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SORPTION OF NITROAROMATICS BY AMMONIUM- AND ORGANIC AMMONIUM-EXCHANGED SMECTITE: SHIFTS FROM ADSORPTION/COMPLEXATION TO A PARTITION-DOMINATED PROCESS

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Abstract—Nitroaromatic compounds (NACs) are components of munitions commonly found as soil contaminants at military training sites and elsewhere. These compounds pose possible threats to human health and ecological systems. Recent studies indicate that these compounds are strongly retained by smectite clays. The adsorption mechanisms are not fully reconciled, but it is known that the type of exchangeable cation strongly affects NAC affinity for smectites. This study examined the sorption of 1,3-dinitrobenzene, 2,4-dinitrotoluene and naphthalene from water by a smectite clay (SWy-2) saturated with ammonium, tetramethylammonium (TMA), trimethylphenylammonium (TMPA) and hexadecyltrimethylammonium (HDTMA). In all cases, we observed greater sorption of 2,4-dinitrotoluene compared with 1,3-dinitrobenzene. The sorption isotherms for 2,4-dinitrotoluene and 1,3-dinitrobenzene displayed a concave-downward curve for NH_4-SWy-2 and TMA-SWy-2, whereas the isotherms for sorption of HDTMA-SWy-2 and TMPA-SWy-2 were essentially linear. The magnitude of sorption followed the order: NH_4-SWy-2 > TMA-SWy-2 > TMPA-SWy-2 > HDTMA-SWy-2 for both compounds. The greater affinity of NACs for NH_4- and TMA-SWy-2 is due in part to complex formation between the exchangeable cation and $-NO_2$ groups. These clays also provide near optimal interlayer distances that approximate the molecular thickness of NACs hence promoting the simultaneous interaction of the planar aromatic rings with opposing siloxane surfaces and solute dehydration. Both processes are energetically favorable. In HDTMA-SWy-2, sorption of all solutes is *via* a partition-dominated process. Solute competition (diminished uptake of one solute in the presence of a second) was observed for TMA-SWy-2 but not HDTMA-SWy-2. This is consistent with an adsorptive mechanism for TMA-SWy-2 and a partitioning mechanism for HDTMA-SWy-2. This study demonstrates that the dominant molecular mechanism of NAC sorption by smectite changes fundamentally from complexation between $-NO_2$ groups and the exchangeable cation (viz. NH_4 and TMA) to partitioning for a systematic series of ammonium and quaternary ammonium cations in which the locus of positive charge (the central N atom) is progressively shielded by organic moieties of increasing size.

Key Words—Munitions, Nitroaromatic Compounds, Smectite, Soil Contamination.

INTRODUCTION

Smectites are layered 2:1 aluminosilicates with structural negative charges that arise from isomorphous substitution. In nature, inorganic cations (*e.g.* Ca^{2+}, Mg^{2+}, Al^{3+}, K^+ and Na^+) are commonly associated with the clay surfaces to balance these negative charges. In the presence of water, inorganic exchangeable cations are hydrated causing the interlayer to expand. Among the clay minerals commonly found in soils, smectites are especially important because of their widespread occurrence, large surface areas, large cation exchange capacities and significant expansibility. Smectite clays can be modified through ion-exchange reactions utilizing inorganic or organic cations. Previous studies have shown that these simple modifications can dramatically alter the affinities of smectites for organic contaminants and pesticides and that this capability could enhance the successful implementation of a variety of *in situ* and *ex situ* remediation/immobilization technologies (Boyd *et al.*, 1998a, 2001; Lee *et al.*, 1989; Xu *et al.*, 1997; Sheng *et al.*, 1998; Weissmahr *et al.*, 1999; Li *et al.*, 2004a).

Replacing the inorganic exchangeable cations of smectites with organic cations typically causes an increase in the hydrophobic nature of the clay interlayer environment (Barrer, 1961; Boyd *et al.*, 1988b; McBride, 1977; Mortland *et al.*, 1986; Wolfe *et al.*, 1985; Xu and Boyd, 1995). For instance, as naturally occurring inorganic exchangeable cations of clay minerals are replaced with organic cationic surfactants such as hexadecyltrimethylammonium (HDTMA), the resultant organoclays are rendered more effective sorbents for removing poorly water soluble organic compounds from aqueous solution (Boyd *et al.*, 1988b; Burris and Antworth, 1992; Lee *et al.*, 1989; Sheng *et al.*, 1996). In HDTMA-modified clays, the association of the C-16 alkyl carbon chains of HDTMA creates an organic phase in the clay interlayer that covers most clay siloxane surface. In the case of aromatic hydrocarbons, solute

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partitioning into this organic phase was shown to be the primary sorptive process (Jaynes and Boyd, 1991a). Increasing the amount of HDTMA in the clay interlayer enlarges the partitioning domains as indicated by an expansion of the clay basal spacing from 12 up to 18 and 23 Å. The increased interlayer distances of HDTMA-modified smectites correspond to the formation of bilayers and paraffin complexes by the alkyl-carbon chains of HDTMA.

