

HYDROPHOBICITY OF SILOXANE SURFACES IN SMECTITES AS REVEALED BY AROMATIC HYDROCARBON ADSORPTION FROM WATER

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Abstract—The nature of the siloxane surface in smectites was investigated by measuring the adsorption of aromatic hydrocarbons from water by organo-clays. The organo-clays were prepared by replacing the hydrophilic, inorganic exchange cations of a series of smectites with the small, hydrophobic organic cation, trimethylphenylammonium (TMPA). Smectites with a range in charge densities were used that resulted in different TMPA contents in the organo-clays. Adsorption isotherms of benzene, alkylbenzenes, and naphthalene from water by the TMPA-smectites indicated that sorption was inversely related to TMPA content. The Langmuir form of the isotherms suggests that the aromatic compounds adsorb to the clay surface. Possible adsorptive sites in TMPA-smectites are limited to the TMPA cations and the siloxane oxygen surfaces. Because sorption increased as layer charge and TMPA content decreased, the organic compounds must adsorb to the siloxane surfaces.

Calculations based on an adsorbed compound monolayer, which was estimated by fitting adsorption data to the Langmuir equation, and the N_2 specific surface area of each TMPA-clay, indicate that the surface area occupied by each adsorbed molecule increases as the planar area of the molecule increases. This strongly indicates that the planar surfaces of the compounds adsorb directly to the clay surface. Apparently, the TMPA cations function to keep the smectite interlayers open. Interactions between the phenyl groups of TMPA cations on opposing interlayer clay surfaces may act to increase the size of the adsorptive regions. These results show that the siloxane surfaces of smectites can effectively adsorb aromatic hydrocarbons from water if the hydrophilic, inorganic exchange cations are replaced with small, hydrophobic organic cations. The strong adsorption of hydrophobic organic molecules from water demonstrates the hydrophobicity of the siloxane surfaces in smectites.

Key Words—Adsorption isotherm, Alkylbenzene, Benzene, Langmuir equation, Naphthalene, Organo-clay, Surface area.

INTRODUCTION

Early research on clays emphasized the importance of the surface silicate oxygens on water adsorption due to hydrogen bonding (Hendricks and Jefferson, 1938; Bradley, 1945; Low, 1961). Conversely, Graham (1964) concluded that the interlayer cations have a major effect on fixing the sites of water adsorption, and that the surface oxygens have only a minor effect. Similarly, Sposito and Prost (1982) concluded that the spatial arrangement of adsorbed water molecules is largely controlled by the exchangeable cations, but they argued that the role of the silicate surface cannot be neglected.

The capability of the basal oxygens to form hydrogen bonds with water (hydrophilicity) is determined by the Lewis base (i.e., electron pair donor) character of the (Si,Al)-O bonds. Sposito and Prost (1982), Sposito (1984), and Bleam (1990) stated that the Al-O surface oxygens in tetrahedrally-substituted phyllosilicates should have relatively strong Lewis basicities and would be expected to form strong hydrogen bonds. Similarly, Chen (1976) found that synthetic zeolites (mordenite) became more hydrophilic as the Al content was in-

creased. He concluded that the hydrophilic character of the zeolite was caused by the alumina tetrahedra.

Farmer and Russell (1971) stated that because the negative charge in octahedrally-substituted clays must be distributed over at least 10 surface oxygens, these surface oxygens should be weaker electron donors (Lewis bases) than those in tetrahedrally-substituted clays. Similarly, Sposito and Prost (1982) suggested that the surface oxygens in octahedrally-substituted smectites should form weak hydrogen bonds with water due to delocalization of the octahedral charge deficit. In contrast, Bleam (1990) maintained that the octahedral charge deficit cannot be delocalized beyond the cation-oxygen coordination polyhedra. He further argued that the surface oxygens both in octahedrally-substituted smectites (e.g., montmorillonite, hectorite) and neutral-layer phyllosilicates (e.g., talc, pyrophyllite) should have Lewis basicities too low to hydrogen-bond effectively.

Neutral-layer phyllosilicates such as talc and pyrophyllite are known to be rather hydrophobic. However, for smectites, the strong hydration of metal exchange cations obscures the inherent hydrophilicity or hydro-

phobicity of the siloxane surfaces. If the hydrophilic character of smectites is due predominately to the exchangeable metal cations, replacement of the inorganic cations with hydrophobic organic cations should greatly diminish the hydrophilic nature of the clay. This might facilitate the direct adsorption of hydrophobic organic compounds to the clay surface. Alternatively, if the siloxane surfaces are inherently hydrophilic, significant adsorption of hydrophobic organic molecules from water should not occur due to the preferential adsorption of water.

We have examined the sorptive removal of hydrophobic organic contaminants from water by several organo-clays formed by displacing the inorganic exchange cations with different organic cations. These studies have shown that when small organic cations such as tetramethylammonium (TMA) are used, the clays act as surface adsorbents, although the nature of the adsorptive interaction is poorly understood. Lee *et al.* (1989) found that the sorption of benzene from water by TMA-smectites yielded a Langmuir-type isotherm. However, sorption of alkylbenzenes by TMA-smectite decreased sharply as the size of the alkyl substituent increased, resulting in a variety of isotherm types. Jaynes and Boyd (1990) found that organo-smectites formed using trimethylphenylammonium (TMPA) consistently yielded Langmuir-type isotherms for benzene and many alkylbenzenes. Giles *et al.* (1960) stated that Langmuir-type isotherms (L curves) are usually indicative of molecules adsorbed flat on the surface.

