

## SORPTION OF BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENE (BTEX) COMPOUNDS BY HECTORITE CLAYS EXCHANGED WITH AROMATIC ORGANIC CATIONS

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**Abstract**—Adsorptive-type organoclays, where hydrocarbons adsorb directly to the siloxane surfaces, were studied to find new organic cations and to determine the parameters that produce effective sorbents. Organoclays were prepared from hectorite by cation exchange with small, aromatic organic cation salt solutions. Trimethylphenylammonium (TMPA) chloride was obtained and iodide salts of commercially-unavailable aromatic cations were synthesized and used to prepare organoclays. An aqueous mixture of benzene, toluene, ethylbenzene, and xylenes (BTEX) consistent with the composition of unleaded gasoline was used in sorption isotherms to compare the sorptive properties of the organoclays. Only the TMPA, methylphenylpyridinium (MPPyr), and trimethylammonium indan (Indan) organoclays were effective BTEX sorbents. Organoclays prepared from methylpyridinium (MPyr), trimethylammonium biphenyl (Biphenyl), and trimethylammonium fluorene (Fluorene) were poor sorbents. The MPPyr and TMPA organoclays preferentially sorbed ethylbenzene, whereas the Indan organoclay preferentially sorbed benzene and toluene. Langmuir-type sorption isotherms for the TMPA, MPPyr, and Indan organoclays implied surface adsorption, whereas linear isotherms suggested that partitioning was the sorptive mechanism for the MPyr, Biphenyl, and Fluorene organoclays. Water hydrating the small MPyr cation and the larger bulk of the Biphenyl and Fluorene cations may have blocked BTEX access to the interlayer siloxane surfaces. Although the rather bulky MPPyr and Indan cations produced effective organoclays, compact size and low hydration are organic cation properties that typically yield effective adsorptive-type organoclays.

**Key Words**—Adsorptive Organoclays, Aromatic Cations, BTEX, Hectorite, Natural Clays, Organophilic Organoclays, Smectite, Sorption, Unleaded Gasoline, X-Ray.

### INTRODUCTION

Natural clays are ineffective sorbents for nonpolar, nonionic organic compounds (NOCs) that can migrate from contaminated sites to subsurface and groundwater environments. The inorganic exchange cations of natural clays (*i.e.*, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) are strongly hydrated in water, producing a hydrophilic environment at the clay surface. The replacement of inorganic exchange cations with organic cations of the form [(CH<sub>3</sub>)<sub>3</sub>NR]<sup>+</sup> or [(CH<sub>3</sub>)<sub>2</sub>NR<sub>2</sub>]<sup>+</sup>, where R is a large (C<sub>12</sub> or greater) alkyl hydrocarbon, yields organoclays with organophilic properties (Boyd *et al.*, 1988). The organic cation alkyl groups reside in the interlayer region of the clay structure and function as a partition medium for NOCs. Thus, the organic cation alkyl groups effectively remove NOCs from water. Sorption by partitioning occurs by a process similar to the extraction of NOCs from water by a bulk organic-solvent phase such as hexane or octanol (Chiou *et al.*, 1983).

Jaynes and Boyd (1991a) and Jaynes and Vance (1996) prepared organoclays using large, alkyl organic cations such as hexadecyltrimethylammonium (HDTMA) and clay minerals with a range of layer charge. They found that NOC sorption increased as the organic-cation molecular weight and clay-layer charge were increased. In contrast, Lee *et al.* (1989,

1990) and Jaynes and Boyd (1990, 1991b) found that NOC sorption decreased as the clay-layer charge increased for organoclays prepared using the small, alkyl cation tetramethylammonium (TMA) or the small, aromatic cation trimethylphenylammonium (TMPA). Smith *et al.* (1990) noted that organoclays prepared using large alkyl cations and small aromatic cations yielded markedly different tetrachloromethane sorption isotherms. Smith and Galan (1995) found that organoclays prepared using small organic cations have internal surfaces which can act as hydrocarbon adsorption sites. Similarly, Boyd *et al.* (1991) showed that increasing the size of the alkyl groups on a series of organic cations similar to TMPA (*i.e.*, benzyltrimethylammonium to benzyltributylammonium) decreased ethylbenzene sorption. Based on the different sorptive characteristics, Boyd and Jaynes (1992) divided organoclays into two types, organophilic and adsorptive. Organophilic clays are formed using large alkyl cations, and adsorptive organoclays are formed using small alkyl or small aromatic organic cations.