Lee *et al.* (1989, 1990) showed that smectite clays exchanged with smaller organic cations such as tetramethylammonium (TMA) or trimethylphenylammonium (TMPA) cations display adsorptive properties as indicated by curvilinear isotherms for sorption of benzene and other aromatic hydrocarbons. They concluded that TMA and TMPA cations function as weakly hydrated pillars which prop open the smectite interlayers providing access to adsorption domains on the siloxane surface. Jaynes and Boyd (1991b) and Lee *et al.* (1990) studied the effect of clay surface charge density on the adsorption of organic contaminants by such organo-smectites. High-charged smectites exchanged with a correspondingly greater amount of TMA or TMPA sorbed less benzene compared to TMA- or TMPA-modified smectites derived from clays with lesser charge densities. The authors suggest this observation as additional evidence for organic solute adsorption by mineral siloxane surfaces between the exchangeable TMA or TMPA cations. Also, sorption of benzene vapor by dry TMA-smectite was greater compared to sorption of benzene from bulk water. Hydration of the TMA cations, albeit weak, diminished the size of adsorption domains between exchangeable TMA ions. Thus there are at least two primary mechanisms for sorption of organic solutes by organo-clays, *i.e.* partitioning into organic phases derived from organic cations containing large alkyl hydrocarbon chains (*e.g.* HDTMA-clay) and adsorption to the available siloxane surfaces in organoclays comprising smaller organic cations such as TMA.

So, for TMA-and TMPA-smectites, the small, weakly-hydrated organic ammonium cations serve to prop open the clay interlayers without the organic cation or its hydration waters fully occupying the interlayer environment, hence rendering the clay siloxane surfaces available for adsorption of organic solutes. Recent studies have shown that several weakly-hydrated inorganic cations (*e.g.* K^+ and Cs^+) can manifest similar changes in the clay interlayer environment leading to greater adsorption of certain organic solutes (Haderlein and Schwarzenbach, 1993; Haderlein *et al.*, 1996; Boyd *et al.*, 2001; Sheng *et al.*, 2002). For example, NACs demonstrate strong affinities for smectites exchanged with K^+ or Cs^+, but much less adsorption by smectites saturated with Na^+, Ca^{2+} or Mg^{2+}. This was attributed to the comparatively stronger hydration of Na^+, Ca^{2+} and Mg^{2+} cations which create an inhospitable (*i.e.* hydrophilic) environment for organics in clay interlayers. This is, in part, because strongly bound water is more difficult to displace, thus restricting access of the organic contaminants to potential adsorption sites in smectite.

The hydration of inorganic exchangeable cations strongly influences the interlayer environment in smectites where NAC sorption predominantly occurs. Besides determining the abundance of adsorptive sites of sufficient size (between exchangeable cations), interlayer cation hydration is a major determinant of the distance between clay layers in smectites. A d_{001} spacing of ~12.5 Å is commonly observed for K^+- and Cs^+-smectite clays. This appears to provide an optimal interlayer spacing which allows the planar aromatic rings of NACs to orient parallel to and interact directly with the opposing clay sheets, thereby minimizing contact with water molecules, which is energetically favorable (Li *et al.*, 2004b). This is consistent with the now common observation that smectite clays saturated with relatively weakly hydrated K^+ or Cs^+ ions have a strong affinity for NACs (Boyd *et al.*, 2001; Haderlein and Schwarzenbach, 1993; Haderlein *et al.*, 1996; Johnston *et al.*, 2001; Johnston *et al.*, 2002; Li *et al.*, 2004b; Sheng *et al.*, 2002; Weissmahr *et al.*, 1998). In contrast, those saturated with more strongly hydrated cations, such as Na^+ or Ca^{2+}, are much less effective adsorbents for NACs. Such an arrangement of NACs in the interlayers of K^+-, Cs^+- or NH_4^+-smectites might also allow the formation of electron donor-acceptor complexes involving the electron deficient aromatic ring of NACs and the electron-rich siloxane oxygens of smectites (Haderlein and Schwarzenbach, 1993; Haderlein *et al.*, 1996; Weissmahr *et al.*, 1998). Weakly hydrated exchangeable cations on clay surfaces can also interact favorably with the $-NO_2$ groups of NACs. Boyd *et al.* (2001) demonstrated that one mechanism responsible for the strong sorption of NACs is the formation of inner-sphere and/or outer-sphere complexes with weakly-hydrated exchangeable cations in the clay interlayers.

Smectite clays are strong sorbents for many organic compounds. The dominant sorption mechanism(s) on a given smectite varies depending on properties of the exchangeable cations and the organic solutes. Previous studies indicated that organic compounds could be retained by partition interactions with organic phases derived from exchanged organic cations and by adsorption on clay siloxane surfaces. The latter process results from additive processes including hydrophobic interactions between the solute and the clay siloxane surfaces, solute dehydration in the clay interlayers, formation of complexes between polar functional groups of the solute and exchangeable cations and/or formation of electron-donor acceptor complexes. The size, structure and hydration properties of exchangeable cations associated with smectites strongly influence the clay interlayer environment, hence determining the degree of sorption

of organic compounds and the operative sorption mechanism(s). To further understand the dominant sorptive mechanism(s) of smectite clays responsible for the retention of NACs where multiple mechanisms are possible, we measured the sorption from water of 1,3-dinitrobenzene (1,3-DNB) and 2,4-dinitrotoluene (2,4-DNT) and naphthalene in single- and binary-solute systems by a reference smectite (SWy-2) saturated with ammonium and a series of organic quaternary ammoniums, *i.e.* TMA, TMPA and HDTMA, of increasing size and hydrophobicity. A central goal of this study was to determine the predominance of complex formation between the exchangeable cation and the $-NO_2$ groups of NACs (Boyd *et al.*, 2001) as the locus of positive charge, *i.e.* the central N atom, is progressively shielded by organic moieties of increasing size (methyl, phenyl, hexadecyl). X-ray diffraction and surface area determination of clays were used to gain insight into the effects of exchangeable cation on the nature of the clay interlayer environment and hence sorption of NACs.

