with concentration gradually over the low and intermediate range of relative concentrations, and then more sharply at relative concentrations of ~ 0.58 and above. The amount sorbed (per unit mass of HDTMA) was consistently lower than that by HDTMA-ILL until the relative concentration reached ~ 0.73 , after which *m*-DCB sorption by HDTMA-SWy-2 exceeded that by HDTMA-ILL.

Sorption of *p*-DCB immediately expanded the interlayers of HDTMA-SAZ-1, whereas the basal spacing of HDTMA-SWy-2 remained constant over the entire range of concentrations (Figure 4). Interlayer expansion was not observed when either HDTMA-SWy-2 or HDTMA-SAZ-1 was dried and then redispersed in water. With addition of CB, the $d(001)$ of HDTMA-SWy-2 increased from ~ 18.5 to ~ 20.2 Å (in the absence of *p*-DCB). Sorption of *p*-DCB further expanded (by a maximum of ~ 2.5 Å) the interlayers of HDTMA-SWy-2.

Increases in basal spacings occurred for both HDTMA-SAZ-1 and HDTMA-SWy-2 as a result of *o*-DCB sorption (Figure 5). Sorption of *o*-DCB by HDTMA-SAZ-1 caused an immediate interlayer expansion. At low aqueous concentrations of *o*-DCB, the interlayers of HDTMA-SWy-2 did not expand following *o*-DCB sorption. Rather, the interlayers expanded only at *o*-DCB relative concentrations greater than ~ 0.25 .

DISCUSSION

HDTMA contents and basal spacings of organoclays are determined by the CEC values and related charge densities of the clays. This determines the HDTMA arrangements in the interlayers, and greatly influences the sorptive properties of organoclays (Solomon and Hawthorne, 1983). The low-charge

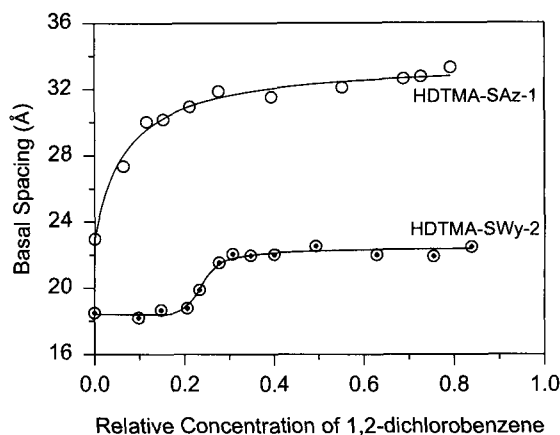


Figure 5. Basal-spacing variations in homoionic HDTMA high-charge smectite (HDTMA-SAz-1) and low-charge smectite (HDTMA-SWy-2) owing to 1,2-dichlorobenzene sorption.

HDTMA-SWy-2 formed a densely packed bilayer structure with a $d(001)$ -value of ~ 18.5 Å. The high-charge HDTMA-SAz-1 showed a $d(001)$ -value of ~ 22.9 Å, consistent with a pseudotrimolecular layer or interstratified mixtures of bilayers and paraffin complexes (Jaynes and Boyd, 1991b; Xu and Boyd, 1995a). For HDTMA-ILL, the $d(001)$ -value remained at 10 Å indicating that interlayer K was not exchangeable by HDTMA. The higher-unit surface-charge density of illite, greater than montmorillonite and similar to vermiculite, presumably resulted in more dense packing of HDTMA on these external surfaces, as compared to those of the smectites.

The physicochemical properties of dichlorobenzene isomers depend in part on the relative positions of chlorine atoms on the aromatic ring (Table 2). The water solubilities decrease in the order o -DCB $>$ m -DCB $>$ p -DCB, whereas the octanol-water partition coefficients (K_{ow}) are similar (Howard and Meylan, 1997). The relative positions of two Cl atoms strongly influence the polarities of the dichlorobenzene isomers. Another Cl atom at the *ortho*-position results in the high polarity of o -DCB, as indicated by the dipole moment (Table 2). m -DCB has an intermediate polarity, and the additional Cl atom at the *para*-position results in a dipole moment of zero for p -DCB. Although K_{ow} predicts similar partition interactions of the three dichlorobenzene isomers with HDTMA clays, their differing polarities appeared to show differences in overall uptake.