Jaynes and Boyd (1991b) prepared TMPA organoclays and attributed the retention of benzene, alkylbenzenes, and naphthalene to adsorption on the siloxane surfaces in interlayer micropores. Using Fourier transform infrared spectroscopy (FTIR), Stevens *et al.*

Table 1. Organic cations used to prepare organoclays for BTEX sorption isotherms.

Designation	Cation name	Formula	M.W.	Source compound
MPyr	methyl pyridinium	$C_5H_5NCH_3^+$	94	pyridine
TMPA	trimethyl phenylammonium	$C_6H_5N(CH_3)_3^+$	136	phenyltrimethyl ammonium chloride
MPPyr	methyl phenylpyridinium	$C_6H_5C_5H_4NCH_3^+$	170	4-phenylpyridine
Indan	trimethylammonium indan	$C_9H_9N(CH_3)_3^+$	176	5-amino indan
Biphenyl	trimethylammonium biphenyl	$C_{10}H_9N(CH_3)_3^+$	212	4-amino biphenyl
Fluorene	trimethylammonium fluorene	$C_{13}H_9N(CH_3)_3^+$	224	2-amino fluorene
HDTMA	hexadecyltrimethylammonium	$CH_3(CH_2)_{15}N(CH_3)_3^+$	285	hexadecyltrimethylammonium bromide

(1996) found that the adsorption of arenes, such as benzene and ethylbenzene, occurs primarily at the siloxane surface of TMA- and TMPA-smectites. Furthermore, Stevens and Anderson (1996) used FTIR to show that water preferentially hydrates the organic cations in TMA and TMPA organoclays and not the siloxane surface. Lee *et al.* (1989) found that water sorption by TMA limited the sorption of aromatic molecules larger than benzene by TMA-smectites. Sheng *et al.* (1997) found that the heterogeneous charge density of smectites noted by Stul and Mortier (1974) leads to micropores with a heterogeneous size distribution in TMPA-smectites. Similarly, Sheng and Boyd (1998) examined mixed Ca/TMPA-smectites and found that TMPA cations function as nonhydrated interlayer pillars, and organic-solute adsorption occurs predominantly on the siloxane surfaces and is not associated with the TMPA cations.

A great variety of large, alkyl organic cations are commercially available and are used in many studies to prepare organophilic-type organoclays. However, fewer of the small, aromatic organic cations are commercially available. Most studies on the sorptive characteristics of adsorptive-type organoclays used organic cations such as TMA, TMPA, and the benzylalkylammonium cations, but other small aromatic cations may form more effective organoclay sorbents.

In this study, organoclays were prepared from hectorite using a variety of small, aromatic organic cations. Previous research (Jaynes and Boyd, 1990, 1991b) has shown that a smectite with a small layer charge, such as hectorite, yields more effective adsorptive-type organoclays. Commercially-unavailable organic cations were synthesized from amines. The organic cations were selected to evaluate the effects of cation size on benzene, toluene, ethylbenzene, and xylenes (BTEX) sorption from water by organoclays. Objectives of the research were to identify new organic cations for the preparation of adsorptive-type organoclays and to distinguish organic cation properties

that lead to effective organoclay sorbents. A BTEX mixture consistent with the composition of unleaded gasoline was used to prepare organoclay sorption isotherms. From this data, organoclay BTEX sorption was related to organic cation size, organoclay basal spacing, and organoclay surface area.

## MATERIALS AND METHODS

### Samples

A hectorite (H) sample from Hector, California was obtained from Wards Natural Science Establishment, Rochester, New York (hectorite #34). A Na-montmorillonite obtained from the Source Clay Repository of the Clay Minerals Society in Columbia, Missouri (SWy-1) was used for comparison. The hectorite sample was Na-saturated by treatment with excess NaCl followed by dialysis in distilled water. The hectorite and montmorillonite samples were dispersed in water and the <2  $\mu\text{m}$ -size fractions were separated using wet sedimentation.

