

RELATION OF WATER AND NEUTRAL ORGANIC COMPOUNDS IN THE INTERLAYERS OF MIXED Ca/TRIMETHYLPHENYLAMMONIUM-SMECTITES

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Abstract—Organoclays were prepared by exchanging Ca^{2+} in a Ca^{2+} -saturated smectite partially or fully with trimethylphenylammonium (TMPA) cations. The mechanistic function of these organoclays as adsorbents for neutral organic compounds in aqueous solution was examined. TMPA cations were found to take a random distribution on the surfaces of mixed Ca/TMPA-smectites. The presence of TMPA, and its random distribution, resulted in water associated with the clay surfaces being held more weakly. Apparently, the interspersing of TMPA and Ca^{2+} ions prohibits the formation of a stable network of water molecules around Ca^{2+} . Water molecules associated with the siloxane surface in mixed Ca/TMPA-clays are removed during the adsorption of neutral organic compounds from bulk water, leaving only ~ 11 strongly held water molecules around each Ca^{2+} , as opposed to ~ 58 water molecules in homoionic Ca^{2+} -smectite. These results demonstrate that the amount of water associated with the clay surfaces and interlayers depends on the nature of the exchange cation(s), and not on the amount of available siloxane surface area by itself. We conclude that in TMPA-smectites the TMPA cations function as nonhydrated pillars, and sorption of organic solutes occurs predominantly on the adjacent siloxane surfaces, which are hydrophobic in nature. The water molecules around Ca^{2+} in mixed Ca/TMPA-smectites obscures some of the siloxane surfaces. This diminishes sorption capacity, in an amount roughly equivalent to the fraction of the CEC occupied by Ca^{2+} , because organic solutes cannot displace the waters of hydration of Ca^{2+} .

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 renders 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 nonpolar organic compounds are not strongly adsorbed on such hydrated 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 $[(\text{CH}_3)_3\text{NR}]^+$ or $[(\text{CH}_3)_2\text{NRR}']^+$. Previous studies have shown (Mortland et al. 1986; Boyd, Lee et al. 1988; Boyd, Mortland et al. 1988; Boyd, Sun et al. 1988; Boyd et al. 1991) that the organoclays are effective sorbents for removing organic compounds from water, and may therefore be useful in treating contaminated waters, and as components of clay barriers in waste disposal reservoirs. Soil clays can be converted to organoclays in this fashion, and this substantially enhances their sorptive capabilities for organic contaminants (Boyd, Lee et al. 1988; Lee et al. 1989). The formation of subsurface organoclay sorptive zones via *in-situ* injections of cationic surfactant solutions has been suggested (Boyd et al. 1991; Burris and Antworth

1992). If properly placed, such zones could intercept and immobilize subsurface chemical plumes, perhaps followed by degradation of the immobilized contaminants (Nye et al. 1994).

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; Boyd, Sun et al. 1988). 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 showed that clays modified with hexadecyltrimethylammonium (HDTMA) effectively sorb neutral organic contaminants via either singular or multiple mechanism(s) (Sheng et al. 1996a). 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, similar to solute partitioning into soil organic matter (Chiou et al. 1979, 1983). However, the isotherms describing sorption of aliphatics by HDTMA-clays are generally type III (Gregg and Sing 1982) compared to the linear isotherms commonly observed for sorption by 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

Table 1. Properties of TMPA-smectites.

Clay	Sample name	OC%	% of CEC occupied by TMPA	<i>d</i> (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

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, yielding 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, organoclays formed with small organic cations display adsorptive properties. Due to their small size, organic cations such as tetramethylammonium (TMA) or 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 (Gregg and Sing 1982) 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 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 the strong shape-selective adsorption characteristics of TMA-smectite. It was suggested that the lower degree of hydration of TMPA as compared to TMA accounted for the different adsorption characteristics of the corresponding organoclays. In a subsequent study (Jaynes and Boyd 1991), the charge density of smectite was chemically reduced, resulting in different TMPA contents in the organoclays. Adsorption was found to increase as layer charge and TMPA content decreased. Jaynes and Boyd (1991) concluded that the siloxane surface of smectite is hydrophobic, and aromatic molecules were mainly adsorbed on the siloxane surfaces between TMPA cations. TMPA cations had little direct effect on adsorp-

tion, and functioned as nonhydrated "pillars" to keep the smectite interlayers open for adsorption.

