

## SORPTIVE CHARACTERISTICS OF TETRAALKYLAMMONIUM-EXCHANGED SMECTITE CLAYS

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**Abstract**—The size of quaternary  $\text{NH}_4^+$  cations defines their packing configurations in the interlayers and the basal spacings of organoclays, and hence strongly influences the sorptive properties of organoclays. A series of organoclays (TAA-SACs) was prepared from a smectite (SAC) fully exchanged with symmetrical tetraalkylammonium (TAA) cations of progressively increasing sizes with the carbon number of single alkyl group from 1 to 6. X-ray diffraction analysis indicated the packing configurations of monolayer, monolayer-to-bilayer transition, bilayer, and bilayer-to-trilayer transition in the interlayers of SAC. Calculations of the interionic distances between TAA ions support such packing configurations. Sorption of benzene by TAA-SACs displayed a high-low-high uptake trend and progressively weaker sorptive interactions as the size of TAA ions increased. Both the siloxane surfaces and TAA ions contributed to the overall sorption, with their relative contributions dependent on the TAA interionic distances and the basal spacings of TAA-SACs. High benzene sorption by small TAA-SAC (tetramethylammonium(TMA)-SAC) was attributed to the strong interactions between the siloxane surfaces and benzene molecules. With large TAAs, high sorption was due to the effective solute partitioning. Compared to benzene sorption, TCE sorption by small TAA-SACs (TMA-SAC and tetraethylammonium(TEA)-SAC) was less effective and displayed an abnormal trend, due largely to the lack of the siloxane surface-TCE interactions and to the stronger hydration of TMA as compared to TEA ions. The results provide strong evidence to support the use of either small or large quaternary  $\text{NH}_4^+$  cations in preparation of organoclays as effective sorbents for removing organic contaminants from water.

**Key Words**—NOC, Organoclay, Smectite, Sorption, Tetraalkylammonium.

### INTRODUCTION

The potential of organoclays as effective sorbents for neutral organic contaminants (NOCs) in pollution prevention and abatement has lead to extensive studies of their sorptive properties. Enhanced sorptivity of organoclays results from the ion exchange between the desired organic cations and exchangeable inorganic cations (*e.g.* alkali-metal cation  $\text{Na}^+$  and alkaline-earth-metal  $\text{Ca}^{2+}$ ) in the interlayers of natural clays. The inorganic-organic ion-exchange process is favored by the hydrophobicity of the siloxane surfaces (Jaynes and Boyd, 1991), lower hydration of organic cations compared to inorganic cations, reduced solvent shielding in the interlamellar environment, and strong hydrophobic interactions between organic cations (Solomon and Hawthorne, 1983). The replacement of inorganic cations by organic cations via ion exchange converts the clay surfaces from hydrophilic (due to strong hydration of inorganic cations) to hydrophobic. As a result, organoclays are highly effective sorbents for aqueous phase NOCs, and may find their potential use in a variety of environmental applications and technologies. Examples are the use of organoclays as extenders for activated

carbons for water treatment (Beall, 1985), as components of clay barriers to immobilize dissolved NOCs and to prevent hydraulic failure of the barrier when exposed to concentrated or pure organic liquids (Smith and Jaffé, 1994; Li *et al.*, 1996; Gullick and Weber, 2001), as adsorbents for airborne NOCs (Harper and Purnell, 1990), and as adsorbents for aqueous-phase anionic contaminants when organic cations are loaded in excess of clay CECs (Stapleton *et al.*, 1994; Haggerty and Bowman, 1994; Bors *et al.*, 1997; Li *et al.*, 2002).