### Organic cation preparation

Phenyltrimethylammonium chloride and hexadecyltrimethylammonium bromide organic cation salts were obtained from the Aldrich Chemical Company (Table 1). Aromatic amines (Table 1) obtained from Aldrich Chemical Company were used to prepare iodide salts of the organic cations methylpyridinium (MPyr), methylphenylpyridinium (MPPyr), trimethylammonium indan, (Indan) trimethylammonium biphenyl (Biphenyl), and trimethylammonium fluorene (Fluorene). The amines were methylated by refluxing with excess methyl iodide for three hours according to the procedure described by Cumming *et al.* (1950). After methyl iodide treatment, a rotary-vacuum evaporator was used to reduce solvent volume and maximize precipitation of the organic-cation salts. The resulting iodide salts were recrystallized from a minimum volume of solvent, filtered, and dried. Structures for the organic cations are presented in Figure 1.

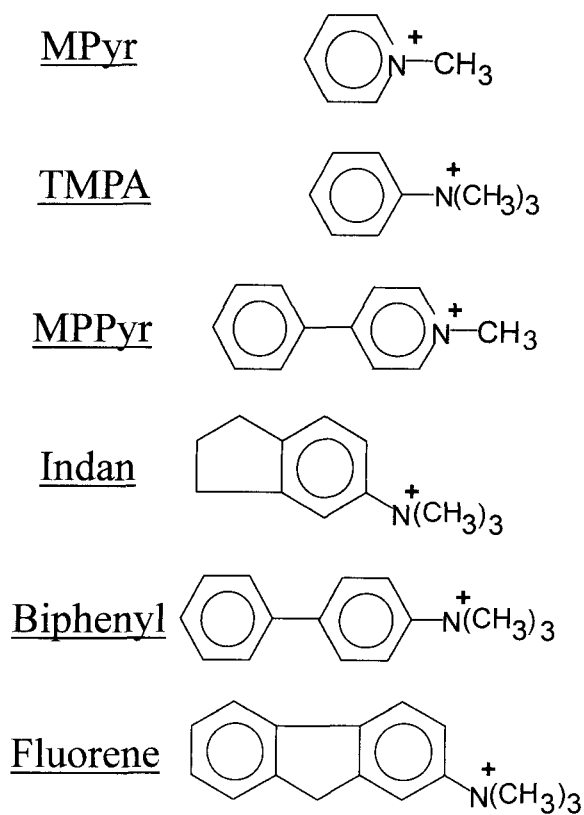


Figure 1. Chemical structures of organic cations used to prepare hectorite organoclays.

#### Organoclay preparation

Previous research (Jaynes and Boyd, 1990) indicated that TMPA in excess of the cation exchange capacity (CEC) is needed to fully saturate the clay exchange sites. The MPyr and TMPA organoclays were prepared by adding the organic-cation salt equivalent to twice the CEC of the clay. In the absence of specific information on the adsorptive behavior of the other organic cations, molecular weight was used as an estimator. The molecular weights of the MPPyr, Indan, Biphenyl, and Fluorene organic cations were judged sufficiently large for stoichiometric cation exchange. Hence, organoclays H-MPPyr, H-Indan, H-Biphenyl, and H-Fluorene were prepared by adding amounts of the organic-cation salts approximately equal to the CEC of the clay. Aqueous solutions of the organic cations were added to agitated clay suspensions. After mixing for 2–4 h, the organoclays were transferred to dialysis tubing and dialyzed in distilled water until free of salts. Each organoclay was subsequently frozen and freeze-dried. Organic carbon and inorganic carbon analyses were performed in duplicate on the unexchanged clay and organoclays.

#### X-ray diffraction analysis (XRD)

Samples (20 mg) of the organoclays were ultrasonically dispersed in 1 ml of 95% ethanol and dried as oriented aggregates on 2.5 cm diameter circular glass slides. Sodium-saturated samples (20 mg) of SWy-1 and hectorite clays were dispersed in 1 ml of water and dried on glass slides. The  $d(00l)$ -values were recorded using  $\text{CuK}\alpha$  radiation and a computer-controlled Scintag automated X-ray diffractometer with a graphite monochromator, a solid-state detector, and an autosampler.