Considering the important effects of charge reduction and TMPA density 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 reduced-charge TMPA smectite and mixed Ca/TMPA-smectite because charge reduction leaves the hydrophobic siloxane surfaces available for the adsorption of organic compounds while Ca²⁺ in mixed Ca/TMPA-smectite will occupy the surfaces and may be hydrated. The overall objective of the current work is to evaluate the function of TMPA and Ca²⁺ cations in the adsorption of organic compounds on mixed Ca/TMPA-smectites.

MATERIALS AND METHODS

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⁻¹ (centimoles of charge kg⁻¹) (Jaynes and Boyd 1990) was obtained from the American Colloid Company (Chicago, Illinois). The <2 μm clay fractions were obtained by the wet sedimentation method, and subsequently Ca-saturated. TMPA bromide (Aldrich Chemical Co., Milwaukee, Wisconsin) was used to prepare organoclays. To obtain mixed Ca/TMPA clay, aqueous TMPA solutions were added to 2 L of smectite suspensions containing 25 g 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 (no white AgBr precipitate from addition of AgNO₃), and subsequently quick-frozen and freeze-dried. Organic carbon (OC) contents were determined using Dohrmann DC-190 high temperature TOC analyzer (Rosemount Analytical Inc., Santa Clara, California), and used to calculate the percent of CEC occupied by TMPA cations (Table 1).

The batch equilibration technique was used to quantify TMPA adsorption and Ca²⁺ release. Ca²⁺-saturated smectite (0.1 g) was weighed into a series of 25-mL Corex glass centrifuge tubes containing different volumes of aqueous TMPA bromide solutions (3.6 cmol L⁻¹), 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 d. After centrifugation at 8000 rpm (relative centrifugal force, RCF = 4302 g) for 10 min, a portion of each supernatant was taken and diluted to a concentration of be-

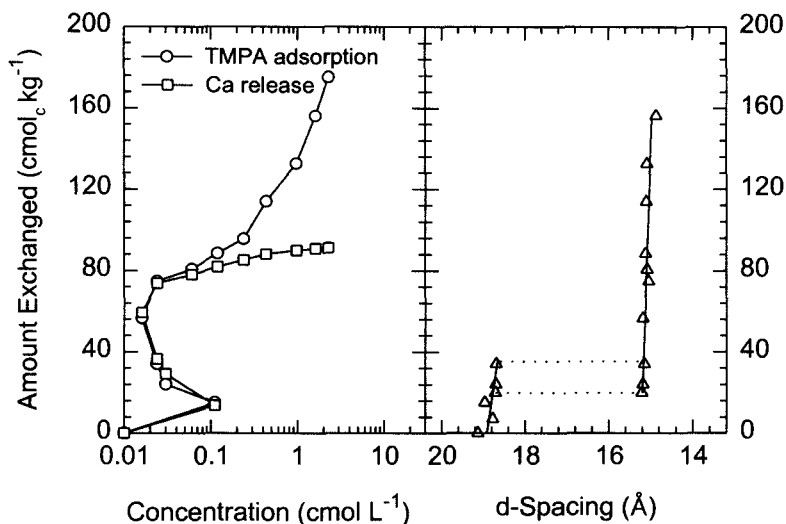


Figure 1. Adsorption of TMPA cations by, and release of Ca^{2+} , from a Ca^{2+} -smectite (left), and corresponding basal spacings (right).

tween 1 and 10 mg L⁻¹. TMPA concentrations were measured using an ultraviolet absorption spectrophotometer (Hewlett-Packard 8452A, Diode Array, Germany) at 254 nm. The Ca^{2+} concentrations were measured using an atomic absorption spectrophotometer (Perkin-Elmer 1100B, Norwalk, Connecticut). The amounts of TMPA adsorbed were calculated by the differences between the initial and equilibrium concentrations.