Organoclays are often prepared using quaternary ammonium cations (QACs) of the general form  $[(\text{CH}_3)_3\text{NR}]^+$  or  $[(\text{CH}_3)_2\text{NRR}']^+$ , where *R* and *R'* are hydrocarbon groups. Depending on the molecular sizes of *R* and *R'*, organoclays display distinct sorptive properties and abilities. When *R* and *R'* are small in size, *e.g.*  $\text{CH}_3$ - and phenyl, such sorbents are classified as adsorptive organoclays. In these organoclays, QACs are separate from each other and function as pillars to permanently open the interlayers of clay. Both the siloxane surfaces and QACs in the interlayers are potential sites for NOC adsorption. Most studied within this category are tetramethylammonium (TMA)-smectite (Lee *et al.*, 1989, 1990; Jaynes and Boyd, 1990) and trimethylphenylammonium(TMPA)-smectite (Jaynes and Boyd, 1990, 1991; Sheng and Boyd, 1998). These organoclays are effective adsorbents of water-soluble NOCs, and sorption of aromatic compounds, in particular, is often greater (larger amount sorbed at the same

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relative concentration of sorbate) and stronger (isotherm more concave-downward) than that of aliphatic compounds and chlorinated solvents (Barrer and Macleod, 1955). The adsorption is characterized by a Langmuir-type isotherm (sorptive leveling-off at high concentrations), strong solute competition and solute molecular shape selectivity (Lee *et al.*, 1989, 1990). These characteristics suggest that adsorptive organoclays are highly effective in sorbing low concentrations of small aromatic molecules from water not contaminated with multiple contaminants, but may not be suitable for sorbing NOCs from highly contaminated wastewater.

With large  $R$  and  $R'$ , *e.g.* hexadecyl and dodecyl, clay sorbents are classified as organophilic organoclays. In these organoclays, QACs conglomerate to form a continuum of organic phase in the interlayers of clay available as a partition medium for contaminant sorption. Hexadecyltrimethylammonium (HDTMA)-smectite, dodecyltrimethylammonium-smectite and dioctadecyldiammonium-smectite are some of the most studied organoclays in this category. Sorption of NOCs by organophilic organoclays is controlled primarily by solute partitioning, which is characterized by an essentially linear isotherm, low heat of sorption, dependence of sorption on organic content, and lack of solute competition (Boyd *et al.*, 1988). Synergistic NOC sorption by HDTMA-smectites in multisolute systems was reported in the literature (Sheng *et al.*, 1996; Jaynes and Vance, 1996). These characteristics and observations suggest the potential of organophilic organoclays as sorbents for high concentrations of NOCs in multi-contaminant water and that they may not be effective for sorbing low concentrations of NOCs.

It is clear that the molecular size of QACs substantially affects the sorptive properties of organoclays and that QACs must be chosen carefully so that the organoclays meet the specific environmental need. Current knowledge does not adequately address the effect of QAC size on the sorptive characteristics of both categories of organoclays. In this paper, we prepared a series of organo-smectites using symmetrical tetraalkyl QACs of the  $[NR_4]^+$  form, where  $R$  is an  $n$ -alkyl group of progressively increasing size with the number of carbons in a single alkyl group ranging from 1 to 6. The organoclays were characterized by X-ray diffraction (XRD). Sorption of benzene and trichloroethylene (TCE) from water was measured. Our objective was to investigate the effect of increasing size of QACs on the interlayer structure of organoclays and subsequent sorption of NOCs.

## MATERIALS AND METHODS

### *Samples*

Smectite (SAC), obtained from the American Colloid Company (Chicago, Illinois), has  $Na^+$  as the primary exchangeable cation and a cation exchange capacity

(CEC) of 90 cmol<sub>c</sub>/kg. The  $<2 \mu m$  clay fractions were obtained by wet sedimentation of the Na-saturated clay suspension, quick frozen, and freeze dried. All tetraalkylammonium (TAA) bromide compounds (purity  $\geq 98\%$ ), including TMA bromide, tetraethylammonium (TEA) bromide, tetrapropylammonium (TPPrA) bromide, tetrabutylammonium (TBA) bromide, tetrapentylammonium (TPeA) bromide, and tetrahexylammonium (THA) bromide, were purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin), and used as received.

The TAA-SACs were prepared following the procedures below. The TAA bromide (5 g) was dissolved in distilled water (200 mL), and subsequently added to SAC suspensions containing 5 g of SAC. For TPeA and THA bromides, the solution was heated at 80°C while stirring for 2 h to facilitate TAA dissolution prior to mixing with SAC suspension. The TAA-SAC suspension was shaken overnight at room temperature (23°C). The TAA in suspension was 2.6–7 times the amount required to saturate the clay. The suspension was then centrifuged to remove supernatant liquid, and the mixture (TAA-SAC) was washed with distilled water several times to remove extra TAA bromide salt. The resulting TAA-SACs were quick frozen and freeze dried. Organic carbon and nitrogen contents were determined using a LECO CN2000 C/N analyzer (LECO, Inc.), and used to calculate the percent of CEC occupied by TAA cations.