The adsorptive behavior of TMA- and TMPA-smectites are in direct contrast to the partition behavior of organo-clays made with large organic cations such as hexadecyltrimethylammonium (HDTMA). The effectiveness of HDTMA-smectites as sorbents of alkylbenzenes was increased if high-charge clays were used. Sorption was enhanced by the greater basal spacings and greater organic carbon contents of the high-charge HDTMA-clays (Jaynes and Boyd, 1991). In contrast, Lee *et al.* (1990) and Jaynes and Boyd (1990) found that the adsorptive capacity of TMA- and TMPA-smectites for aromatic hydrocarbons was much greater for organo-smectites formed from low-charge rather than high-charge smectites.

The objective of this study was to determine the nature of the adsorptive interaction of aromatic hydrocarbons with TMPA-smectite. To this end, the sorptive removal of several aromatic hydrocarbons from water by TMPA-smectites was evaluated using adsorption isotherms. The montmorillonite charge reduction technique of Hofmann and Klemen (1950) was used to prepare reduced-charge montmorillonites and determine whether the greater sorptivity of low-charge TMPA-smectites is increased by further decreases in layer charge and thus TMPA content. Our results show that the siloxane surfaces are the most probable ad-

sorptive sites and demonstrate the hydrophobic nature of these surfaces.

MATERIALS AND METHODS

Samples

A Wyoming montmorillonite (SAC) was obtained from the American Colloid Company. Two other smectites, an Arizona montmorillonite (SAz) and a Washington nontronite (SWa) were obtained from the Source Clays Repository of The Clay Minerals Society. The <2- μm fractions were obtained by wet sedimentation and were subsequently Mg-saturated, frozen, and freeze-dried.

Lithium charge reduction

A series of reduced-charge montmorillonites were prepared from sample SAz by mixing Li-saturated and Na-saturated clay suspensions in the ratios 0.3Li/0.7Na, 0.6Li/0.4Na, 0.8Li/0.2Na, and 1.0Li/0.0Na according to the procedure described by Brindley and Ertem (1971). The suspensions were thoroughly mixed, quick-frozen, and freeze-dried. The freeze-dried clays were later heated in beakers at 250°C for 8–12 hours. These reduced-charge clays are subsequently referred to as 0.3Li-250, 0.6Li-250, 0.8Li-250, and 1.0Li-250, respectively. Jaynes and Bigham (1987) found that the cation-exchange capacity (CEC) of heated, Li/Na-saturated SAz clay was directly proportional to the exchangeable Li fraction prior to 250°C heating. Hence, the CEC of the reduced-charge clays was estimated to be 0.7, 0.4, 0.2, and 0.1 times the CEC of the natural clay (i.e., estimated CECs = 91, 52, 26, and 13 meq/100 g, respectively). A cation-exchange capacity of 13 meq/100 g was assumed for the 1.0Li-250 clay to allow for any residual charge due to tetrahedral substitutions and crystal edge sites.

Organo-clay preparation

Trimethylphenylammonium (TMPA) organo-clays were prepared by adding quantities of TMPA chloride equal to 5–10 times the CEC of the clay. The TMPA chloride was dissolved in distilled water and added to clay suspensions that were agitated on a magnetic stirrer. After mixing for 4 hours, the TMPA clay suspensions were sealed in dialysis tubing and dialyzed in distilled water until a chloride test with AgNO_3 indicated that the samples were free of salts.

Organo-clays were also prepared from the reduced-charge clays. However, the reduced-charge clays were first ultrasonically dispersed in 1:1 ethanol/water to promote reexpansion prior to TMPA exchange. Brindley and Ertem (1971) found that this treatment would effectively reexpand reduced-charge clays. Trimethylphenylammonium chloride was dissolved in ethanol and mixed with the reduced-charge clay suspensions in an amount equal to 10 times the estimated CEC.

The suspensions were placed on a reciprocating shaker for 8–12 hours and were subsequently sealed in dialysis tubing and dialyzed as above until free of salts. The resulting suspensions of the natural and reduced-charge TMPA-clays were quick-frozen and freeze-dried. Organic carbon analyses were performed on the natural clays and organo-clays by Huffman Laboratories, Inc., Golden, Colorado.

Physical characterization

Surface areas were determined using the BET equation (Brunauer *et al.*, 1938) and 3-point N₂ gas adsorption isotherms. A Quantasorb Junior (Quantachrome Corp.) sorption meter was used on samples that were degassed at 120°C under vacuum for 8–12 hours. Surface areas were determined at liquid N₂ temperatures using N₂ as the adsorbate and He as the carrier gas. Monolayer surface areas were then calculated after fitting the 3 points ($P/P^{\circ} = 0.06, 0.11, 0.26$) of each isotherm to the BET equation.

Basal spacings (d001) of the natural clays and organo-clays were determined by X-ray diffraction. Samples (30 mg) of the TMPA-clays were ultrasonically dispersed in 2 ml of 95% ethanol and dried as oriented aggregates on glass slides. Oriented aggregates of the natural clays were prepared by allowing aqueous suspensions containing 30 mg of clay to dry on glass slides. Basal X-ray diffraction spacings were then recorded using CuK α radiation and a Philips APD 3720 automated X-ray diffractometer using an APD 3521 goniometer fitted with a theta-compensating slit, a 0.2-mm receiving slit, and a diffracted beam graphite monochromator.