Sorption of nonpolar p -DCB by HDTMA clays produced type-III isotherms for all HDTMA clays (Figure 1). This suggests solute partitioning as the predominant sorptive mechanism. The type-III isotherms for p -DCB sorption are explained as an increase in solvency (*i.e.*, solubility parameter) of the HDTMA phases for p -DCB as a result of increasing p -DCB concen-

tration in the phase as sorption proceeds (Chiou *et al.*, 1992; Sheng *et al.*, 1996a, 1996b). The initial interlayer spacing of the high-charge HDTMA-SAz-1 was sufficiently large for the direct intercalation of p -DCB molecules in the interlayers, as indicated by the immediate interlayer expansion from ~ 23 to ~ 29 Å (Figure 4). The nonpolar p -DCB molecules did not cause an expansion of the interlayers of HDTMA-SWy-2. The lower extent of sorption of p -DCB by HDTMA-SWy-2 as compared to HDTMA-ILL (~ 2.5 times lower per unit mass of HDTMA) indicates that overall the HDTMA in HDTMA-SWy-2 was a less effective partition medium than that in HDTMA-ILL. This, and the lack of interlayer expansion, suggests that p -DCB sorption occurred largely on the external surfaces of HDTMA-SWy-2. In contrast, the HDTMA in HDTMA-SAz-1 was a more effective partition medium than that in HDTMA-ILL.

The double-sigmoid isotherms for o -DCB sorption by HDTMA clays (Figure 2) indicates both solvation and partition interactions, similar to those described previously for CB sorption by HDTMA clays (Sheng *et al.*, 1996a). The direct intercalation of o -DCB molecules in the interlayers of high-charge HDTMA-SAz-1 was indicated by the interlayer expansion from ~ 23 to ~ 33 Å (Figure 5). The extent of expansion of HDTMA-SAz-1 by o -DCB is substantially greater than that caused by p -DCB (from ~ 23 to ~ 29 Å). The greater expansion caused by o -DCB reflects the combined effect of solvation and partition interactions. This and the much higher extent of o -DCB sorption, as compared to p -DCB, indicates an additional sorptive process, *i.e.*, solvation of the HDTMA-ammonium centers. This mechanism shows a sigmoid-cooperative sorption isotherm (Slabaugh and Hiltner, 1968; Pyda and Kurzynski, 1982, 1983; Solomon and Hawthorne, 1983). Concurrently, o -DCB molecules also partition into the interlamellar HDTMA-organic phases. This is facilitated by the interlayer expansion and characterized by a type-III partition isotherm. Combination of solvation and partition interactions manifests a double-sigmoid isotherm. The solvation-type interactions of o -DCB are apparently promoted by its high polarity, and do not occur substantially for p -DCB which is nonpolar. In the case of HDTMA-ILL, where only an external HDTMA-organic phase exists, solvation-type interactions are apparently less important as indicated by the lower uptake of o -DCB per unit mass of HDTMA of HDTMA-ILL and the less pronounced double-sigmoid shape of the isotherm. Closer packing of adsorbed HDTMA on the ILL surface owing to its higher charge density as compared to SAz-1 (Jaynes and Boyd, 1991b) may inhibit penetration of o -DCB, reducing the solvation-type interactions with the ammonium centers. The much higher o -DCB sorption by HDTMA-SAz-1 than that by HDTMA-ILL reveals the importance of the solvation effect.

Table 3. Logarithm of HDTMA-normalized distribution coefficients ($\log K_{\text{HDTMA}}$, l/kg) of dichlorobenzene isomers at a relative concentration of 0.5, and respective $\log K_{\text{HDTMA}}/K_{\text{OW}}$ in parentheses.

Chemical	$\log K_{\text{HDTMA}}$ ($\log K_{\text{HDTMA}}/K_{\text{OW}}$)		
	HDTMA-SAz-1	HDTMA-SWy-2	HDTMA-ILL
1,2-dichlorobenzene	4.23(0.80)	4.27(0.84)	3.97(0.54)
1,3-dichlorobenzene	4.13(0.60)	3.45(-0.08)	3.66(0.13)
1,4-dichlorobenzene	3.63(0.19)	2.89(-0.55)	3.27(-0.17)
1,4-dichlorobenzene in the presence of chlorobenzene	—	3.73(0.29)	—

Sorption of *o*-DCB by HDTMA-SWy-2 does not cause interlayer expansion until the relative concentration of *o*-DCB reaches ~ 0.25 (Figure 5). Beyond this concentration, the interlayers of HDTMA-SWy-2 are expanded from ~ 18.5 to ~ 22 Å, and the extent of sorption increases dramatically (Figure 2). The interlayer expansion and increased sorption suggest both solvation- and partition-type interactions. The solvation-type interactions with HDTMA-SWy-2 appear to contribute more to overall sorption as compared to HDTMA-ILL. The lower packing density of HDTMA in HDTMA-SWy-2 as compared to HDTMA-ILL may cause this, as discussed above.

Sorption of *m*-DCB represents the intermediate case. Similar to *o*-DCB, the sorptive characteristics of *m*-DCB by HDTMA-SAz-1, *i.e.*, a double-sigmoid isotherm and a much higher uptake than that by HDTMA-ILL (Figure 3), suggest that *m*-DCB is directly intercalated in the interlayers of HDTMA-SAz-1 via both solvation and partitioning. However, the polarity of *m*-DCB molecules is reduced compared to *o*-DCB (Table 2) and this reduces the solvation of HDTMA. Thus uptake of *m*-DCB is reduced as compared to *o*-DCB, but uptake is much higher than that for *p*-DCB (Figure 3).