### *X-ray diffraction analysis*

The basal spacings of TAA-SACs were determined by XRD analysis. The TAA-SAC suspensions were dropped on glass slides, and dried overnight at room temperature. The XRD patterns were recorded using  $CuK\alpha$  radiation and a Philips APD3720 automated X-ray diffractometer using an APD3521 goniometer fitted with a  $\theta$  compensating slit, a 0.2 mm receiving slit and a diffracted-beam graphite monochromator, from 3 to 8°2 $\theta$ , in steps of 0.02°2 $\theta$ , at 1 s/step. Basal spacings were calculated using Bragg's Law equation,  $d = \lambda/2\sin\theta$ , where  $\lambda = 1.54041 \text{ \AA}$  with  $CuK\alpha$  radiation.

### *Liquid-phase NOC sorption*

Benzene representing aromatic compounds and TCE representing aliphatic chlorinated solvents were used in the sorption measurements. Batch sorption isotherms of benzene and TCE on TAA-SACs were made by weighing 40 to 200 mg of TAA-SAC samples into Correx centrifuge tubes (25 mL for benzene; 4 mL for TCE) (Corning Glass, Corning, New York) that contained distilled water (25 or 4 mL). Hamilton micro-syringes (Hamilton Co. Reno, Nevada) were used to deliver solute into the tubes. Benzene was added directly as neat liquid. Various amounts (5, 10, 14, 18, 22, 26, 30 and 34  $\mu L$ ) were delivered to yield a range of initial concentrations. The TCE was delivered as acetone solution (1:3 ratio). The volumes of TCE/acetone solution delivered into 4 mL of solution were 1.6, 3.2, 4.8, 6.4, 8.0 and 10  $\mu L$ . The

Table 1. Selected physicochemical properties of TAA smectites.

Sample	Number of carbons in cation	Organic C (%)	Organic N (%)	% of CEC occupied by TAA	Free interionic distance (Å)
TMA-SAC	4	4.60	1.31	109	7.3
TEA-SAC	8	8.48	1.25	108	4.4
TPrA-SAC	12	11.5	1.11	101	1.5
TBA-SAC	16	14.5	1.06	101	-1.4
TPeA-SAC	20	17.2	1.00	99	<0
THA-SAC	24	22.2	1.06	110	<0

amount of acetone in solution was <0.5%, and was assumed to have a negligible effect on TCE sorption. The tubes were sealed immediately with Teflon-lined septa, placed on a rotator (Glas-Col, Terre Haute, Indiana), and rotated at 30 rpm for 24 h at room temperature. Previous experiments demonstrated that sorptive equilibrium was reached within 18 h. The tubes were centrifuged at 8000 rpm (RCF = 4302 g) for 15 min to separate liquid and solid phases, and 5 mL (benzene) or 2 mL (TCE) of the supernatant liquid was extracted with hexane (5 mL or 2 mL) in a glass vial by agitating for 30 min on a reciprocating shaker. A portion of the hexane containing the extracted benzene or TCE was then analyzed using gas chromatography.

Blank samples containing 25 mL of distilled water and 20  $\mu$ L of benzene or 4 mL of distilled water and 1  $\mu$ L of TCE but not TAA-SACs were also prepared and analyzed following the same procedure. Measured recoveries were 87–98%. Concentration data were adjusted for the recoveries. The amount of benzene or TCE sorbed was calculated from the difference between the amount added and that remaining in the final solution. All measurements were in duplicate, and the difference was generally <5%. Isotherms were obtained by plotting the average amount sorbed against the equilibrium concentration remaining in solution.