Adsorption isotherms

Batch adsorption isotherms of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and naphthalene on the TMPA-clays were made by weighing 5 to 200-mg samples into 25 ml Corex centrifuge tubes that contained 25 ml of distilled water. Hamilton microliter syringes were used to deliver a range of concentrations of each compound up to 70% of the water solubility. Benzene was added directly as the neat liquid, whereas toluene, ethylbenzene, propylbenzene, butylbenzene, and naphthalene were delivered as methanol solutions. All samples were prepared in duplicate. Effective adsorption of the added organic compounds made it necessary to repeat many of the isotherms using smaller sample weights. Blank samples containing 25 ml of distilled water and the added organic compounds were also prepared to estimate vaporization losses and adsorption to the glass. Samples were placed on a reciprocating shaker and agitated for 12–18 hours under ambient conditions. After centrifugation, a 1–5-ml aliquot of the supernatant was extracted with 10 ml of CS₂ in a glass vial. A portion of

the CS₂ extract containing the extracted compound was then analyzed using gas chromatography.

Isotherms were constructed by plotting the amounts sorbed (Q) versus the concentrations remaining in solution (C_e). The amount sorbed was calculated from differences between the quantity of organic compound added and that remaining in the equilibrium solutions. The amount remaining in solution ranged from 0 to 75% and typical blank recoveries ranged from 85 to 95%. The data were not adjusted for these recoveries. The average of duplicate samples was plotted for each point in the presented isotherms. The agreement between duplicates was generally good enough that both points plotted within the area covered by the point marker.

Gas chromatography

Concentrations of the organic compounds in the CS₂ extracts were measured with a Hewlett Packard 5890A gas chromatograph using a flame ionization detector. A packed column with N₂ as the carrier gas was used for all separations. Peak areas were determined with a Hewlett Packard 3392A integrator and a Hewlett Packard 7673A automatic sample changer was used to automate runs.

Langmuir equation

Adsorption isotherm data for the organic compounds were fitted to the Langmuir equation (i.e., $C_e/Q = mC_e + b$) by plotting C_e/Q versus C_e . Data sets that conform to the Langmuir model yield a straight line with slope m and intercept b (Hiemenz, 1986). Linear regression analyses of C_e/Q versus C_e (values converted to molar units) were made on the isotherm data. The slope m , the intercept b , and the r^2 value (a measure of linearity) were determined for each isotherm. If adsorption data fully conform to the model, the parameters m and b have physical significance. Then the Langmuir parameters and the measured organo-clay surface areas can be used to calculate the surface area occupied per molecule (σ°) using the relation: $\sigma^{\circ} = m \times A_{sp}/N_A$; where m = the slope from fit to Langmuir equation, A_{sp} = specific surface area, and N_A = Avogadro's number. The value of $1/m$ is an estimate of the number of moles of the adsorbed compound per g of organo-clay at monolayer coverage. Isotherm data sets that yielded r^2 values less than 0.65 were not deemed to be of the Langmuir type and were fitted to a constant partitioning model (i.e., $Q/C_e = \text{constant}$). Linear regression analyses of Q versus C_e were subsequently made on these data sets with slope K and the intercept forced through the origin (i.e., $K = Q/C_e + 0$). K is also termed the sorption coefficient. Confidence intervals at the 95% level were calculated for the parameters m , b , σ° , and K (Steel and Torrie, 1980).

Table 1. Properties of reference clays and organo-clays.

Sample	CEC	O.C.	d001 ¹	BET surface area
	meq/100 g	%	Å	m ² /g
SAC-Mg <2 μm	90	0.19	15.5 (10.4)	43.9
SAC-TMPA	—	9.12	14.8	109.1
SWa-Mg <2 μm	107	0.18	15.0 (10.4)	85.5
SWa-TMPA	—	9.70	15.4	105.6
SAz-Mg <2 μm	130	0.15	15.3 (10.4)	85.0
SAz-TMPA	—	11.39	15.3	71.1
SAz-0.3Li-250-TMPA	—	9.33	14.9	146.7
SAz-0.6Li-250-TMPA	—	6.70	14.4	239.6
SAz-0.8Li-250-TMPA	—	3.42	12.7	168.5
SAz-1.0Li-250-TMPA	—	1.33	9.8	110.5

¹ The d001 values in parentheses are those expected under the conditions in which the BET N₂ surface areas were performed (i.e., evacuated, 120°C).

RESULTS AND DISCUSSION

Physical characterization

Characteristics of the natural clays and the prepared organo-clays are presented in Table 1. The CEC values of SAC, SWa, and SAz indicate that the relative charge densities of these smectites are low, intermediate, and high, respectively. The organic carbon contents of the organo-clays reflect the charge density. The carbon content is higher in the clays with greater charge. This is especially clear for SAz-TMPA and the reduced-charge SAz-TMPA clays. Organic carbon contents in these clays vary from 11.4% in SAz-TMPA to 1.3% in 1.0Li-250-SAz-TMPA.