MATERIALS AND METHODS

Chemicals

1,3-DNB and 2,4-DNT were purchased from Aldrich Chemical Company Inc. (Milwaukee, WI) with a reported purity >97% and naphthalene was obtained from Sigma Chemical Company Inc. (St. Louis, MO) with a reported purity of 99%. Methanol (HPLC grade) was purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ). The HDTMA bromide, TMA bromide, TMPA chloride and NH_4 chloride were purchased from Aldrich with chemical purities >98%. All chemicals were used as received.

Clay preparation

A reference smectite (Wyoming montmorillonite, SWy-2) was obtained from the Source Clays Repository of The Clay Minerals Society at Purdue University (West Lafayette, IN) and used throughout this study. It has a cation exchange capacity (CEC) of 82 $cmol_c/kg$ and a theoretical surface area of 750 m^2/g (van Olphen and Fripiat, 1979). The <2 μm sized fraction was extracted by wet sedimentation. The clay suspensions were then quick frozen and freeze dried. Cation exchange reactions were used to prepare the homoionic clays. The naturally occurring inorganic exchangeable cations were replaced by ammonium, TMA, TMPA and HDTMA. The NH_4-smectite was prepared by washing the clay three times with 0.2 M NH_4Cl solution. The TMA- and TMPA-clays were prepared by adding TMPA chloride and TMA bromide in amounts which were three times the clay CEC. HDTMA-saturated clays were prepared by adding HDTMA bromide equal to the clay CEC. Then the clay suspensions were washed four to five times with Milli-Q water to remove excess electrolytes and $AgNO_3$ was used to check that the samples were free of chloride and bromide. The clay suspensions were then quick-frozen and freeze dried. The clay organic carbon content was measured using the combustion method and the surface area was determined using the N_2 BET method.

Single-solute sorption

The sorption of 1,3-DNB, 2,4-DNT and naphthalene by NH_4-, TMA-, TMPA- and HDTMA-SWy-2 was measured using a batch equilibration method. First, 0.05−0.10 g clay samples, depending on the type of solute and prepared clay, were placed in glass centrifuge tubes. Then a series of initial solute concentrations in water, ranging from 5 to 200 mg/L for 1,3-DNB and 2,4-DNT and 1.0 to 25 mg/L for naphthalene, was added. The tubes were closed immediately with Teflon-lined screw caps and shaken end-over-end at 40 rpm for 24 h at room temperature (23ºC). Previous studies demonstrated that sorption equilibrium in such systems was reached within 18 h (Sheng *et al.*, 2002). The tubes were centrifuged at 2600 g for 30 min to separate liquid and solid phases. Concentrations of 1,3-DNB and 2,4-DNT and naphthalene (NAPH) in the supernatant liquids were measured by a high-performance liquid chromatography (HPLC) system consisting of a Perkin-Elmer Binary 250 LC pump, a Series 200 autosampler and a Series 200 UV-visible detector. The optimal wavelength was set at 270 nm for 1,3-DNB, 250 nm for 2,4-DNT and 260 nm for NAPH. The mobile phase composition was a mixture of methanol and water and optimized for each compound. Controls consisted of the aqueous organic solutes in the absence of clay. The amount sorbed was calculated from the concentration difference between the aqueous solute concentrations in the control and supernatant solutions in the clay suspensions. Sorption isotherms were obtained by plotting sorbed *vs.* equilibrium aqueous phase concentrations. No changes in solute concentrations were detected in the control tubes, therefore solute mass lost from the aqueous phase in the presence of clay was assumed to be sorbed by clay.

Binary-solute sorption

To evaluate the competitive sorption of NACs by clays, we conducted binary-solute sorption experiments using the batch equilibration method. A series of initial solutions was prepared by mixing 2,4-DNT and 1,3-DNB with molar ratios of 1:1 and 1:3 in aqueous solution. The initial solutions were added to centrifuge tubes containing HDTMA-SWy-2 or TMA-SWy-2. The equilibration and clay-solution separation procedures were the same as described above. The supernatant solutions were sampled and subjected to simultaneous measurements of 1,3-DNB and 2,4-DNT by HPLC. The mobile phase was an isocratic mixture of methanol and water (50:50) with the flow rate at 1.0 ml/min. The wavelength of the UV-vis detector was set at 270 nm.

Table 1. Properties of reference smectite (SWy-2) and SWy-2 exchanged with ammonium, trimethylammonium (TMA), trimethylphenylammonium (TMPA) and hexadecyltrimethylammonium (HDTMA).

Clay	% organic C	% CEC occupied by organic cation*	N_2 BET surface area (m^2/g)	d_{001} (Å)
Reference smectite (SWy-2)	0.1	–	21.3	12.0
NH_4-SWy-2	0.1	–	43.4	11.2
TMA-SWy-2	3.0	76.5	132.3	13.5
TMPA-SWy-2	7.4	83	19.5	14.2
HDTMA-SWy-2	15.7	83	13.7	17.5

* The percentage of CEC occupied by organic C was calculated by the measured organic C content divided by the organic C from organic cations assuming CEC sites are fully saturated with organic cations.

X-ray diffraction analysis

After the supernatant solutions were removed for HPLC analysis, ~2 mL of clay suspension remained in the tubes. The clay slurries were mixed using a vortex mixer, dropped onto glass slides using a disposable glass pipette, air dried to produce oriented clay films, then subjected to X-ray diffraction (XRD) analysis. The XRD patterns of clay films were recorded using a Philips APD 3720 automated X-ray diffractometer equipped with CuKα radiation, an APD 3521 goniometer and a diffracted-beam monochromator. The scanning angle ranged from 3 to 15º2θ at steps of 0.02º and the scanning time was 2 s per step.