#### Gas chromatography

Concentrations of benzene and TCE in hexane extracts were measured by gas chromatography. A Shimadzu GC-14A gas chromatograph fitted with a flame ionization detector and a packed column with 10% AT-1000 on 80/100 Chromosorb W-AW (Alltech Co.) was used for all separations. Helium was used as the carrier gas. A Shimadzu AOC-20i autoinjector was used to automate runs. No dilution of extracts was necessary because the concentrations of benzene and TCE were within the analytical linear range. Peak areas were recorded from a Nelson 900 series interface, and compared to external standards to determine the concentrations of benzene or TCE.

## RESULTS

Table 1 lists the selected physicochemical properties of the TAA-exchanged SACs. All TAAs have one N but

a progressively increasing number of total carbons from TMA to THA by an increment of 4. The measured C contents of TAA-SACs increased in direct proportion to the number of total C atoms in TAAs. Measured N contents remained relatively constant with a slight decrease with increasing the number of C atoms in TAAs, in accordance with the molecular formula of the TAAs. Both the C and N contents were used to calculate the percentage of CEC occupied by the TAAs. For each TAA-SAC, two values were obtained and generally agreed well with <5% difference. Only the average values are given in Table 1. The percentage of the CEC occupied by the TAAs was generally ~100%, indicating a complete exchange between TAAs and the original inorganic cations.

The XRD patterns of the TAA-SACs showed broad and generally symmetrical diffraction peaks (Figure 1a). The peak positions remained relatively unchanged (only small shift) for TMA-, TEA- and TPrA-SACs. An abrupt shift in peak position towards smaller angles occurred with TBA-SAC, followed by a further but smooth shift with TPeA-SAC and THA-SAC. Basal spacings corresponding to the centroid of diffraction peaks increased slightly (from 13.8 to 14.2 Å) with increasing the carbon number in single alkyl group up to 3 (from TMA to TPrA) (Figure 1b). A sharp increase in the basal spacing of TBA-SAC (16.6 Å) occurred. Smaller increases in the basal spacings of TPeA-SAC and THA-SAC were observed.

Sorption of benzene, with respect to both magnitude and isotherm shape, depended on TAA cations used to prepare the organoclays (Figure 2). The TMA-SAC sorbed most. An increase in the carbon number in single TAA alkyl group from 1 to 2 (*i.e.* from TMA to TEA) dramatically decreased the benzene sorption by the respective TAA-SACs. Sorption was minimal with TPrA and TBA cations. Further increase in the carbon number of TAAs (*i.e.* TPeA and THA) resulted in an increase in benzene sorption. A noticeable transition in the isotherm shape is also seen from Figure 2. Sorption of benzene by TMA-SAC displayed a Langmuir-type concave-downward isotherm, consistent with the literature results (Lee *et al.*, 1989, 1990). The isotherm for benzene sorption by TEA-SAC, although still concave downward, was much less curvilinear. The isotherms for benzene sorption by other TAA-SACs were essentially linear or concave

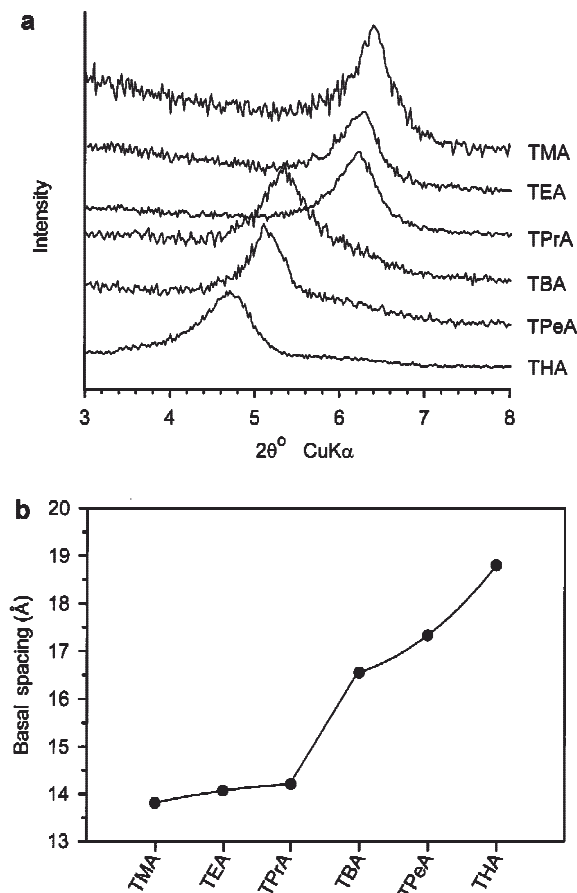


Figure 1. (a) XRD patterns of TAA-SACs, and (b) TAA size-dependent variation in the basal spacing of TAA-SACs.