Basal spacings were determined by X-ray diffraction (XRD) analysis. TMPA-smectites with different degrees of TMPA exchange by Ca^{2+} 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 $\text{CuK}\alpha$ 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 $^{\circ}2\theta$, in steps of 0.02 $^{\circ}2\theta$, at 1 s/step.

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, Wisconsin). TMPA-smectites (0.2 g) 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 micro-liter syringe. The maximum amount of each compound added corresponded to a final equilibrium concentration of $\sim 50\%$ of its water solubility. The tubes were capped immediately with Teflon-backed septa and

shaken for 24 h on a reciprocating shaker at room temperature. Preliminary experiments showed that adsorption reached equilibrium within 18 h. After equilibration, the tubes were centrifuged at 8000 rpm (RCF = 4302 g) for 10 min. Supernatant (5 mL) was extracted with 10 mL of CS_2 in a glass vial.

Organic compounds in the CS_2 extracts were analyzed by gas chromatography. A Hewlett-Packard 5890A gas chromatograph was used with a flame ionization detector and a packed column (5% sp-1200/1.5% Bentonite 34 on 100/120Supelcoport, steel) with N_2 as the carrier gas. Concentrations were calculated from the measured peak areas using a series of external standards. Recoveries in blanks not containing TMPA-smectites were $\sim 90\%$; data were adjusted for the recoveries. Amounts adsorbed were calculated from differences between the amount of organic compounds added and that remaining in the final equilibrium solutions. Isotherms were obtained by plotting the amounts adsorbed against the equilibrium concentrations in solution.

RESULTS

The adsorption of TMPA cations by a Ca^{2+} -saturated smectite, and the release of Ca^{2+} are shown in Figure 1. The curves relating TMPA uptake and Ca^{2+} release to the equilibrium concentration of TMPA were initially superimposable, and formed a unique S-shaped isotherm. At a TMPA loading of about 80 cmol kg⁻¹, 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⁻¹. 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^{-1} , 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 sorption of TMPA in this study is higher than that reported in a previous study using Mg-smectite (Jaynes and Boyd 1990). The difference appears to be a lack of TMPA sorption beyond the CEC of the Mg-smectite, although this is only indicated by a single datum. The cause of this difference is unclear, but the greater TMPA sorption observed here may be due to the longer equilibration time (4 d vs. 8–12 h) and higher initial TMPA concentrations (8.0 vs 6.0 CEC). Washing with distilled water removes the excess of TMPA cations from smectite over the CEC, as indicated by OC content measurements in Table 1. The lowest equilibrium concentrations of TMPA cations in solution are associated with intermediate degrees of exchange of Ca^{2+} with TMPA cations, that is, from about 20 to 90% of the CEC.

Changes in basal spacings with the degree of TMPA exchange (Figure 1) show that at TMPA loadings up to about 16 cmol kg^{-1} , a single spacing of $\sim 19 \text{ \AA}$ was observed. Between 16 and 38 cmol kg^{-1} of TMPA loading, 2 spacings of about 19 and 15 \AA were present. The intensity of the 15-\AA peak increased and the intensity of the 19-\AA peak decreased as the TMPA loading increased over this range. At TMPA loadings above 38 cmol kg^{-1} , a single spacing of $\sim 15 \text{ \AA}$ was present. The peaks remained sharp and symmetrical over the range of TMPA loadings.