RESULTS AND DISSCUSSION

The properties of the clays used in this study are presented in Table 1. Reference SWy-2 and NH_4-SWy-2 clays each contained ~ 0.1% organic C, presumably present as an impurity. The organic C values of the organoclays increased in the expected order: TMA-SWy-2 < TMPA-SWy-2 < HDTMA-SWy-2. Comparisons of measured organic C content with the calculated organic C percentages at full saturation indicated that 76.5, 83 and 83% of the cation exchange sites were occupied by organic ammonium cations for TMA-SWy-2, TMPA-SWy-2 and HDTMA-SWy-2, respectively. The basal spacing (d_{001}) increased with the size of the predominant exchangeable cation: NH_4-SWy-2 < TMA-SWy-2 < TMPA-SWy-2 < HDTMA-SWy-2. For the organoclays, the measured N_2 BET surface areas were inversely proportional to the size of the organic ammonium, *i.e.* HDTMA-SWy-2 < TMPA-SWy-2 < TMA-SWy-2. This ordering results from the fact that the larger organic ammonium cations occupy a greater proportion of the interlayer volume and obscure a larger portion of the siloxane surfaces where N_2 adsorption occurs. This also accounts for the measured N_2 BET surface areas of the organo-clays being less than the theoretical surface area of SWy-2.

Sorption of nitroaromatic compounds

Sorption isotherms of 2,4-DNT and 1,3-DNB by HDTMA-, TMPA-, TMA- and NH_4-SWy-2 from water are shown in Figure 1 with amount sorbed per unit mass of clay plotted *vs*. the equilibrium aqueous concentration of the solute. All sorption isotherms were fitted to the Freundlich equation (shown as solid lines in Figure 1):

$$Q = K_f\, Ce^N$$

where Q (mg/kg) is the sorbed concentration, Ce (mg/L) is the equilibrium aqueous concentration, K_f ($mg^{1-N}L^N/kg$) is the Freundlich sorption coefficient and N is an empirical constant (unitless) that describes isotherm non-linearity. The Freundlich equation fitting parameters are listed in Table 2.

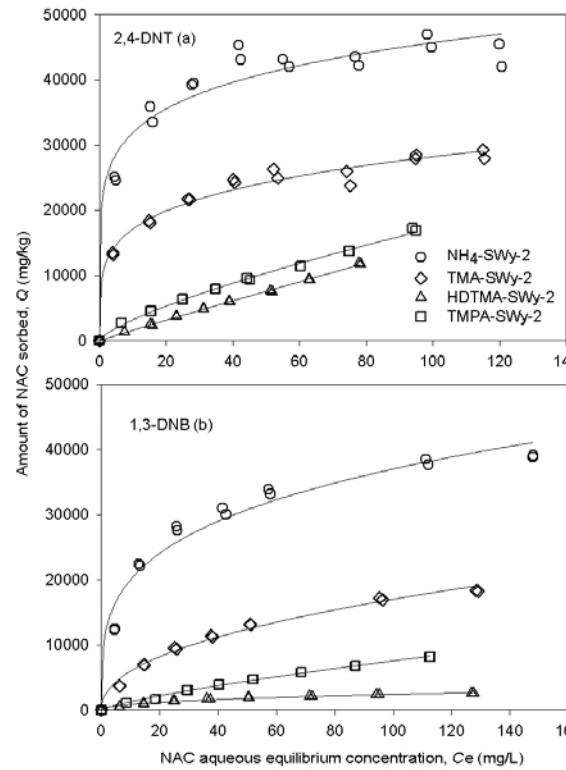

Figure 1. Sorption isotherms of nitroaromatic compounds (NACs) (a) 2,4-dinitrotoluene (2,4-DNT) and (b) 1,3-dinitrobenzene (1,3-DNB) by smectite (SWy-2) saturated with ammonium, tetramethylammonium (TMA), hexadecyltrimethylammonium (HDTMA) or trimethylphenylammonium (TMPA).

Table 2. Freundlich sorption isotherm parameters K_f (mg^{1-N} L^N/kg), N and r^2 for 2,4-dinitrotoluene, 1,3-dinitrobenzene and naphthalene by smectite clay (SWy-2) exchanged with ammonium, tetramethylammonium (TMA), trimethylphenylammonium (TMPA) and hexadecyltrimethylammonium (HDTMA). Standard errors are reported in parentheses.

	NH_4-SWy-2			TMA-SWy-2			TMPA-SWy-2			HDTMA-SWy-2		
Solute	K_f	N	r^2	K_f	N	r^2	K_f	N	r^2	K_f	N	r^2
1,3-dinitrobenzene	10860	0.27	0.97	2120	0.45	0.99	228	0.27	0.97	331	0.43	0.98
	(940)	(0.02)		(180)	(0.02)		(21)	(0.02)		(29)	(0.02)	
2,4-dinitrotoluene	22260	0.16	0.95	10380	0.22	0.98	582	0.74	0.99	174	0.96	0.99
	(1760)	(0.02)		(610)	(0.01)		(44)	(0.02)		(9)	(0.02)	
Naphthalene	3.1	1.30	0.97	11.7	3.28	0.95	23527	1.14	0.98	331	1.39	0.99
	(1.2)	(0.17)		(5.74)	(0.37)		(747)	(0.07)		(41)	(0.03)	