upward. The transition in the isotherm shape from Langmuir-type to linear or concave upward with increase in the C number of the TAAs indicated progressively weaker interactions between benzene molecules and TAA-SACs (Gregg and Sing, 1982).

The sorption isotherms of TCE on TAA-SACs were clearly different from those of benzene (Figure 3). Overall, the amount of sorption by TAA-SACs was much lower for TCE than for benzene. Surprisingly, the TCE sorption by TEA-SAC was greater than by TMA-SAC, in direct contrast to the benzene sorption. Similar to the benzene sorption, the TCE sorption was the lowest by TPrA- and TBA-SACs. Again, the TCE sorption increased with further increase in the C number of the TAAs (TPeA and THA). With respect to the isotherm shape, a linear isotherm was observed for the sorption of TCE by TMA-SAC, in contrast to the Langmuir-type shape for the benzene sorption. This indicated weaker interactions between TMA-SAC and TCE compared to benzene. Also surprising was that the isotherm of TCE sorption by TEA-smectite was concave downward, indicating stronger interactions of TCE with TEA-SAC than with TMA-SAC. All other isotherms for TCE sorption were linear or concave upward.

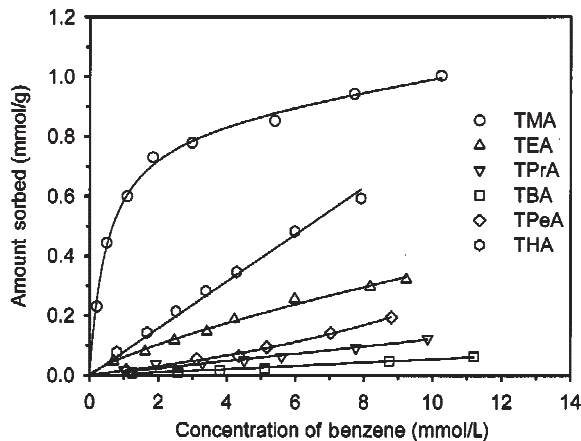


Figure 2. Sorption of benzene from water by TAA-SACs.

## DISCUSSION

The interlamellar packing of QACs, and hence the basal spacing of organoclays, depend on the sizes of the QACs. For small QACs (*e.g.* TMA), they are separate from each other, and the siloxane surfaces of clay are not fully covered by QACs. The basal spacing of such organoclays is largely defined by the molecular size of single QACs. The basal spacing of TMA-SAC of 13.8 Å indicates an interlayer separation of 4.4 Å, slightly smaller than the height of the TMA ion (4.9 Å), suggesting some keying of the hydrogen atom into the silicate sheets and possible deformation of tetrahedral structure of TMA ions as these ions assume the flattest configuration possible in the interlayers (Jaynes and Boyd, 1990; Barrer and Macleod, 1955). This corresponds to a monolayer configuration of TMA ions in the interlayers. In TEA-SAC and TPrA-SAC, TAA cations apparently remain separated from each other. The slightly larger basal spacings than that of TMA-SAC are consistent with the larger sizes of TEA and TPrA ions.