The lower uptake of *m*-DCB by HDTMA-SWy-2 as compared to HDTMA-ILL (~ 2 times lower) at low-solute concentrations indicates some restricted access to the HDTMA phase in the interlayers of HDTMA-SWy-2. For both organoclays, sorption of *m*-DCB is much greater than that of *p*-DCB indicating both partition and solvation interactions. However, uptake of *o*-DCB is greater than that of *m*-DCB suggesting a greater degree of solvation-type interactions for *o*-DCB, resulting from the higher polarity of this solute as compared to *m*-DCB. At comparatively high relative concentrations (>0.58) of *m*-DCB, sorption by HDTMA-SWy-2 increases sharply suggesting an expansion of the interlayers of HDTMA-SWy-2. The requirement of a higher relative concentration compared to *o*-DCB to cause expansion reflects the weaker solvation effect.

The different dichlorobenzene uptake illustrates the importance of solute polarity on sorption. This is further illustrated by the effect of a polar solute (*e.g.*, CB) on the uptake of a nonpolar solute (*e.g.*, *p*-DCB). We

have observed substantial enhancement of *p*-DCB sorption by HDTMA-SWy-2 in the presence of CB (Figure 1). In this bisolute system, the relative concentrations of CB at equilibrium were between 0.34–0.44, which exceeded that needed to expand the interlayers of HDTMA-SWy-2 (Sheng *et al.*, 1996a). The interlayer expansion was observed by XRD (Figure 4). Immediate further interlayer expansion after *p*-DCB sorption demonstrates the intercalation of *p*-DCB, which is not the case in the single-solute system, and the extent of sorption by HDTMA-SWy-2 resembles that by HDTMA-SAz-1. Another factor that enhances *p*-DCB sorption by HDTMA-SWy-2 in the presence of CB is a cosolvent effect, as described in previous studies (Sheng *et al.*, 1996b, 1998).

To separate the relative contributions of solvation and partition interactions to sorption of dichlorobenzene isomers by HDTMA clays, the HDTMA-normalized distribution coefficients of *o*-DCB, *m*-DCB, and *p*-DCB at a relative concentration of 0.5 are compared ($\log K_{\text{HDTMA}}$ in Table 3). The values of K_{HDTMA} divided by K_{OW} approximate the relative effect of solvation and partition, owing to the lack of solvation interactions in the partitioning of these molecules between octanol and water. Generally, the K_{HDTMA} values are high compared to K_{OW} , indicating the effectiveness of the HDTMA clays for dichlorobenzene sorption. The effectiveness of HDTMA-SAz-1, where the interlayers are directly accessible for dichlorobenzenes owing to its initial large basal spacing, differs among dichlorobenzene isomers depending on molecular polarities. The $K_{\text{HDTMA}}/K_{\text{OW}}$ ratios show that HDTMA-SAz-1 is more effective than octanol in the uptake of all the dichlorobenzene isomers. *o*-DCB is the most polar solute and shows the strongest solvation-type interactions. *m*-DCB has an intermediate molecular polarity, and the $K_{\text{HDTMA}}/K_{\text{OW}}$ ratio, although greater than unity, is lower than that of *o*-DCB. For nonpolar *p*-DCB, uptake by HDTMA-SAz-1 is comparable to that by bulk octanol. The effectiveness of HDTMA-SWy-2 is influenced by both solute polarity and the interlayer spacing. For *o*-DCB, solvation expands the interlayers, which makes the interlayers accessible for *o*-DCB. Uptake of *o*-DCB by HDTMA-SWy-2 is much higher than that by bulk octanol, and similar to that by HDTMA-SAz-1. In contrast, the inability of the non-

polar solute *p*-DCB to expand the interlayers of HDTMA-SWy-2 owing to a lack of solvation-type interactions results in HDTMA-SWy-2 being less effective for *p*-DCB uptake than bulk octanol.

In summary, HDTMA clays are effective sorbents for dichlorobenzene isomers, although the effectiveness varies depending on the initial interlayer spacing of HDTMA clays and the polarities of solute molecules. Sorption is enhanced by greater interlayer separation and higher solute polarity. The presence of a polar solute (e.g., CB) greatly enhances the sorption of a nonpolar solute (e.g., *p*-DCB) by a low-charge HDTMA clay with a smaller interlayer spacing (e.g., HDTMA-SWy-2). Owing to the wide use of dichlorobenzene isomers, they often exist as mixtures in wastewater and groundwater. HDTMA clays should be effective sorbents for removing dichlorobenzene isomers from contaminated water.

ACKNOWLEDGMENTS

This research was supported by the National Institute of Environmental Health Sciences grant P42ES04911, the Michigan State University Institute for Environmental Toxicology, and the Michigan Agricultural Experiment Station.

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E-mail of corresponding author: Boyds@pilot.msu.edu
(Received 12 February 1998; accepted 16 June 1999; Ms. 314; A.E. George F. Vance)