Sorption isotherms of 2,4-DNT and 1,3-DNB by the clays were non-linear except for that representing the sorption of 2,4-DNT by HDTMA-SWy-2. The magnitude of sorption on clays was greater for 2,4-DNT than for 1,3-DNB. The greater affinity of clays for 2,4-DNT compared to 1,3-DNB is probably due in part to the lesser water solubility of the toluene derivative. Our previous studies of NAC sorption by K-SWy-2 and aromatic hydrocarbon sorption by HDTMA-smectites have shown that solute uptake from water is favored by lesser water solubility (Boyd *et al.*, 2001; Li *et al.*, 2004b; Jaynes and Boyd, 1991a). The sorption of 1,3-DNB and 2,4-DNT by clays followed the order of NH_4-SWy-2 > TMA-SWy-2 > TMPA-SWy-2 > HDTMA-SWy-2. The strong affinities of the NACs for NH_4-SWy-2 and TMA-SWy-2, along with the sorption non-linearity, are characteristics of adsorption on the basal surfaces of smectite clays. Compared to naturally occurring inorganic exchangeable cations commonly associated with smectites (*e.g.* Na^+, Ca^{2+}, Mg^{2+}), the relatively low hydration free energies for ammonium (−292 kJ/mol) (Marcus, 1985) and TMA (-219kJ/mol) (Ford and Wang, 1992) result in less water surrounding the cations rendering more mineral siloxane surface available for adsorption (Boyd *et al.*, 2001). The NH_4-SWy-2 was at least 1.5 times more effective (on a unit mass basis) than TMA-SWy-2 for sorption of 2,4-DNT and 1,3-DNB over the concentration range studied. The greater affinity of NH_4-SWy-2 for these solutes may result from the formation of complexes between exchanged ammonium and the $-NO_2$ groups of the NACs, as in the case of NAC sorption by K-smectites (Boyd *et al.*, 2001). The larger molecular size of TMA than that of ammonium would inhibit direct interactions between $-NO_2$ and TMA ions since the locus of positive charge in TMA is buried inside four methyl groups. Thus $-NO_2$ complexes with ammonium would be expected to be stronger than those with TMA, leading to greater NAC sorption by NH_4-SWy-2.

The 2,4-DNT and 1,3-DNB molecules differ by only a methyl group. The weaker sorption by NH_4- and TMA-SWy-2 observed for the smaller molecule 1,3-DNB than 2,4-DNT cannot be explained by steric hindrance or surface-filling arguments. Rather, it probably results from stronger complexes between 2,4-DNT and surfaces and/or cations. The methyl group is expected to donate electron density to the ring, which should decrease the strength of electron-donor-acceptor complexes with the surface as proposed by Haderlein *et al.* (1996). In fact, much of the donated electron density would probably flow to the nitro groups in para- and ortho-positions (Boyd *et al.*, 2001), which may enable stronger formation of complexes with interlayer cations. Another factor that helps to account for the stronger sorption of 2,4-DNT over 1,3-DNB is that hydrophobic effects make a contribution to the sorption of NACs (Boyd *et al.*, 2001; Li *et al.*, 2004b). 2,4-DNT is less water-soluble than 1,3-DNB so that there should be more impetus to remove it from water.

The NACs sorbed from water by HDTMA- and TMPA-clays exhibited sorption properties distinct from those of NH_4- and TMA-clays. Sorption of NACs by HDTMA- or TMPA-clays was less than sorption by NH_4- or TMA-SWy-2 clays and the isotherms were more linear (Table 2 and Figure 1). In HDTMA-SWy-2, the association of alkyl chains creates an organic partitioning phase that covers most clay siloxane surfaces; solute partitioning into this organic phase is believed to be the primary process occurring in this clay for aromatic hydrocarbons (Boyd *et al.*, 1988b; Jaynes and Boyd, 1991a). The linear isotherms and inverse relationship between sorption and solute water solubility are consistent with a partition-dominated process (Chiou, 2002). The basal spacing of HDTMA-SWy-2 used here was 17.5 Å, corresponding to the formation of a bilayer of alkyl chains (Jaynes and Boyd, 1991a). In this configuration, the densely packed alkyl chains adopt a horizontal orientation relative to clay layers forming an organic partition phase in which mineral surfaces are largely covered and hence contribute minimally to the sorption of organic compounds. Sorption of NACs by TMPA-smectite is slightly greater than that by HDTMA-clay, which may be due to some contribution by interlayer surfaces to adsorption. Overall, sorption by the TMPA-clay is intermediate between HDTMA-clay where NAC sorption is predominantly *via* partitioning and TMA-clay which functions as an adsorbent. The underlying mechanism(s) for NAC sorption by TMPA-clay is uncertain.

Naphthalene sorption

In contrast to the sorption order of NACs, the magnitude of naphthalene sorption followed the order: TMPA-SWy-2 > HDTMA-SWy-2 > TMA-SWy-2 > NH_4-SWy-2 (Figure 2). As we observed previously (Jaynes and Boyd, 1990), TMPA-SWy-2 appeared to have an unusually high affinity for naphthalene. In all cases, sorption of naphthalene by clays produced upward curvature in the isotherms (Figure 2 and Table 2) indicating that the increased concentration of naphthalene promotes further sorption in the interlayers. Hundal *et al.* (2001) suggested that sorption of phenanthrene by smectites was primarily *via* a process of capillary condensation in interlayer nanopores and micropores; phenanthrene was physically entrapped in the nanopores and micropores of the clay driven primarily by hydrophobic effects. Zhu *et al.* (2004) have shown a strong correlation between Freundlich sorption constants and indices of cation-π bonding. They suggested that cation-π bonding occurred between polycyclic aromatic hydrocarbons and inorganic exchangeable cations in smectite interlayers. A comparison of sorption between the two types of compounds in this study (naphthalene and NACs) by organoclays suggests that the prepared organoclays possess different sorption sites/mechanisms for retention of the test compounds. The much greater affinity of NH_4- and TMA-SWy-2 for NACs compared to naphthalene indicates that interlayer adsorption on the siloxane surfaces and complex formation involving the $-NO_2$ groups are the predominant sorptive interactions for polar NACs; the latter mechanism is not available for adsorption of non-polar naphthalene. In contrast, TMPA-SWy-2 has a particularly high affinity for naphthalene with upward curvature of the isotherm, suggesting capillary condensation as a possible mechanism. Regardless of sorption mechanisms, it seems plausible that the aromatic groups on TMPA would prop the smectite interlayer at a *d* spacing (14.2 Å, Table 2) that might be optimal for naphthalene.