The adsorption isotherms for benzene, *o*-xylene, ethylbenzene, *n*-butylbenzene and trichloroethylene with mixed Ca/TMPA-smectites (Figure 2) were type I (L-type) (Gregg and Sing 1982; McBride 1994) 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 for the alkylbenzenes. The isotherms of *o*-xylene were type V (S-type) (Gregg and Sing 1982; McBride 1994), 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 loading increased from 0.17 CEC (17% of the CEC) to 0.65 CEC. TMPA loadings higher than 0.75 CEC, however, caused a decrease in the adsorptive ability of the clay; the adsorptive ability of SAC-TMPA1.0 is lower than that of SAC-TMPA.65 and SAC-TMPA.75 (Figure 2).

DISCUSSION

The unique S-shaped adsorption isotherm of TMPA, and the adsorption of TMPA in excess of the CEC indicate lateral interactions 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 edges of the aggregates. This promoted lateral interactions among adsorbed HDTMA molecules even at very low loadings, resulting in a monotonic isotherm. The fully expanded clay sheets in Na-smectite manifested a more random distribution of HDTMA at low loadings, and minimized lateral interactions. As the HDTMA 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 and a collapse of the clay layers occurred after about 20% of the CEC was satisfied by TMPA. In analogy to the exchange of Na^+ by HDTMA on smectite, the S-shaped isotherm of TMPA exchange with Ca^{2+} also indicates 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 more 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 of TMPA and Ca^{2+} is further evidenced by the 2 distinct basal spacings of 19 and 15 \AA , observed at low and high TMPA loadings, respectively. No XRD peaks were observed between 15 and 19 \AA . Initially, the interlayer spacing (19 \AA) is defined by the fully hydrated (inner plus outer sphere water molecules) Ca^{2+} ions. At a TMPA loading of about 20% of the CEC, the layers collapse to 15 \AA , apparently accompanied by a partial dehydration of the clay sheets. The 2 peaks occurred simultaneously over a range of TMPA loadings corresponding to ~ 17 to 42% of the CEC. This may indicate some variation in the charge density of the clay layers, producing a sequential collapse of clay layers of different charge densities. That is, some degree of clay nonhomogeneity with respect to surface charge density of the layers appears to exist. As such, some particles may dehydrate and collapse before others as the exchange reaction proceeds.

The distribution and interaction of organic cations in the interlayers of smectite has a pronounced effect