#### Sorption isotherms

Batch sorption isotherms were prepared by weighing 0.10–0.40 g organoclay samples into 25 ml Corex centrifuge tubes (Corning Glass Works, Corning, New York) with 25 ml of distilled water containing known concentrations of a BTEX mixture. The BTEX mixture contained benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene in proportions consistent with the composition of super unleaded (92 octane) gasoline (Hewlett Packard, 1994). The BTEX mixture was prepared by dissolving appropriate proportions of the BTEX compounds in methanol. The maximum volume (24  $\mu\text{l}$  BTEX/methanol solution) added to the 25 ml tubes yielded benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene concentrations of 11, 84, 28, 48, 48, and 39 mg/l, respectively. Initial studies determined that volumes  $>24 \mu\text{l}$  would not readily dissolve in 25 ml of water.

To monitor vaporization losses and adsorption to the glass centrifuge tubes, blank samples containing 25 ml of distilled water and the added BTEX compounds were also prepared. Hamilton microliter syringes (Hamilton Co., Reno, Nevada) were used to deliver a range of concentrations (2 replicates, 6 concentrations) of the BTEX mixture. Some isotherms were repeated using larger sample weights to obtain satisfactory sorption. Vaporization losses of BTEX were minimized by sealing the centrifuge tubes with aluminum foil before applying the caps and by inverting the sealed tubes on the reciprocating shaker. Sample tubes were subsequently agitated for 12 to 18 h under ambient conditions. After centrifugation, a 10-ml aliquot of the supernatant was extracted with 10 ml of hexane in a septum-capped, 20-ml vial, and the hexane extract was analyzed for BTEX using gas chromatography.

Concentrations of the BTEX compounds in the hexane extracts were measured with a Hewlett Packard 5890 series II gas chromatograph using a flame-ionization detector, a Hewlett Packard Chemstation, and an automatic sample changer. A Supelco 30-m, 0.75 mm Supelcowax 10, megabore capillary column with He as carrier gas (Supelco, Bellefonte, Pennsylvania) was used for BTEX analysis. Sample peak areas were

Table 2. Properties of natural clays and derived organoclays.<sup>1</sup>

Sample	Phases	Organic cation fraction of CEC	OC %	IC %	d(001) nm	Surface area m <sup>2</sup> /g
Na-hectorite <2 μm	hectorite + calcite	n.a. <sup>2</sup>	<0.05	3.51	1.13	40
H-MPyr	organoclay + calcite	0.70	3.36	2.42	1.23	104
H-TMPA	organoclay + calcite	0.89	5.94	2.79	1.40	116
H-MPPyr	organoclay + calcite	0.95	8.75	2.12	1.36	36
H-Indan	organoclay + calcite	0.73	6.34	2.90	1.31	65
H-Biphenyl	organoclay + calcite	0.86	9.30	2.62	1.45	34
H-Fluorene	organoclay + calcite	1.14	13.3	1.95	1.50	51
SWy-1 <2 μm	montmorillonite	n.a.	<0.05	0.04	1.10	26
SWy-HDTMA	organoclay	1.06	16.8	0.15	1.81	28

<sup>1</sup> Data on SWy-1 <2 μm and SWy-HDTMA taken from Jaynes and Vance (1996).

<sup>2</sup> n.a. = not applicable.

quantified by reference to five BTEX standards that were included in each analysis.

Each isotherm was constructed by plotting the amount sorbed vs. the concentration remaining in solution. The amount sorbed was calculated from the difference between the quantity of compound added and the quantity remaining in the equilibrium solution. Typical blank recoveries ranged from 90 to 100% and the data were not adjusted for these recoveries. The isotherms were fitted to the Freundlich equation (Hiemenz, 1986) to facilitate comparisons between all organoclays. This permitted the calculation of sorption coefficients ( $K_d$  = amount sorbed/equilibrium concentration) from the Freundlich coefficients and equilibrium concentrations.

The BTEX-equilibrium concentrations used to calculate  $K_d$  values from the Freundlich coefficients were 2.2 mg/l benzene, 16 mg/l toluene, 5.5 mg/l ethylbenzene, 9.3 mg/l p-xylene, 9.3 mg/l m-xylene, and 7.6 mg/l o-xylene. When combined those concentrations equal 50 mg/l total BTEX. These BTEX concentrations delineate the low-concentration range of the sorption isotherms, where BTEX retention by adsorptive-type organoclays is greatest.