X-ray diffraction indicates a basal spacing of about 15 Å for SAC-TMPA, SWa-TMPA, and SAz-TMPA. Charge does not appear to affect the spacings. The d001 spacings of the reduced-charge SAz-TMPA samples vary from about 14.9 Å down to 9.8 Å. The 12.7 Å spacing of 0.8Li-250 SAz-TMPA indicates an interstratification between expanded layers and collapsed layers. The 9.8 Å spacing in the 1.0Li-250 SAz-TMPA clay indicates a complete collapse of the interlayer region. Here, the adsorbed TMPA must be largely confined to external sites on the clay particles.

The surface areas of the natural, Mg-saturated clays are comparable to values reported by van Olphen and Fripiat (1979) for a Wyoming montmorillonite (SWy, 31 m²/g) and for an Arizona montmorillonite (SAz, 94 m²/g). Because Mg-saturated clays collapse to 10.4 Å at 110°C (MacEwan and Wilson, 1980; table 3.5, p. 213), the measured N₂ surface areas should primarily reflect the external area. In contrast, the TMPA cations should maintain interlayer expansion in SAC-TMPA, SWa-TMPA, and SAz-TMPA. Hence, the surface areas of the TMPA-clays should be greater than the Mg-saturated clays. The surface areas of SAC-TMPA and SWa-TMPA are greater than the corresponding Mg-saturated clays. But, SAz-TMPA has a somewhat lower

surface area than SAz-Mg. This implies that much of the interlayer surface of SAz-TMPA is covered by TMPA cations and is therefore, not accessible to N₂. Reducing the charge of SAz prior to TMPA exchange substantially increases the surface area. Surface areas of the reduced-charge SAz-TMPA clays increase with 0.3Li-250 up to 0.6Li-250. With greater charge reduction, partial and complete collapse of the interlayers in 0.8Li-250 and 1.0Li-250, respectively, resulted in lower surface areas.

Adsorption isotherms

The adsorption of benzene and propylbenzene to the SAC-, SWa-, and SAz-TMPA organo-clays is shown in Figure 1. Benzene and propylbenzene adsorption to these organo-clays is inversely related to charge; the TMPA-clay derived from the low-charge clay (SAC-TMPA) is the best sorbent. All of the benzene isotherms and two of the propylbenzene isotherms are of the Langmuir type, which suggests adsorption to the clay surface and not partitioning into an organic phase derived from the TMPA cations. The latter interactions would be expected to result in characteristically linear isotherms, as in the case of HDTMA-smectites (Jaynes and Boyd, 1991). The drawings in Figure 2 suggest a possible explanation for the inverse dependence of adsorption on charge. Trimethylphenylammonium is a small organic cation which forms monolayers (15 Å) in the interlayers of both high-charge and low-charge smectites. The TMPA cations in low-charge smectites should be more isolated physically than those in high-charge smectites. This would leave more of the interlayer clay surface available as adsorption sites.

Benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and naphthalene isotherms for SAz-TMPA and two reduced-charge SAz-TMPA organo-clays are presented in Figure 3. The charge density of the clays used to prepare TMPA organo-clays affected both the

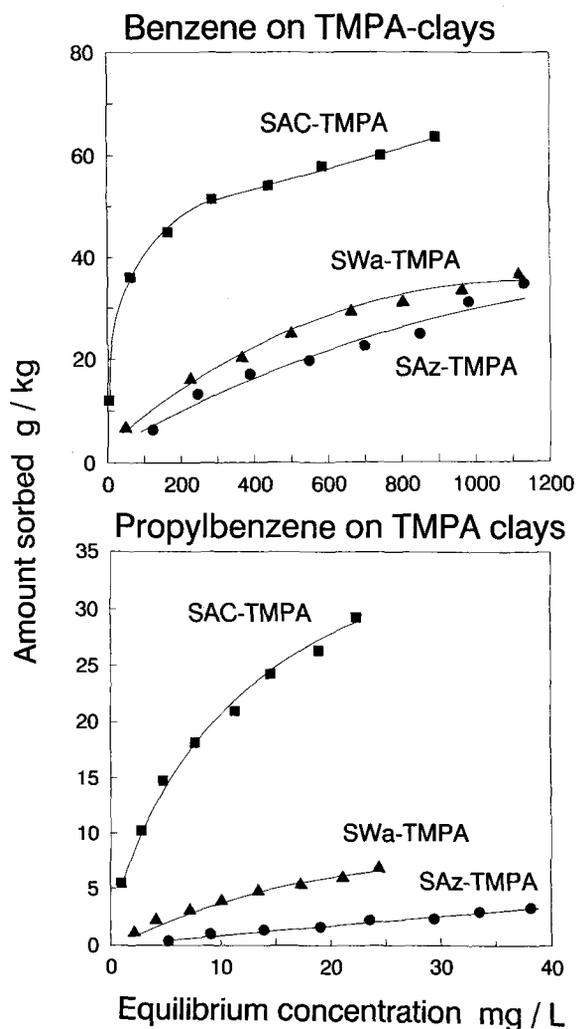


Figure 1. Adsorption isotherms of benzene and propylbenzene to SAC-TMPA, SWa-TMPA, SAz-TMPA.

shape of the isotherm and the resultant sorptive capacity. Although benzene sorption on SAz-TMPA was appreciable, the sorption progressively decreased as the size of the aromatic hydrocarbon increased in the order: toluene > ethylbenzene > propylbenzene \approx butylbenzene \approx naphthalene. The linear isotherms observed for the alkylbenzenes and naphthalene indicate weak sorptive interactions with SAz-TMPA. The TMPA cations in SAz-TMPA may be too closely spaced to permit adsorption of molecules larger than benzene to the clay surface. In contrast, the sorption of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and naphthalene to the reduced-charge SAz-TMPA clays (0.3Li-250, 0.6Li-250) yields Langmuir-type isotherms.