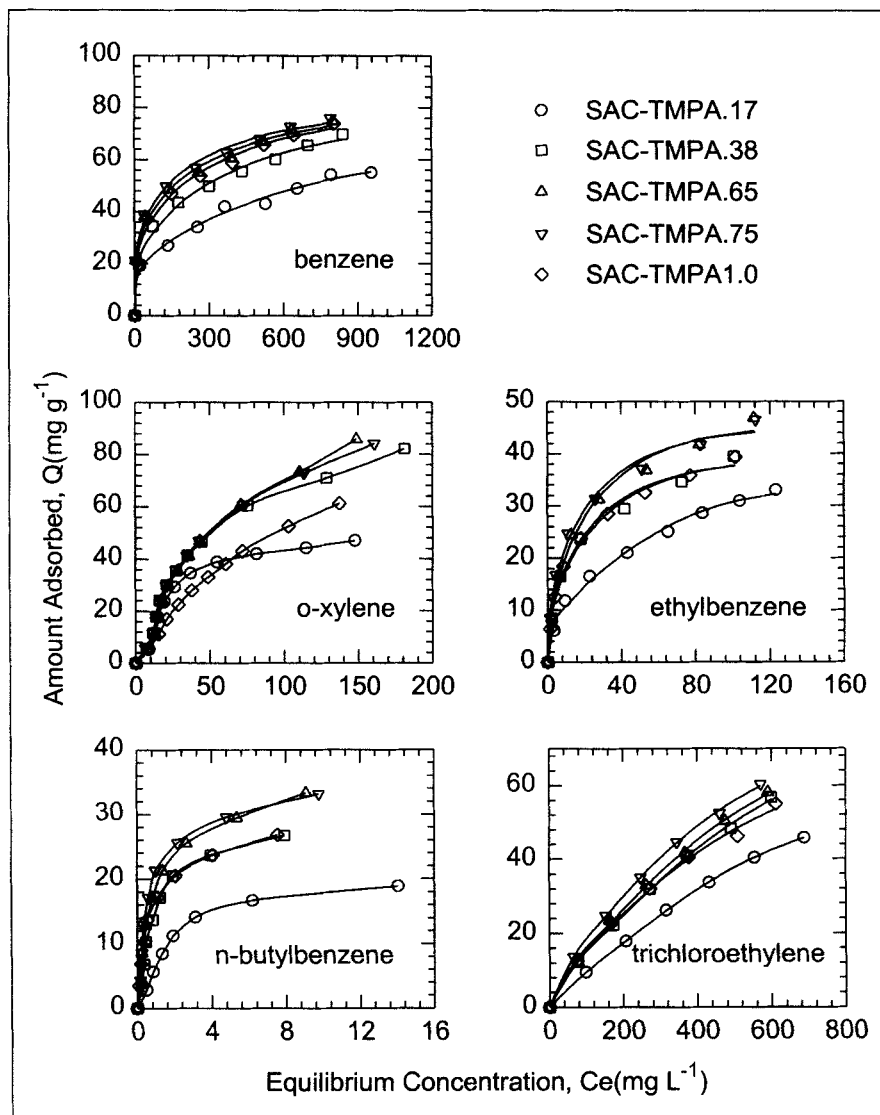


Figure 2. Adsorption of neutral organic compounds by TMPA-smectites from aqueous solutions.

on the adsorption of organic compounds. 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 the 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+} (Jaynes and Boyd 1991). Although adsorption isotherms on TMPA-smectites for neutral organic compounds are better described by the Dubinin–Radushkevich (DR) equation (Sheng et al. 1996b), the data can be adequately fitted to the Langmuir equation, and this allows comparison to the data reported by Jaynes and Boyd (1991), as described below. The monolayer adsorption capacities Q_m of benzene, ethyl-

benzene and *n*-butylbenzene on the mixed Ca/TMPA-smectites are summarized in Table 2. The steep initial rise of the curves generated from plots of the monolayer capacities versus OC (from TMPA) (Figure 3) is additional evidence that Ca^{2+} and TMPA cations are not segregated by layers. Otherwise, the monolayer adsorption capacity would be linearly correlated to TMPA content (OC content) in the smectite (dashed lines in Figure 3). A random distribution was also indicated for mixed Ca/TMA-smectite based on the surface area measurements (Lee et al. 1989).

In order to determine the effect of TMPA and Ca^{2+} on the adsorption of organic compounds, the adsorption capacities of SAC-TMPA.75 in our study and SAz-0.6Li-250-TMPA (a high-charge smectite from

Table 2. Monolayer adsorption capacities of benzene and mono-alkylbenzenes on TMPA-smectites.

Organo-clay type	OC%	Monolayer adsorption capacity (mg g ⁻¹)		
		Benzene	Ethylbenzene	<i>n</i> -butylbenzene
Ca/TMPA-smectite				
SAC-TMPA.17	1.66	61.4	38.3	22.4
SAC-TMPA.38	3.57	74.4	42.7	30.7
SAC-TMPA.65	5.88	77.3	50.5	36.8
SAC-TMPA.75	6.75	78.2	48.8	35.5
SAC-TMPA1.0	8.84	77.0	42.1	28.6
SAz-0.6Li-250-TMPA†	6.70	94.8	59.3	46.3

† Data from Jaynes and Boyd (1991).