#### Surface areas

Surface areas were determined using 3-point (P/P<sub>0</sub> = 0.06, 0.11, 0.26) N<sub>2</sub> gas adsorption isotherms. A Quantasorb (Quantachrome Corp.) sorption meter was used on samples that were degassed for 8–12 h at 120°C under a 30 ml/min flow of pure He or N<sub>2</sub>. Surface areas were determined at liquid N<sub>2</sub> temperatures using N<sub>2</sub> as the adsorbate and He as the carrier gas. Monolayer surface areas were calculated by fitting

each isotherm to the BET equation (Brunauer *et al.*, 1938).

## RESULTS AND DISCUSSION

Treatment with organic cations modified the appearance and physical properties of the clays. Exchangeable Na<sup>+</sup> replacement in hectorite by the MPyr, TMPA, and MPPyr organic cations formed white-colored organoclays, whereas replacement with Indan, Biphenyl, and Fluorene organic cations formed gray-, light gray-, and olive green-colored organoclays. The H-MPyr, H-TMPA, H-MPPyr, H-Indan, and H-Fluorene organoclays readily flocculated and settled to the bottom of the container. In contrast, the H-Biphenyl organoclay was more hydrophilic and did not readily flocculate.

#### Organic and inorganic carbon contents

The organic C content of the unexchanged hectorite sample is very low in comparison to the organoclays (Table 2). Hence, the organic C is derived almost entirely from the exchanged organic cations. The organic C contents generally increased with increases in the molecular weight of the organic cation. Jaynes and Bigam (1986) measured a CEC of ~90 cmol/kg for a carbonate-free, <2-μm sample of SHCA-1 hectorite from Hector, California. Based on the organic C content of each organoclay, the C content of the organic cation, and the CEC of the clay, the fraction of cation-exchange sites covered by organic cations was calculated. Inorganic carbon (IC) contents of the organoclays were 2.9% or less, which was present as clay-sized CaCO<sub>3</sub>; the CaCO<sub>3</sub> acts only as an inert diluent.

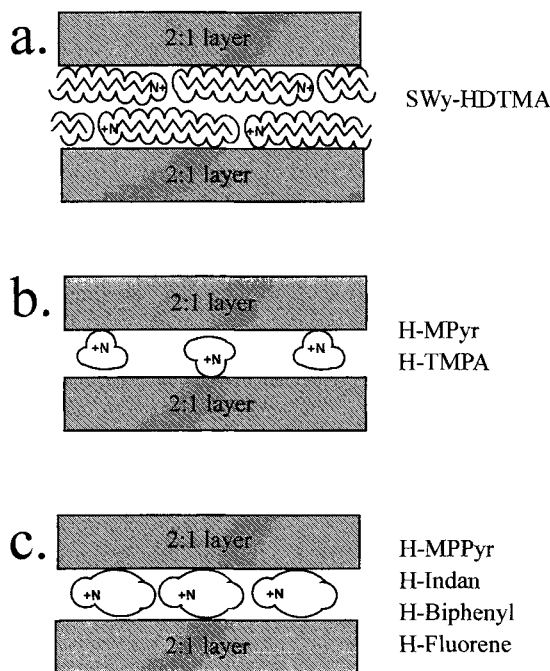


Figure 2. Possible arrangements of organic cations in interlayer: (a) bilayer complex, after Lagaly and Weiss, 1969; (b) monolayer complex with interlayer voids; (c) monolayer complex with smaller interlayer voids.

The fraction of cation-exchange sites occupied by organic cations ranged from 0.70 to 1.14. About  $\frac{1}{3}$  and  $\frac{1}{2}$  of the added MPyr and TMPA cations were adsorbed by hectorite. In contrast, adsorption of the MPPyr, Indan, Biphenyl, and Fluorene organic cations is nearly stoichiometric. Molecular weight provided a reasonably accurate estimate of organic-cation adsorption.

#### XRD analysis and surface area determination

The XRD analyses generally indicated a small increase in the  $d(001)$ -value as the molecular weight of the organic cations increased. Based on the  $d(001)$ -values and surface areas (Table 2), the organoclays were classified according to interlayer alkylammonium complexes (Figure 2). Examples of the alkylammonium complexes from the present study are shown also. The SWy-HDTMA large alkyl-cation type organoclay (Jaynes and Vance, 1996) was included for comparison. Alkyl cations formed 1.8 nm bilayers in the interlayers of the SWy-HDTMA organoclay (Figure 2a). Surface areas of the SWy-HDTMA organoclay and the untreated SWy-1 clay were equivalent.