Naphthalene was strongly sorbed by the low-charge clays (i.e., 0.6Li-250 SAz-TMPA and SAC-TMPA) and yielded Langmuir-type isotherms. Naphthalene sorption by SAC-TMPA was intermediate between that of

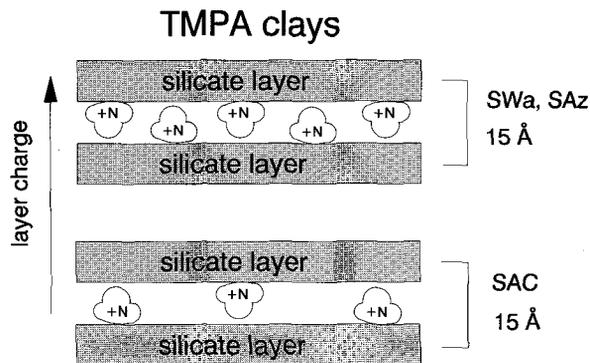


Figure 2. Trimethylphenylammonium cations in smectite interlayer.

0.6Li-250 SAz-TMPA and 0.3Li-250 SAz-TMPA (Figure 3). In contrast, the higher-charge clays SAz-TMPA, 0.3Li-250-SAz-TMPA, and SWa-TMPA did not sorb naphthalene as effectively and yielded linear isotherms over the concentration range evaluated. The linear sorption coefficients ($K = 2769, 644, 9138$; Table 2) of SWa-TMPA, SAz-TMPA, and 0.3Li-250-SAz-TMPA, respectively, are comparable to those determined on HDTMA-smectites ($K = 1130$ to 4818, Jaynes and Boyd, 1991).

The effect of Li charge reduction on the sorptive capacity of the Li-250, SAz-TMPA clays is similar to that of the natural TMPA clays; the lower the charge, the greater the sorptive capacity. Because lower charge clays have less TMPA (see %O.C. Table 1), the TMPA cations must have little direct effect on sorption and may only function to prop open the interlayers. The isotherms in Figure 4 argue even more strongly that the TMPA cations only indirectly affect adsorption. Benzene and ethylbenzene sorption by 1.0Li-250 SAz-TMPA is much greater than that by SAz-TMPA despite the fact that the latter has 10 times more TMPA. Calculated with a benzene monolayer, the benzene to TMPA molar ratio is 0.5/1 in SAz-TMPA and 7.0/1 in 1.0Li-250 SAz-TMPA. Hence, the organic compounds must adsorb to the siloxane surface rather than to the TMPA.

The increased retention of the organic compounds with the decreased charge and TMPA content suggests that exchanged TMPA cations are not directly involved in the adsorption. The TMPA cations may only function as "pillars" to keep the interlayers apart. Thus, the siloxane surface of the clay appears to be the actual adsorptive surface. The preferential adsorption of hydrophobic organic compounds to smectites in the presence of bulk water implies that the siloxane surface is hydrophobic. This view is supported by Skipper *et al.* (1989) who made computer calculations of the water-clay interactions in talc using atomic pair potentials. They asserted that the surface oxygens can be regarded as hydrophobic because the bonding between the surface oxygens and water are not as strong as the inter-

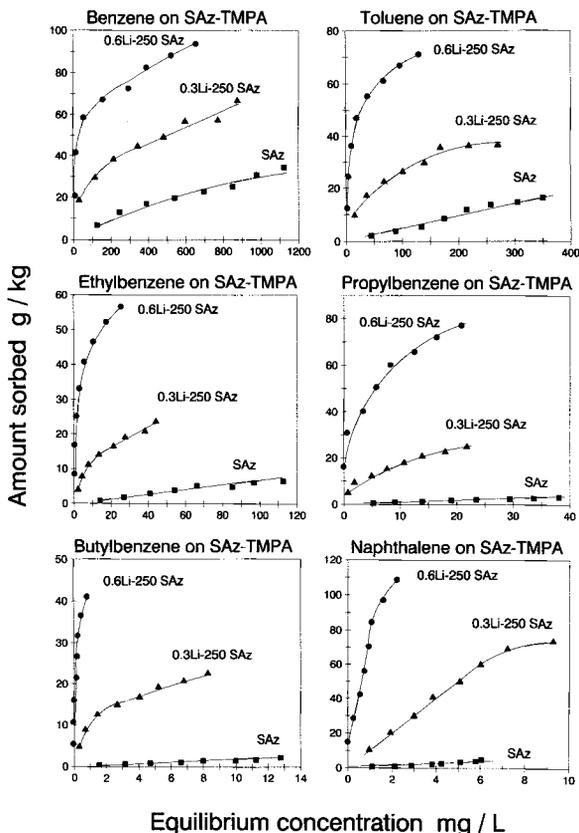


Figure 3. Adsorption isotherms of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and naphthalene to SAz-TMPA, 0.3Li-250 SAz-TMPA, and 0.6Li-250 SAz-TMPA.

molecular bonding in water. Similarly, studies on the sorption of water and hydrocarbons by zeolites have shown that the Si-O-Si bonds are probably hydrophobic in nature (Chen, 1976). In TMPA-smectites, the exchanged TMPA cations displace the hydrophilic, inorganic exchange cations enabling hydrophobic organic molecules to interact directly with the siloxane surfaces.