Arizona, SAz, with Li added in an amount of 60% of the CEC to reduce charge) from Jaynes and Boyd (1991) were compared. The basis for comparison was that these 2 smectites have similar TMPA loadings (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 17.6% for benzene, 17.7% for ethylbenzene and 23.2% for *n*-butylbenzene (Table 2). This is near to but slightly less than the 25% of the CEC occupied by Ca²⁺. This implies that a portion of the siloxane surface in the mixed Ca/TMPA-smectite is covered by hydrated Ca²⁺ ions, roughly equal to the percent of the CEC occupied by Ca²⁺, leading to a diminution of adsorption capacity. This is consistent with the conclusion of Jaynes and Boyd (1991) that the siloxane surface between TMPA ions functions as the adsorptive region for neutral organic compounds in TMPA-smectite.

To further illustrate this, SAC-TMPA.75 is again chosen to calculate the area covered by Ca²⁺ cations, and their waters of hydration. A crystal radius of 0.99 Å for Ca²⁺ is used in the calculation. For SAC-TMPA.75, in which 25% of CEC is occupied by Ca²⁺ ions, the area covered by dehydrated Ca²⁺ ions per gram of the clay would be 2.09 m² g⁻¹. Jaynes and Boyd (1991) reported a surface area of 239.6 m² g⁻¹ for SAz-0.6Li-250-TMPA. If it is supposed (based on their nearly identical TMPA contents) that the surface areas of SAC-TMPA.75 without Ca²⁺ ions and of SAz-

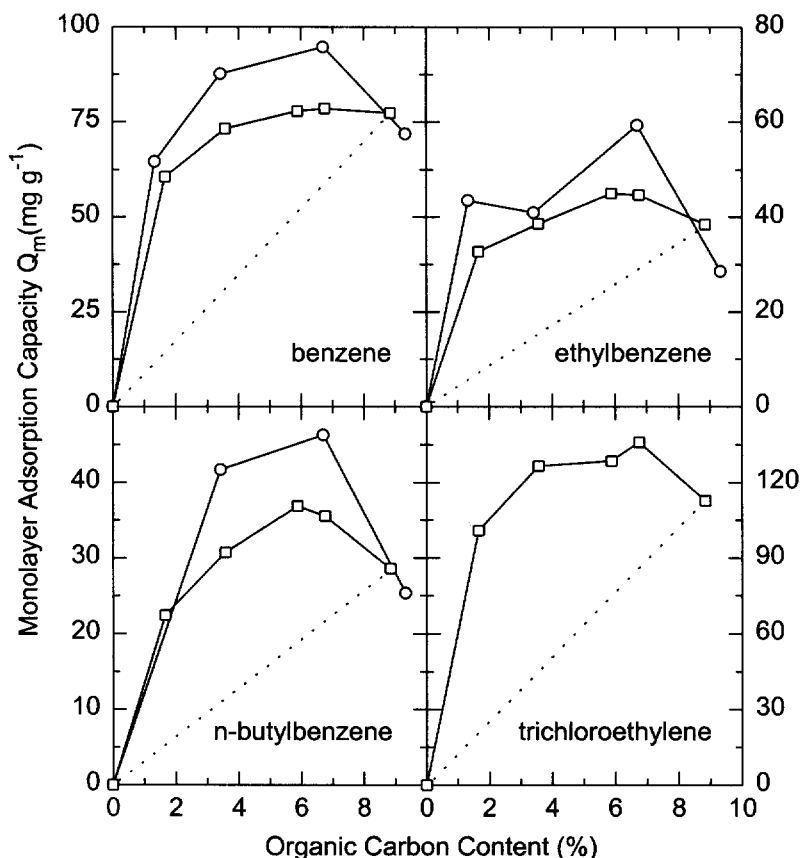


Figure 3. Dependence of monolayer adsorption capacity on organic carbon content for Ca/TMPA-smectites (squares) and reduced-charge TMPA-smectites from Jaynes and Boyd (1991) (circles).