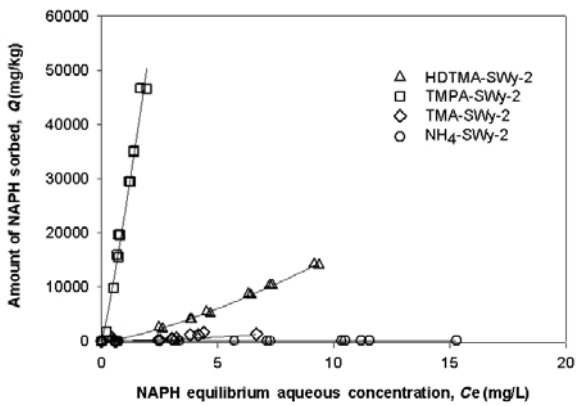

Figure 2. Sorption isotherms of naphthalene by smectite (SWy-2) saturated with ammonium, tetramethylammonium (TMA), trimethylphenylammonium (TMPA) or hexadecyltrimethylammonium (HDTMA).

Sorption from binary solute mixtures

Sorption of NACs from binary solute mixtures by clays was measured to evaluate solute competition as a means of further revealing the operative sorption mechanisms. Isotherms representing sorption of a binary mixture of 1,3-DNB and 2,4-DNT from water by HDTMA-SWy-2 and TMA-SWy-2 are shown in Figures 3 and 4 along with the corresponding single solute sorption isotherms. The Freundlich fitting parameters are reported in Table 3. The binary solutions of 2,4-DNT and 1,3-DNB were prepared at initial molar ratios of 1:1 and 1:3. Sorption isotherms of 2,4-DNT from the binary solute mixtures by HDTMA-SWy-2 were coincident with the single solute isotherm demonstrating a total lack of solute competition. Sorption of 1,3-DNB in binary solute mixtures by HDTMA-SWy-2 was somewhat greater than the single solute sorption at aqueous concentration >50 mg/L, indicating a cooperative sorption process. The lack of a negative effect on sorption in binary solute systems is consistent with a partition-dominated process involving the organic phase formed by HDTMA (Chiou, 2002).

Sorption of 1,3-DNB and 2,4-DNT from binary solute mixtures by TMA-SWy-2 are compared to the sorption of the single solutes in Figure 4. Sorption isotherms of

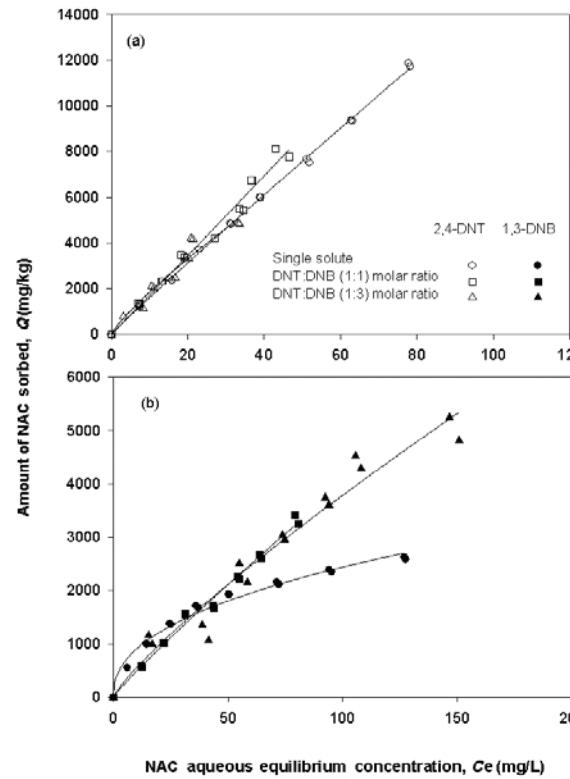

Figure 3. Sorption isotherms of nitroaromatic compounds (NACs) (a) 2,4-dinitrotoluene (2,4-DNT) and (b) 1,3-dinitrobenzene (1,3-DNB) by hexadecyltrimethylammonium (HDTMA)-smectite (SWy-2) in single- and binary-solute systems.

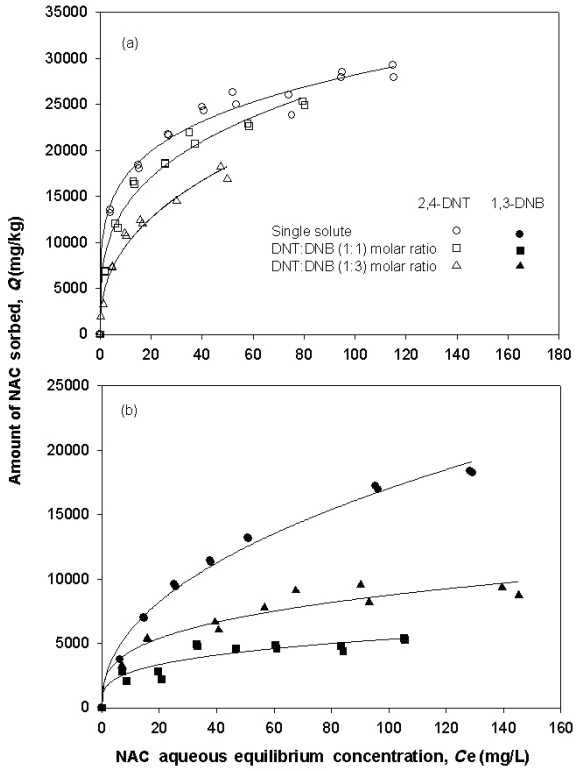

Figure 4. Sorption isotherms of nitroaromatic compounds (NACs) (a) 2,4-dinitrotoluene (2,4-DNT) and (b) 1,3-dinitrobenzene (1,3-DNB) by tetramethylammonium (TMA)-smectite (SWy-2) in single- and binary-solute system.