Fit of adsorption data to Langmuir model

The parameters of a fit of the adsorption data to the Langmuir model are presented in Table 2. The r^2 values in Table 2 of samples marked "L" are all greater than 0.89 and are typically greater than 0.98. This indicates that the isotherm data are at least empirically consistent with the Langmuir model. The naphthalene sample marked "L?" had an r^2 value less than 0.80, but the isotherm is more consistent with the Langmuir model than with a linear model. The samples marked "C" are more consistent with a linear model and were fitted to the line $K = Q/C_e + 0$ using linear regression.

Calculations based on Langmuir parameters

The surface area per molecule (σ°) of the adsorbed compounds was calculated using the Langmuir coef-

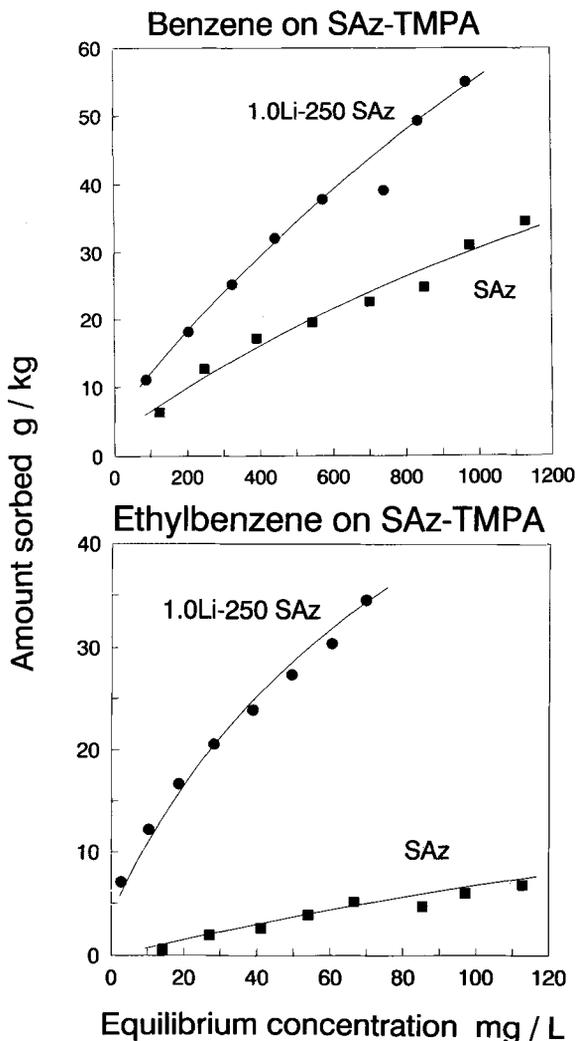


Figure 4. Adsorption isotherms of benzene and ethylbenzene to SAz-TMPA and 1.0Li-250 SAz-TMPA.

ficients (Table 2) and the measured N_2 surface areas (Table 1). In general, the calculated σ° values increase as the molecules increase in size from benzene to butylbenzene. According to Hiemenz (1986), a progressive increase of σ° values with increases in the planar dimensions of the adsorbed molecules strongly suggests that the adsorbed molecules lie flat on the adsorbent surface. However, Barrer and Perry (1961) argued that the separation of TMA cations in TMA-smectite is not large enough to allow adsorption of benzene to the siloxane surface. They argued that benzene must instead adopt a tilted orientation in contact with the tetrahedral faces of TMA cations. Yet, their arguments were implicitly based on the assumption that the TMA cations on opposing interlayer clay surfaces adopt a staggered arrangement. Larger areas of the clay surface would be available if the organic cations on opposing clay surfaces interacted, as shown schematically in Figure 5. This might also be a more stable arrangement

Table 2. Parameters of adsorption data fitted to Langmuir equation.