An abrupt increase in the basal spacing of TBA-SAC compared to TPrA-SAC was observed. Presumably, TBA ions are too large to be accommodated in the

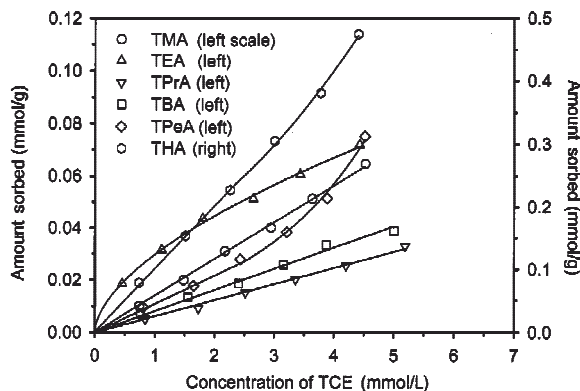


Figure 3. Sorption of trichloroethylene from water by TAA-SACs.

monolayer configuration in the interlayers. Instead, they adopt a monolayer-to-bilayer transition configuration, as manifested by an interlayer expansion from the basal spacing of 14.2 Å for TPrA-SAC to 16.6 Å for TBA-SAC, although the close packing of TBA ions in the interlayers may not be reached (Solomon and Hawthorne, 1983). Such a configuration would be favored by hydrophobic interactions between alkyl groups (chain-chain overlapping). A larger basal spacing of TPeA-SAC at 17.4 Å suggests a bilayer configuration for TPeA ions in the interlayers. The THA ions may adopt a bilayer-to-trilayer transition configuration with a further interlayer expansion to a basal spacing of 18.8 Å. The basal spacings of 13.7 Å with monolayer, 17.7 Å with bilayer, and 21.7 Å with trilayer configurations were reported in the alkylammonium-exchanged expandable clays (Lagaly and Weiss, 1969; Lagaly, 1982). The monolayer to bilayer transition with TAA ions was also observed with other smectites by Mercier and Detellier (1994), who used the transition to determine the internal surface area of various clays.

The monolayer-to-bilayer transition argument is further supported by the TAA molecular structural calculations. We assume that the negative charges of clay are distributed regularly on 750 m<sup>2</sup>/g of clay surface, using the CEC of SAC (90 cmol/kg), calculations show the average distance between adjacent charges to be 11.8 Å. We further assume that the triangular base of the TAA tetrahedron adhered parallel to the siloxane surfaces deforms to fit three alkyl groups within the same plane to allow for the maximal TAA adsorption on the siloxane surfaces and occupies a round-shaped clay surface. Using the carbon-based bond lengths of 1.479 Å for C–N, 1.541 Å for C–C and 1.06 Å for C–H, and the covalent radius of 0.299 Å for H, calculations show the radii of 2.68 Å, 4.13 Å, 5.58 Å, 7.04 Å for TMA, TEA, TPrA and TBA ions adsorbed on the clay surface, respectively. Thus, the free interionic distances (between TAA ions), listed in Table 1, are 7.3, 4.4, 1.5 and –1.4 Å for TMA-SAC, TEA-SAC, TPrA-SAC and TBA-SAC, respectively. The distances for TPeA-SAC and THA-SAC are even more negative than –1.4 Å. The greater than zero distances result in a monolayer packing of TAAs in the interlayers. The negative values indicate insufficient spacings for monolayer coverage, and TAAs must adopt a configuration thicker than monolayer that leads to a basal spacing larger than 14.2 Å.

The packing configurations of TAAs in the interlayers of SAC strongly influence NOC sorption by TAA-SACs. There are two distinct sorption sites in the interlayers of clay, *i.e.* the siloxane surfaces and TAA ions. Barrer and Perry (1961) concluded that, in TMA-exchanged Wyoming smectite, benzene molecules were packed in the interlayers in a tilted orientation relative to the siloxane surfaces onto the triangular faces of TMA tetrahedra. In TMPA-exchanged Arizona smectite and its

reduced-charge smectites, the organic cations were found to function as ‘pillars’ to open the interlayers and the siloxane surfaces were the sole sorptive sites for aromatic molecules (Jaynes and Boyd, 1991). However, the relative contributions of the two types of sites to sorption may depend on several factors. The free interionic distance larger than the molecular size of NOCs may allow direct interaction between the siloxane surfaces and NOC molecules. In the presence of water, hydration of TAAs may reduce the interaction between TAA ions and NOC molecules. These two sorptive interactions may be strongly influenced by the molecular structure of NOC molecules. Greater uptake of aromatic compounds than of aliphatic hydrocarbons was reported in the literature (Barrer and Macleod, 1955), as was observed with sorption of benzene and TCE in this study. This was attributed to the sheet-like aromatic structure and delocalized  $\pi$ -electron system (Lee *et al.*, 1989). If TAA ions are sufficiently large that they form a discrete organic hydrocarbon phase in the interlayers, they may function as an effective partition medium for NOC sorption. Sorption of benzene and TCE by TAA-SACs was influenced by these factors.