1,3-DNB and 2,4-DNT in both single and binary solute systems are non-linear indicating adsorption to clay surfaces rather than a partitioning process, as described above. In both cases the presence of a second solute depressed the uptake of the primary solute, clearly demonstrating that 1,3-DNB and 2,4-DNT were competing for adsorptive sites on TMA-clay. The strong competitive effect on sorption of NACs by TMA-clay is characteristic of an adsorptive process wherein 1,3-DNB and 2,4-DNT compete with each other for the limited available sorptive sites. The greater amount of competitive solute present in the aqueous phase was observed to suppress the sorption of the primary solute more substantially. For example, at *C*e = 80 mg/L, binary sorption of 1,3-DNB was reduced by ~50% with the DNT:DNB molar ratio of 1:3 and by ~70% at a molar ratio of 1:1. In comparing the affinity of 1,3-DNB and 2,4-DNT with TMA-SWy-2, note that 2,4-DNT suppressed sorption of 1,3-DNB by up to 75%, while 1,3-DNB suppressed 2,4-DNT sorption by <30%. The greater competitive inhibition on sorption caused by 2,4-DNT is a logical manifestation of its greater affinity for TMA-SWy-2 compared to 1,3-DNB (Figure 1).

CONCLUSIONS

Sorption of two NACs by smectite exchanged with ammonium and a series of quaternary ammonium ions (TMA, TMPA, HDTMA) revealed a shift in sorption mechanism from a predominantly adsorptive process in the case of NH_4- and TMA-smectite to a partition-dominated process for HDTMA-smectite. Non-linear sorption isotherms and competition between NACs for sorption sites indicated an adsorptive mechanism. Adsorption of NACs was a manifestation of the small size and low hydration energies of ammonium and TMA. The primary adsorptive interaction appeared to be the formation of complexes between exchangeable cation and the $-NO_2$ groups of the NACs. Adsorption domains are primarily the siloxane surface between the exchangeable cations. The small size and weak hydration of these cations (NH_4^+, TMA) facilitates formation of the aforementioned complexes and makes available the siloxane

Table 3. Freundlich sorption isotherm parameters K_f (mg^{1-N} L^N/kg), N and r^2 for 1,3-DNB and 2,4-DNT by tetramethylammonium (TMA)- and hexadecyltrimethylammonium (HDTMA)-smectite (SWy-2) in binary solute systems. The standard errors are reported in parentheses.

Solute system	TMA-SWy-2 K_f	N	r^2	HDTMA-SWy-2 K_f	N	r^2
1,3-dinitrobenzene (1,3-DNB)						
Molar ratio						
DNT:DNB (1:1)	1867	0.23	0.96	58	0.92	0.99
	(216)	(0.03)		(10)	(0.04)	
DNT:DNB (1:3)	2950	0.22	0.85	70	0.84	0.96
	(714)	(0.06)		(26)	(0.07)	
2,4-dinitrotoluene (2,4-DNT)						
Molar ratio						
DNT:DNB (1:1)	6252	0.33	0.99	168	1.0	0.98
	(353)	(0.01)		(36)	(0.06)	
DNT:DNB (1:3)	3790	0.40	0.98	270	0.84	0.96
	(310)	(0.03)		(63)	(0.07)	

surface, which is largely unobscured by water of hydration associated with the exchangeable cations. Solute partitioning was the primary sorption mechanism of clay exchanged with the much larger and hydrophobic cation HDTMA. In this instance, the C-16 alkyl chains of exchanged HDTMA coalesce to form a hydrophobic partition phase into which NACs dissolve. The siloxane surfaces and interlayer volume are essentially fully occupied by exchanged HDTMA. Linear isotherms and lack of solute competition in binary-solute systems provide evidence for a partition-dominated process where the degree of uptake from water is determined mostly by the water insolubility of the solute.

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REFERENCES

Barrer, R.M. and Perry, G. S. (1961) Sorption of mixtures, and selectivity in alkylammonium montmorillonite. Part II. Tetramethylammonium montmorillonite: *Journal of Chemistry Society*, 850–858.

Boyd, S.A., Lee, J.F. and Mortland, M.M. (1988a) Attenuating organic contaminant mobility by soil modification. *Nature*, **333**, 345–347.

Boyd, S.A., Mortland, M.M. and Chiou, C.T. (1988b) Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Science Society of America Journal*, **52**, 652–657.

Boyd, S.A., Sheng, G., Teppen, B.J. and Johnston, C.T. (2001) Mechanisms for the adsorption of substituted nitrobenzenes by smectite clays. *Environmental Science and Technology*, **35**, 4227–4234.

Burris, D.R. and Anthworth, C.P. (1992) *In situ* modification of aquifer material by a cationic surfactant to enhance retardation of organic contaminants. *Journal of Contaminant Hydrology*, **10**, 325–337.

Chiou, C.T. (2002) *Partition and Adsorption of Organic Contaminants in Environmental Systems.* John Wiley & Sons, Inc., Hoboken, New Jersey.