Sample clay	Type ¹	Langmuir		r ²	$\sigma^{\circ 2}$
		m	b		
		g clay/mole cpd	g clay/liter		$\text{\AA}^2/\text{molecule}$
Benzene					
SAC-TMPA	L	1202 ± 93	0.876 ± 0.472	0.994	21.8 ± 1.7
SWa-TMPA	L	1696 ± 256	8.285 ± 1.899	0.978	29.8 ± 4.5
SAz-TMPA	L	1774 ± 344	14.682 ± 2.091	0.981	21.0 ± 4.1
0.3Li-250 SAz-TMPA	L	1086 ± 208	2.267 ± 1.139	0.965	26.5 ± 5.1
0.6Li-250 SAz-TMPA	L	824 ± 96	0.434 ± 0.322	0.987	32.8 ± 3.8
0.8Li-250 SAz-TMPA	L	891 ± 153	1.162 ± 0.664	0.971	24.9 ± 4.3
1.0Li-250 SAz-TMPA	L	1209 ± 341	7.178 ± 1.728	0.960	22.2 ± 6.3
Toluene					
SAC-TMPA	L	2135 ± 147	0.512 ± 0.073	0.995	38.7 ± 2.7
SWa-TMPA	L	2820 ± 609	6.358 ± 0.908	0.955	49.5 ± 10.7
SAz-TMPA	C	K = 49 ± 3		0.979	N.A.
0.3Li-250 SAz-TMPA	L	2030 ± 221	1.382 ± 0.305	0.988	49.5 ± 5.4
0.6Li-250 SAz-TMPA	L	1218 ± 75	0.157 ± 0.038	0.997	48.5 ± 3.0
0.8Li-250 SAz-TMPA	L	918 ± 247	0.565 ± 0.356	0.932	25.7 ± 6.9
Ethylbenzene					
SAC-TMPA	L	2485 ± 314	0.437 ± 0.094	0.984	45.0 ± 5.7
SWa-TMPA	L	4932 ± 365	3.961 ± 0.168	0.995	86.5 ± 6.4
SAz-TMPA	C	K = 63 ± 6		0.944	N.A.
0.3Li-250 SAz-TMPA	L	3708 ± 503	0.453 ± 0.094	0.982	90.4 ± 12.3
0.6Li-250 SAz-TMPA	L	1787 ± 73	0.034 ± 0.005	0.995	71.1 ± 2.9
0.8Li-250 SAz-TMPA	L	2590 ± 492	0.035 ± 0.009	0.965	72.5 ± 13.8
1.0Li-250 SAz-TMPA	L	2436 ± 587	0.600 ± 0.192	0.945	44.7 ± 10.8
Propylbenzene					
SAC-TMPA	L	3310 ± 433	0.190 ± 0.038	0.983	60.0 ± 7.9
SWa-TMPA	L	9696 ± 1002	1.737 ± 0.104	0.969	170.1 ± 17.6
SAz-TMPA	C	K = 88 ± 11		0.980	N.A.
0.3Li-250 SAz-TMPA	L	4067 ± 779	0.191 ± 0.065	0.965	99.1 ± 19.0
0.6Li-250 SAz-TMPA	L	2334 ± 248	0.014 ± 0.005	0.996	92.9 ± 9.9
Butylbenzene					
SAC-TMPA	L	4693 ± 751	0.039 ± 0.013	0.981	85.1 ± 13.6
SWa-TMPA	L	20,146 ± 3485	0.589 ± 0.100	0.971	353.4 ± 61.1
SAz-TMPA	C	K = 165 ± 23		0.976	N.A.
0.3Li-250 SAz-TMPA	L	5285 ± 622	0.062 ± 0.017	0.987	128.8 ± 15.2
0.6Li-250 SAz-TMPA	L	2895 ± 206	0.002 ± 0.001	0.999	115.2 ± 8.2
0.8Li-250 SAz-TMPA	L	3215 ± 227	0.006 ± 0.002	0.997	90.0 ± 6.4
Naphthalene					
SAC-TMPA	L?	—	—	0.767	—
SWa-TMPA	C	K = 2769 ± 175		0.977	N.A.
SAz-TMPA	C	K = 644 ± 196		0.939	N.A.
0.3Li-250 SAz-TMPA	C	K = 9138 ± 1067		0.940	N.A.
0.6Li-250 SAz-TMPA	L	655 ± 260	0.009 ± 0.002	0.894	26.1 ± 10.3

¹ L = Langmuir; C = linear, constant partitioning.

² N.A. = not applicable.

for the organic cations, as, for example, through π - π interactions between the phenyl groups of adjacent TMPA cations attached to opposing clay layers. Translational and/or rotational movement of alternate clay layers (in the a-b plane) would be necessary to allow organic cations on the surfaces of opposing clay layers to interact. Such rearrangements of the clay layers are plausible because structural analyses have determined that the relative positions of alternate clay layers in vermiculite are shifted depending on the exchangeable cation (MacEwan and Wilson, 1980).

A comparison of the σ° values to the actual planar areas of the molecules (calculated from bond lengths) should reveal any restrictions in adsorption of the larger molecules caused by steric factors. A steric factor that might limit adsorption is the distance between the TMPA cations in the clay interlayers. This would effectively control the size of the adsorptive regions. Surface coverages (σ°) per molecule of the adsorbed compounds on the TMPA-clay surfaces were calculated using the surface areas and a Langmuir equation fit to the adsorption isotherms (see Figure 6). The dotted

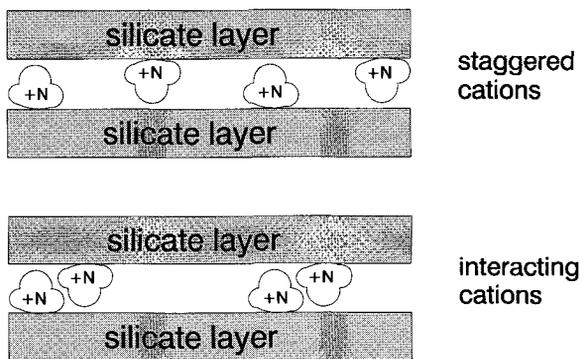


Figure 5. Interactions between interlayer organic cations and the size of adsorption sites.

line in Figure 6 indicates equivalence between σ° values and the planar area of the molecules calculated from bond lengths (see Table 3). The plotted values for SAC-TMPA and SWa-TMPA move above the dotted line as molecular size increases, which indicates that excess surface area is required for adsorption. In other words, the packing efficiency of the adsorbed molecules decreases as molecular size increases.