In contrast, the hectorite organoclays prepared with small, aromatic organic cations formed 1.2–1.5 nm monolayers. Similarly, Polubesova *et al.* (1997) found  $d(001)$ -values of 1.5 nm for the small aromatic cations, benzyltrimethylammonium and benzyltriethylammonium. Crystal structure analysis by Vahedi-Faridi and

Guggenheim (1997) indicated an interlayer structure for TMA-vermiculite similar to the diagram in Figure 2b. They found that the apical methyl groups of TMA tetrahedrons are attached within the ditrigonal cavities of the siloxane surface and proposed that adjacent TMA molecules must alternate apex directions. Vahedi-Faridi and Guggenheim (1997) also found that the offset of the TMA cations from the center of the interlayer region produces a cavity suitable as an adsorption site for small molecules such as benzene. Similarly, methyl groups bonded to N in the organic cations used in this study may be attached to the ditrigonal cavities of hectorite. Yet, many of the organic cations used are larger than TMA and may yield somewhat greater interlayer separations.

The hectorite organoclays were subdivided based on surface area. The H-MPyr and H-TMPA organoclays (the two smallest organic cations) have surface areas that are two or three times greater than untreated clay (see Table 2; Figure 2b). The high surface areas suggest that micropores occur in the interlayer between organic cations. Conversely, the H-MPPyr, H-Indan, H-Biphenyl, and H-Fluorene organoclays have surface areas nearly equal to the untreated hectorite clay (Figure 2c) suggesting minimal interlayer micropores. However, note that the  $d(001)$ -values and surface areas were measured on dry clays. Sorption of BTEX may expand the interlayers of the organoclay and reorient the organic cations. Barrer and Perry (1961) found that, in the presence of benzene vapor, the  $d(001)$ -value of TMA-montmorillonite expanded from 1.36 to 1.46 nm.

#### Sorption isotherms

Total BTEX sorption isotherms (Figure 3) indicate the relative sorptive capacities of the hectorite organoclays. Based on the shape of the isotherms, BTEX sorption to H-TMPA, H-MPPyr, and H-Indan yielded L-type (Langmuir) isotherms according to the classification of Giles *et al.* (1960). The H-MPyr, H-Biphenyl, and H-Fluorene organoclays yielded C- or S-type isotherms. A C-type isotherm is linear and suggests partitioning. Jaynes and Vance (1996) attributed S-type isotherms (concave up) to partitioning and co-sorption of BTEX components by organophilic-type organoclays. Similarly, Sheng *et al.* (1996) noted the co-sorption of organic contaminants by organophilic-type (HDTMA) organoclays.

Sorption coefficients ( $K_d$ ) (Table 3) indicate the relative sorptive capacities of the organoclays. The isotherms in Figure 3 were classified according to the number of aromatic or aliphatic rings in the organic cation (Figure 1) with one ring in Figure 3a, two rings in Figure 3b, and three rings in Figure 3c. The one-ring H-TMPA and two-ring H-MPPyr organoclays were the most effective BTEX sorbents. The BTEX sorptive capacity of the H-MPPyr organoclay was