Strong sorption of benzene by TMA-SAC and the calculated free interionic distance between TMA cations (7.3 Å) greater than benzene molecule (5.6 × 4.8 Å) suggest sorption by both the siloxane surfaces and TMA ions. In contrast, the smaller interionic distance (4.4 Å) in TEA-SAC than benzene suggests that benzene sorption was more or less a result of the interaction between TEA ions and benzene molecules, possibly with a minor contribution from the interactions with some isolated siloxane surfaces larger than benzene molecules due to the heterogeneity of charge distribution on the surfaces. Substantially higher benzene sorption by TMA-SAC than by TEA-SAC reveals that the interaction between the siloxane surfaces and benzene molecules primarily contributes to sorption by TMA-SAC, and when present, is much stronger than that between TAA ions and benzene molecules (Lee *et al.*, 1989, 1990). Low benzene sorption by TPrA-SAC could be a result of the smaller interionic distance (1.5 Å) than the thickness of benzene molecule (3.4 Å) that prohibited the effective packing of benzene molecules between TPrA ions in the interlayers. Lack of sorption enhancement with the monolayer-to-bilayer transition from TPrA-SAC to TBA-SAC indicates a lack of the sufficient interionic distance between TBA ions for the packing of benzene molecules and/or of the close packing of TBA ions in the interlayers to form an effective partition medium. Increased sorption by TPeA-SAC and THA-SAC is consistent with the basal spacings that indicated the bilayer (or thicker) configurations in the interlayers where an effective partition medium may have formed.

Much lower and weaker sorption by TMA-SAC of TCE compared to benzene is expected because the TCE molecule lacks a delocalized  $\pi$ -electron system, even

though its molecular size ( $5.1 \times 5.0 \text{ \AA}$ ) is similar to that of the benzene molecule. Thus, TCE sorption by TMA-SAC could be a sole result of the interaction between TMA ions and TCE molecules. According to Boyd (1969), TEA ions are less hydrated than TMA ions (the hydration enthalpies of TMA and TEA are  $-53$  and  $-42 \text{ kJ/mol}$ , respectively). A similar but stronger interaction between TCE molecules and TEA ions as compared to TMA ions would be expected, as manifested by the higher sorption and curvilinear isotherm for TCE sorption by TEA-SAC. Similar to benzene sorption, sorption of TCE by TPra-SAC and TBA-SAC was low. Sorption of TCE via a partition mechanism by TPeA-SAC and THA-SAC resembled that of benzene to some extent.

### CONCLUSIONS

The size of QACs strongly influences the interlayer configuration of organoclays and subsequent NOC sorption from water. The TAA cations in the interlayers of clay may adopt the monolayer, monolayer-to-bilayer transition, bilayer, or bilayer-to-trilayer transition configurations, resulting in different free interionic distances and basal spacings. NOCs can be sorbed by TAA-SACs via the interactions with the siloxane surfaces and/or TAA ions or via solute partitioning, giving rise to different sorptive characteristics and magnitudes. This work offered strong evidence to support the previous use of either small or large quaternary ammonium cations in preparation of organoclays as sorbents for effective removal of aqueous phase organic contaminants.