Ford, G.P. and Wang, B. (1992) The optimized ellipsoidal cavity and its application to the self-consistent reaction field calculation of hydration energies of cations and neutral molecules. *Journal of Computation Chemistry*, **13**, 229–239.

Haderlein, S.B. and Schwarzenbach, R.P. (1993) Adsorption of substituted nitrobenzenes and nitrophenols to mineral surfaces. *Environmental Science and Technology*, **27**, 316–326.

Haderlein, S.B., Weissmahr, K.W. and Schwarzenbach, R.P. (1996) Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. *Environmental Science and Technology*, **30**, 612–622.

Hundal, L.S., Thompson, M.L., Laird, D.A. and Carmo, A.M. (2001) Sorption of phenanthrene by reference smectites. *Environmental Science and Technology*, **35**, 3456–3461.

Jaynes, W.F. and Boyd, S.A. (1990) Trimethylphenylammonium-smectite as an effective adsorbent of water-soluble aromatic hydrocarbons. *Journal of Air and Waste Management Association*, **40**, 1649–1653.

Jaynes, W.F. and Boyd, S.A. (1991a) Clay mineral type and organic compound sorption by hexadecyltrimethylammonium-exchanged clays. *Soil Science Society of America Journal*, **55**, 43–48.

Jaynes, W.F. and Boyd, S.A. (1991b) Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals*, **39**, 428–436.

Johnston, C.T., Oliveria, M.F. de, Teppen, B.J., Sheng, G. and Boyd, S.A. (2001) Spectroscopic study of nitroaromatic-smectite sorption mechanisms. *Environmental Science and Technology*, **35**, 4767–4772.

Johnston, C.T., Sheng, G., Teppen, B.J., Boyd, S.A. and Oliveira, M.F. de (2002) Spectroscopic study of dinitrophenol herbicide sorption on smectite. *Environmental Science and Technology*, **36**, 5067–5074.

Lee, J.F., Crum, J.R. and Boyd, S.A. (1989) Enhanced retention of organic contaminants by soils exchanged with organic cations. *Environmental Science and Technology*, **23**, 1365–1372.

Lee, J.F., Mortland, M.M., Chiou, C.T., Kile, D.E. and Boyd, S.A. (1990) Adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities. *Clays and Clay Minerals*, **38**, 113–120.

Li, H., Teppen, B.J., Laird, D.A., Johnston, C.T. and Boyd, S.A. (2004a) Geochemical modulation of pesticide sorption on smectite clay. *Environmental Science and Technology*, **38**, 5393–5399.

Li, H., Teppen, B.J., Johnston, C.T. and Boyd, S.A. (2004b) Thermodynamics of nitroaromatic compounds adsorption from water by smectite clay. *Environmental Science and Technology*, **38**, 5433–5442.

Marcus, Y. (1985) Thermodynamic functions of transfer of single ions from water to nonaqueous and mixed-solvents. 2. Enthalpies and entropies of transfer to nonaqueous solvents. *Pure and Applied Chemistry*, **57**, 1103–1128.

McBride, M.B., Pinnavaia, T.J. and Mortland, M.M. (1977) Adsorption of aromatic molecules by clays in aqueous suspension. Pp. 145–154 in: *Fate of Pollutants in the Air and Water Environment. Part 1* (I.H. Suffet, editor). Advances in Environmental Science and Technology, **8**. Wiley-Interscience, New York.

Mortland, M.M., Sun, S. and Boyd, S.A. (1986) Clay-organic complexes as adsorbents for phenol and chlorophenols. *Clays and Clay Minerals*, **34**, 581–585.

Sheng, G., Xu, S. and Boyd, S.A. (1996) Mechanism(s) controlling sorption of neutral organic contaminants by surfactant-derived and natural organic matter. *Environmental Science and Technology*, **30**, 1553–1557.

Sheng, G., Wang, X., Wu, S. and Boyd, S.A. (1998) Enhanced sorption of organic contaminants by smectitic soils modified with a cationic surfactant. *Journal of Environmental Quality*, **27**, 806–814.

Sheng, G., Johnston, C.T., Teppen, B.J. and Boyd, S.A. (2002) Adsorption of dinitrophenol herbicides from water by montmorillonites. *Clays and Clay Minerals*, **50**, 25–34.

Van Olphen, H. and Fripiat, J.J. (1979) *Data Handbook for Clay Minerals and other Non-metallic Minerals*. Pergamon Press, New York.

Weissmahr, K.W., Haderlein, S.B. and Schwarzenbach, R.P. (1998) Complex formation of soil minerals with nitroaromatic explosives and other pi-acceptors. *Soil Science Society of America Journal*, **62**, 369–378.

Weissmahr, K.W., Hildenbrand, M., Schwarzenbach, R.P. and Haderlein, S.B. (1999) Laboratory and field scale evaluation of geochemical controls on groundwater transport of

nitroaromatic ammunition residues. *Environmental Science and Technology*, **33**, 2593–2600.

Wolfe, T.A., Demerirel, T. and Baumann, E.R. (1985) Interaction of aliphatic amines with montmorillonite to enhance adsorption of organic pollutants. *Clays and Clay Minerals*, **33**, 301–311.

Xu, S. and Boyd, S.A. (1995) Cationic surfactant adsorption by swelling and nonswelling layer silicates. *Langmuir*, **11**, 2508–2514.

Xu, S., Sheng, G. and Boyd, S.A. (1997) Use of organoclays in pollution abatement. *Advances in Agronomy*, **59**, 25–61.

Zhu, D., Herbert, B.E., Schlautman, M.A., Carraway, E.R. and Hur, J. (2004) Cation-π bonding: a new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *Journal of Environmental Quality*, **33**, 1322–1330.

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