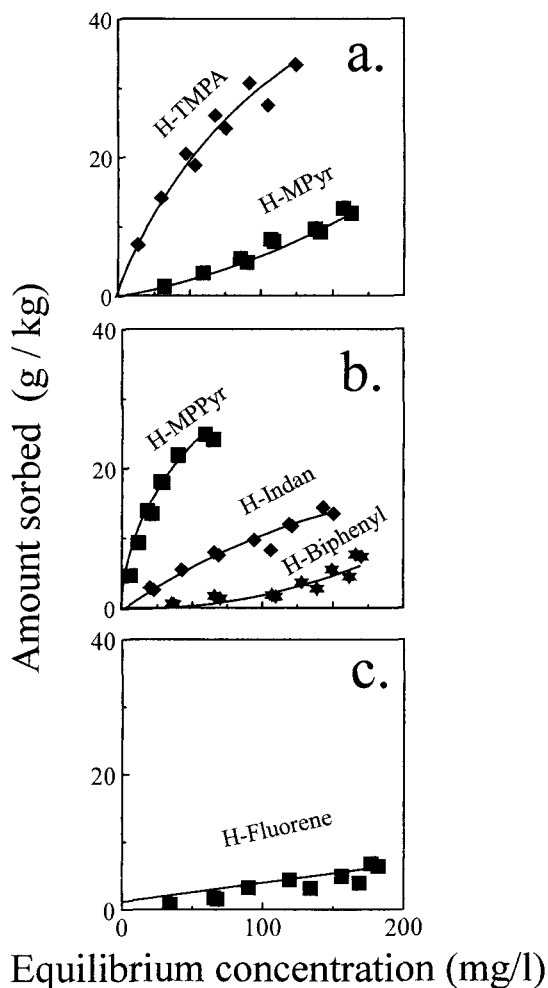


Figure 3. Total BTEX sorption isotherms of hectorite (H) organoclays: (a) H-TMPA and H-MPy; (b) H-MPPy, H-Indan, and H-Biphenyl; (c) H-Fluorene.

~30% greater than the H-TMPA organoclay, although H-TMPA had the greater surface area. The H-MPy and H-Indan organoclays had intermediate BTEX sorptive capacities and the H-Biphenyl and H-Fluorene organoclays were the least effective sorbents.

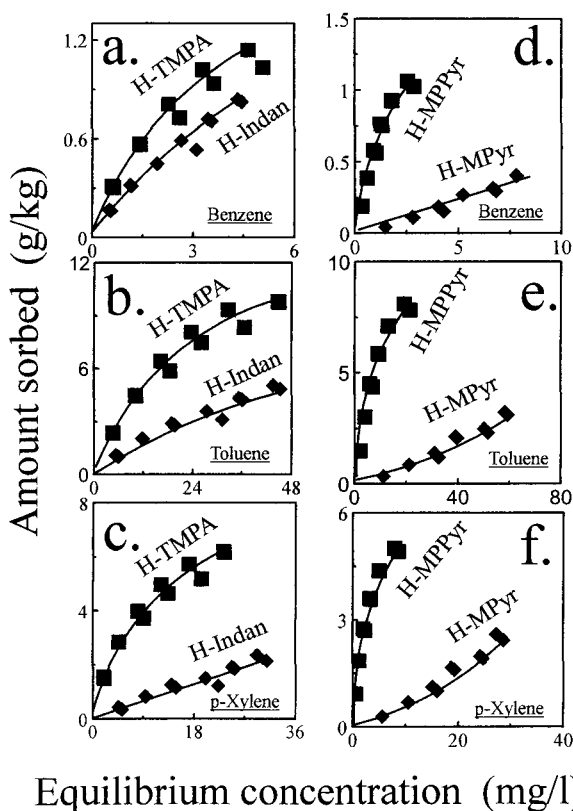


Figure 4. Sorption isotherms of H-TMPA and H-Indan organoclays for (a) benzene, (b) toluene, and (c) p-xylene. Sorption isotherms of H-MPPy and H-MPy organoclays for (d) benzene, (e) toluene, and (f) p-xylene.

Sorption isotherms for benzene, toluene, and p-xylene to H-TMPA and H-Indan organoclays (Figure 4a, 4b, 4c) indicated that H-Indan sorbed comparable amounts of the smaller benzene molecules as H-TMPA. In contrast, H-Indan sorbed much less of the larger toluene and p-xylene molecules than H-TMPA. Preferential sorption of the smaller molecules by H-Indan suggests that the BTEX sorption sites of H-Indan were smaller than in H-TMPA.

Sorption isotherms (Figure 4d, 4e, 4f) indicated that H-MPPy was a much better BTEX sorbent than H-

Table 3. Coefficients ( $K_d$ ) for the sorption of BTEX compounds by the organoclays.<sup>1</sup>

Sample	Benzene	Toluene	Ethylbenzene	p-xylene	m-xylene	o-xylene	Total BTEX
H-MPy	35	35	65	61	65	64	51
H-TMPA	320	347	500	419	492	246	380
H-MPPy	478	495	657	678	568	281	500
H-Indan	226	147	114	81	136	68	116
H-Biphenyl	23	17	19	19	20	14	18
H-Fluorene	22	25	34	37	37	39	32
SWy-HDTMA	89	85	178	199	198	159	140

<sup>1</sup> Sorption coefficients ( $K_d$ ) calculated from Freundlich equation fit to isotherm data at benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, and total BTEX concentrations of 2.2, 16, 5.5, 9.3, 9.3, 7.6, and 50 mg/l.