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### REFERENCES

- Barrer, R.M. and Macleod, D.M. (1955) Activation of montmorillonite by ion exchange and sorption complexes of tetraalkyl ammonium montmorillonites. *Transactions of the Faraday Society*, **51**, 1290–1300.
- Barrer, R.M. and Perry, G.S. (1961) Sorption of mixtures and selectivity in alkylammonium montmorillonite. II. Tetramethylammonium montmorillonite. *Journal of Chemical Society*, 850–858.
- Beall, G.W. (1985) Process for treating organics contaminated water. US patent 4,517,094.
- Bors, J., Gorny, A. and Dultz, S. (1997) Iodide, cesium and strontium adsorption by organophilic vermiculite. *Clay Minerals*, **32**, 21–28.
- Boyd, R.H. (1969) Lattice energies and hydration thermodynamics of tetraalkylammonium halides. *Journal of Chemical Physics*, **51**, 1470–1474.
- Boyd, S.A., Mortland, M.M. and Chiou, C.T. (1988) Sorption characteristics of organic compounds on hexadecyltrimethylammonium-smectite. *Soil Science Society of America Journal*, **52**, 652–657.
- Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption, Surface Area, and Porosity*. Academic Press, New York, 303 pp.
- Gullick, R.W. and Weber, W.J., Jr. (2001) Evaluation of shale and organoclays as sorbent additives for low-permeability soil containment barriers. *Environmental Science and Technology*, **35**, 1523–1530.
- Haggerty, G.M. and Bowman, R.S. (1994) Sorption of chromate and other inorganic anions by organo-zeolite. *Environmental Science and Technology*, **28**, 452–458.
- Harper, M. and Purnell, C.J. (1990) Alkylammonium montmorillonites as adsorbents for organic vapors from air. *Environmental Science and Technology*, **24**, 55–61.
- Jaynes, W.F. and Boyd, S.A. (1990) Trimethylphenylammonium-smectite as an effective adsorbent of water soluble aromatic hydrocarbons. *Journal of Air and Water Management Association*, **40**, 1649–1653.
- Jaynes, W.F. and Boyd, S.A. (1991) Hydrophobicity of siloxane surfaces in smectites as revealed by aromatic hydrocarbon adsorption from water. *Clays and Clay Minerals*, **46**, 10–17.
- Jaynes, W.F. and Vance, G.F. (1996) BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes. *Soil Science Society of America Journal*, **60**, 1742–1749.
- Lagaly, G. (1982) Layer charge heterogeneity in vermiculites. *Clays and Clay Minerals*, **30**, 215–222.
- Lagaly, G. and Weiss, A. (1969) Determination of the layer charge in mica-type layer silicates. Pp. 61–80 in: *Proceedings of the International Clay Conference, Tokyo, Vol. 1*. (L. Heller, editor). Israel University Press, Jerusalem.
- Lee, J.-F., Mortland, M.M., Chiou, C.T. and Boyd, S.A. (1989) Shape selective adsorption of aromatic molecules from water by tetramethylammonium smectite. *Journal of Chemical Society Faraday Transactions 1*, **85**, 2953–2962.
- 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, J., Smith, J.A. and Winquist, A.S. (1996) Permeability of earthen liners containing organobentonite to water and two organic liquids. *Environmental Science and Technology*, **30**, 3089–3093.
- Li, Z., Alessi, D., Zhang, P. and Bowman R.S. (2002) Organophilic as a low permeability sorbent to retard migration of anionic contaminants. *Journal of Environmental Engineering*, **128**, 583–587.
- Mercier, L. and Detellier, C. (1994) Intercalation of tetraalkylammonium cations into smectites and its application to internal surface area measurements. *Clays and Clay Minerals*, **42**, 71–76.
- Sheng, G. and Boyd, S.A. (1998) Relation of water and neutral organic compounds in the interlayers of mixed Ca/trimethylphenylammonium-smectites. *Clays and Clay Minerals*, **46**, 10–17.
- Sheng, G., Xu, S. and Boyd, S.A. (1996) Cosorption of organic contaminants from water by hexadecyltrimethylammonium-exchanged clays. *Water Research*, **30**, 1483–1489.
- Smith, J.A. and Jaffé, P.R. (1994) Benzene transport through landfill liners containing organophilic bentonite. *Journal of Environmental Engineering*, **120**, 1559–1577.
- Solomon, D.H. and Hawthorne, D.G. (1983) *Chemistry of Pigments and Fillers*. John Wiley & Sons, New York, 309 pp.
- Stapleton, M.G., Sparks, D.L. and Dentel, S.K. (1994) Sorption of pentachlorophenol to HDTMA-clay as a function of ionic strength and pH. *Environmental Science and Technology*, **28**, 2330–2335.

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