0.6Li-250-TMPA are similar, 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 associated water molecules, then the area covered by water molecules is approximately $45.83 \text{ m}^2 \text{ g}^{-1}$ ($239.6 \times 20\% - 2.09$). This corresponds to a total number of monolayer water molecules $7.66 \times 10^{20} \text{ g}^{-1}$ (using the radius of water molecule equal to 1.38 Å (Hunt 1965)). Thus, the ratio of the number of water molecules on the surface to that of Ca^{2+} ions in SAC-TMPA.75 is 11.3. If the surface in SAC-TMPA.75 were completely covered by Ca^{2+} and water ($2.09 \text{ m}^2 \text{ g}^{-1}$ by Ca^{2+} , and $237.5 \text{ m}^2 \text{ g}^{-1}$ by water), then the ratio of $\text{H}_2\text{O}/\text{Ca}^{2+}$ would be 58.8. Similarly, if the water vapor isotherm on the same Ca^{2+} -smectite reported by Boyd, Mortland and Chiou (1988) is used to calculate the ratio of $\text{H}_2\text{O}/\text{Ca}^{2+}$ in the smectite, the limiting adsorption amount of water vapor on smectite obtained is $\sim 236 \text{ mg g}^{-1}$ by extrapolating the linear portion of the isotherm to $p/p_0 = 1$. This adsorption amount gives the ratio of $\text{H}_2\text{O}/\text{Ca}^{2+} = 57.4$ at $p/p_0 = 1$. This number is very close to that in SAC-TMPA.75 calculated using an assumed monolayer of water. Thus, the amount of water associated with SAC-TMPA.75 in the presence of bulk water containing organic solutes is much less than the monolayer amount, demonstrating that a large part of the siloxane surface is not covered by water, and therefore available for the adsorption of organic compounds. These calculations indicate that, in the presence of organic solutes, TMPA cations in mixed Ca/TMPA-smectites substantially reduce the amount of water associated with each Ca^{2+} ion, and with the surfaces as a whole. Thus, the nature of the exchange cation(s), not the amount of siloxane surface area by itself, 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. This may be due to a disruption of the network of water molecules around Ca^{2+} ions when TMPA is interspersed with Ca^{2+} in a more or less random distribution. 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 are still strongly held. The ratio of $\text{H}_2\text{O}/\text{Ca}^{2+}$ of ~ 11 suggests that most of the water molecules present in SAC-TMPA.75 are coordinated or strongly associated with Ca^{2+} , since the coordination number for Ca^{2+} with H_2O is 6. The other 47 molecules of water (58–11) per Ca^{2+} are apparently displaced by the sorption of neutral organic compounds from bulk water.

In general, the replacement of Ca^{2+} by TMPA enhances the adsorptive ability of the resultant clay for neutral organic compounds. However, this effect may

be mitigated at high TMPA loadings. At low TMPA loadings, TMPA cations function as weakly hydrated pillars which make the hydrophobic siloxane surface available for adsorption. Up to a point, the higher the TMPA loading, the more surface is available for the adsorption of organic compounds. However, when the amount of TMPA cations in smectite is high enough, that is, 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 loadings of TMPA cations than at intermediate loadings.

Lee et al. (1989) and Kukkadapu and Boyd (1995) 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 $\sim 32 \text{ kcal mol}^{-1}$. TMPA-smectites, like tetramethylphosphonium (TMPP)-smectites, do not show this water-induced shape selectivity, indicating that TMPA (like TMPP) is less strongly hydrated. The lack of hydration water around TMPA maintains the size of the adsorptive regions between TMPA ions, even in the presence of bulk water. However, adsorbates of sufficient size may still be sterically excluded. In TMPA-smectites, all mono-alkylbenzenes with the same width showed high affinity for the surface. However, the presence of methyl groups in adjacent positions of *o*-xylene aromatic ring increases the width of the molecule as compared to mono-alkylbenzenes. This creates steric hindrance, which leads to a weaker adsorbent-adsorbate interaction between *o*-xylene molecules and the siloxane surfaces.

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