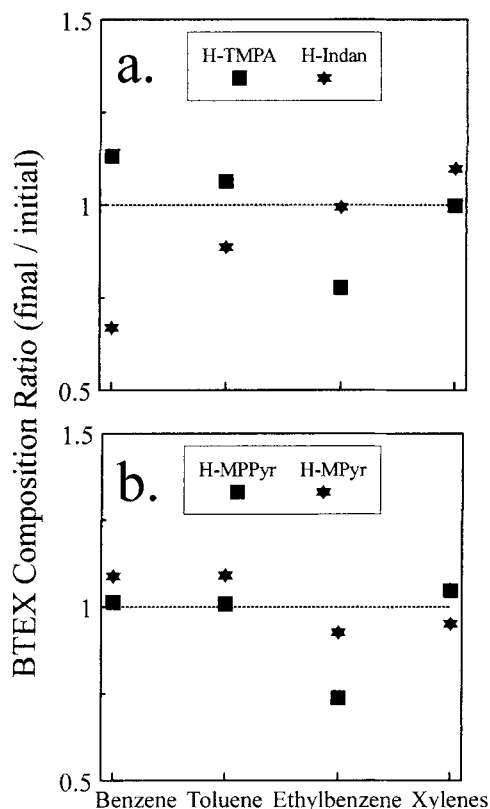


Figure 5. Equilibrium solution composition of BTEX mixture after sorption to organoclays relative to the initial composition: (a) H-TMPA and H-Indan, and (b) H-MPPyr and H-MPyr.

MPyr, although the surface area of H-MPyr was much greater (Table 2). Sorption of BTEX may reorient the organic cations and permit greater expansion of the organoclays. The methypyridinium (MPyr) cation is structurally comparable to TMPA and has a molecular weight only slightly greater than tetramethylammonium (TMA). It was expected that MPyr would form an organoclay as effective as TMPA and TMA. However, the H-MPyr organoclay had a relatively low sorptive capacity for BTEX. Like TMA, the hydration of MPyr may limit BTEX sorption by the H-MPyr organoclay.

#### Preferential sorption

In Figure 5, the composition of the BTEX mixture in equilibrium solutions after sorption are compared to the initial composition of the BTEX mixture. The dotted line indicates the initial composition of the BTEX mixture. Points above this line suggest enrichment and points below the line indicate depletion relative to the initial BTEX mixture. After sorption by H-TMPA (Figure 5a) and H-MPPyr (Figure 5b), the BTEX mixture was enriched with benzene and toluene and depleted of ethylbenzene, which indicates preferential sorption of ethylbenzene. In contrast, the BTEX mix-

ture was greatly depleted in benzene and toluene and enriched in xylenes after sorption by H-Indan, suggesting preferential sorption of benzene and toluene (Figure 5a). Preferential sorption of the smaller, more soluble compounds confirms that many of the adsorption sites are too small to accommodate the larger molecules. After sorption by H-MPyr, the BTEX mixture was slightly enriched with benzene and toluene and depleted in ethylbenzene and xylenes (Figure 5b). Preferential sorption of the larger ethylbenzene and xylene molecules was also noted for H-Biphenyl, H-Fluorene, and SWy-HDTMA. Greater retention of the larger, less soluble molecules is expected for organophilic-type organoclays where partitioning is the dominant sorptive mechanism.

#### SUMMARY AND CONCLUSIONS

A variety of small, aromatic organic cations similar to TMPA were synthesized from hectorite and used to prepare organoclays from hectorite. The H-MPPyr organoclay is a more effective BTEX sorbent than H-TMPA (Table 3), although surface areas of H-MPPyr are lower than H-TMPA. Organoclays prepared using the largest of the organic cations, H-Biphenyl and H-Fluorene, are the least effective BTEX sorbents. The H-Indan organoclay has an intermediate sorptive capacity, but it preferentially sorbs benzene and toluene from the BTEX mixture. Of the new organic cations tested, only the MPPyr and Indan form effective organoclays.

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(Received 10 August 1998; accepted 24 January 1999; Ms. 98-105)