The surface area required for each adsorbed benzene molecule is about equal to the planar area of benzene for all of the TMPA-clays. In contrast, the surface area required for each butylbenzene molecule adsorbed to SAC-TMPA is about 2 times the molecular size. However, each butylbenzene molecule adsorbed to SWa-TMPA requires about 8 times the molecular area. This suggests that many of the adsorptive sites on SWa-TMPA are too small to accommodate butylbenzene efficiently. The TMPA content of SWa-TMPA is only 6% greater than in SAC-TMPA. Nevertheless, SAC-TMPA adsorbs 6 times as much propylbenzene as SWa-TMPA (Figure 1). This implies that an additional factor restricts the adsorption of larger molecules by SWa-TMPA. In contrast to SAC and SAz, the charge defi-

Table 3. Dimensions and planar surface areas of organic compounds.

Compound	Length Å	Width Å	Area/molecule Å ²	
			Calc. ¹	Est. ²
Benzene	5.6	4.8	23.7	30.5
Toluene	7.1	4.8	29.4	34.3
Ethylbenzene	8.4	4.8	35.1	37.7
Propylbenzene	9.6	4.8	40.8	41.1
Butylbenzene	10.8	4.8	45.9	44.3
Naphthalene	7.3	5.6	38.6	39.9

¹ Calculated from bond lengths, covalent radii, and geometry.

² Estimated from the liquid density (ρ_L) and molecular weight (M) of the adsorbate using the relation $A_m = 1.09 \times (M/\rho_L \times N_A)^{2/3}$ where N_A = Avogadro's number (after Gregg and Sing, 1976).

Clay surface coverage by alkylbenzenes

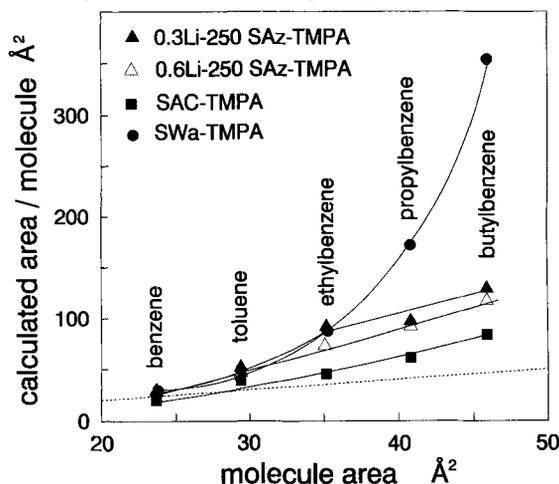


Figure 6. Calculated clay surface coverage by alkylbenzenes.

ciency on SWa is almost entirely in the tetrahedral layers (Rozenon and Heller-Kallai, 1976). Hence, the size of the adsorptive regions in SWa-TMPA may also be limited by water that is hydrogen-bonded to surface oxygens near tetrahedral Al substitution sites (Sposito, 1984). Limited diffusion of larger molecules into the interior of SWa-TMPA particles may further restrict adsorption.

The charge density of SAz, which is greater than SWa, imposes further limitations on organic compound adsorption. For SAz-TMPA, only benzene adsorption isotherms have the Langmuir form. Toluene and large molecules yield linear isotherms. This suggests that the adsorption sites on SAz-TMPA are small and cannot accommodate molecules larger than benzene. In contrast, TMPA-clays made from reduced-charge SAz (0.3Li-250, 0.6Li-250) yield Langmuir-type isotherms for benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, and naphthalene. The calculated σ° values (Figure 6) of 0.6Li-250 SAz-TMPA are generally lower than the 0.3Li-250 SAz-TMPA values. The lower σ° values of 0.6Li-250 SAz-TMPA suggest that further charge reduction has yielded larger adsorptive regions, which allow a more effective packing of the adsorbed molecules. The above discussion was based on data obtained through macroscopic methods (i.e., adsorption isotherms, surface areas) and should be confirmed by molecular scale techniques.

SUMMARY AND CONCLUSIONS

The adsorption isotherms and other data presented in this study suggest the following conclusions: 1. Benzene and alkylbenzene removal from water by TMPA organo-clays yielded adsorption isotherms that are consistent, at least empirically, with the Langmuir monolayer adsorption model. This implies that the

sorptive removal of the organic compounds from water by low-charge TMPA-clays was caused by adsorption to the surface of the organo-clay. 2. The quantity of compound adsorbed was directly proportional to surface area and it was inversely proportional to layer charge and TMPA content. This indicates that the adsorbing surfaces are the siloxane oxygens in the clay interlayer. The interlayer TMPA cations may only function as "pillars" to keep the interlayers apart. 3. Exchanged TMPA cations on opposing clay surfaces appear to interact, freeing larger areas of siloxane surface for adsorption. 4. Calculations based on Langmuir equation parameters and N₂ surface areas give a measure (σ° = area/molecule) of the clay surface area required for each adsorbed molecule. As the planar area of the adsorbed molecules increases, the clay surface area occupied by each molecule also increases. This is strong evidence that the planar surface of the compounds adsorbs to the clay surface. 5. The packing efficiency of adsorbed molecules on the clay surface (molecule area/ σ°) decreased as molecular size and layer charge increased. For example, the adsorption of each butylbenzene molecule required much more surface area on SWa-TMPA (intermediate charge) than on SAC-TMPA (low-charge). This suggests that the placement of interlayer TMPA cations controls the size of the adsorptive regions. 6. The preferential adsorption of hydrophobic organic molecules by these systems in the presence of bulk water demonstrates that a large part of the siloxane surface in smectites has a hydrophobic nature.

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