ADSORPTION OF BENZENE, TOLUENE, AND XYLENE BY TWO TETRAMETHYLAMMONIUM-SMECTITES HAVING DIFFERENT CHARGE DENSITIES

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Abstract—A high-charge smectite from Arizona [cation-exchange capacity (CEC) = 120 meq/100 g] and a low-charge smectite from Wyoming (CEC = 90 meq/100 g) were used to prepare homoionic tetramethylammonium (TMA)-clay complexes. The adsorption of benzene, toluene, and o-xylene as vapors by the dry TMA-clays and as solutes from water by the wet TMA-clays was studied. The adsorption of the organic vapors by the dry TMA-smectite samples was strong and apparently consisted of interactions with both the aluminosilicate mineral surfaces and the TMA exchange ions in the interlayers. In the adsorption of organic vapors, the closer packing of TMA ions in the dry high-charge TMA-smectite, compared with the dry low-charge TMA-smectite, resulted in a somewhat higher degree of shape-selective adsorption of benzene, toluene, and xylene. In the presence of water, the adsorption capacities of both samples for the aromatic compounds were significantly reduced, although the uptake of benzene from water by the low-charge TMA-smectite was still substantial. This lower sorption capacity was accompanied by increased shape-selectivity for the aromatic compounds. The reduction in uptake and increased selectivity was much more pronounced for the water-saturated, high-charge TMA-smectite than for the low-charge TMA-smectite. Hydration of the TMA exchange ions and/or the mineral surfaces apparently reduced the accessibility of the aromatic molecules to interlamellar regions. The resulting water-induced sieving effect was greater for the high-charge TMA-smectite due to the higher density of exchanged TMA-ions. The low-charge Wyoming TMA-smectite was a highly effective adsorbent for removing benzene from water and may be useful for purifying benzene-contaminated water.

Key Words—Adsorption, Aromatic hydrocarbons, Benzene, Charge density, Smectite, Tetramethylammonium, Water.

INTRODUCTION

The type of exchangeable cations on clays strongly influence their sorptive characteristics for non-ionic organic compounds (NOCs). In nature, the net negative charges of clays are usually balanced by inorganic exchange ions, such as Na^+ and Ca^{2+}, which are strongly hydrated in the presence of water. The hydration of these exchangeable metal ions and the presence of Si–O groups in clays imparts a hydrophilic nature to the mineral surfaces. As a result, the adsorption of NOCs by clays is suppressed in the presence of water because relatively nonpolar organic chemicals cannot effectively compete with highly polar water for adsorption sites on the clay surface. In the absence of water, the clay acts as a conventional solid adsorbent; the high adsorptive capacity for organic compounds is attributed to its large surface area (Call, 1957; Jurinak, 1957; Chiou and Shoup, 1985).

The inability of clays to remove substantial amounts of NOCs from aqueous solution can be remedied by replacing natural metal cations with larger organic cations through ion-exchange reactions (McBride *et al.,* 1977; Wolfe *et al.,* 1985; Boyd *et al.,* 1988a). Earlier studies indicated that exchanging quaternary ammonium cations for metal ions on clays greatly modified the sorptive characteristics of dry clays for organic vapors (e.g., White and Cowan, 1958; Barrer and Perry, 1961; McAtee and Harris, 1977). Depending on the size of the organic cation, the exchanged organic ions have been shown to form either a microscopic organic phase, as in hexadecyltrimethylammonium-smectite (Boyd *et al.,* 1988b), or discrete organic-modified surface adsorption sites as in TMA-smectite (Lee *et al.,* 1989). Importantly, the substitution of organic cations reduces the hydration of the clay and concomitantly decreases the "free" aluminosilicate mineral surface area (i.e., that surface not covered by the organic exchange ions). As a result, the surface properties of the clay may change considerably from highly hydrophilic, if the clay contains mainly inorganic cations, to increasingly organophilic, as the inorganic cation is progressively replaced by the organic cation.

Mortland *et al.* (1986) and Boyd *et al.* (1988c) used

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quaternary alkyl ammonium cations as exchangers for metal ions on smectite to enhance the uptake of phenol and chlorophenols from water. They showed that in general the sorptive capacitiy of modified clays exchanged with large quaternary alkyl ammonium ions was greatly increased, compared with that of the unmodified clays. Boyd *et al.* (1988b) also showed that dry hexadecyltrimethylammonium $[(CH_3)_3N(C_{16}H_{33})]^+$-smectite (referred to as HDTMA-smectite) acted as a dual sorbent for the sorption of NOCs, whereby the "free" aluminosilicate mineral surface functioned as a solid adsorbent, and the bulky organic moieties of the exchanged HDTMA ions functioned as a partition medium, analogous to the behavior of mineral and organic matter in dry soil (Chiou and Shoup, 1985). In aqueous solution, however, adsorption on mineral surfaces was suppressed by water, and the uptake of NOCs by HDTMA-smectite was due to solute partitioning into the organic medium formed by the conglomeration of large C_{16} alkyl groups of HDTMA ions. This partitioning behavior of HDTMA-smectite in aqueous solution was suggested by: (1) the highly linear isotherms for the sorption of NOCs by HDTMA-smectite, (2) the dependence of the sorption coefficient on the water solubility of the NOC, (3) the general agreement between the organic matter normalized partition coefficient (K_{om}) of the organo-clay and the corresponding octanol-water partition coefficient (K_{ow}) of the NOC, and (4) the dependence of the sorption by HDTMA-smectite on the organic carbon content of the modified clay (Boyd *et al.,* 1988b). Soils modified by exchange reactions with HDTMA also showed greatly enhanced sorption of NOCs (Boyd *et al.,* 1988a). These studies indicated that the organic matter derived from exchanged HDTMA was 10 to 30 times more effective than natural soil organic matter in the (partition) uptake of benzene, dichlorobenzene, and tetrachloroethylene from water.

By comparison, Lee *et al.* (1989) found from a study of the sorption of aromatic compounds on tetramethylammonium (TMA)-smectite that the characteristics of NOC sorption from water by TMA-smectite were different from the partition behavior of HDTMA-smectite. Most notably, the sorption isotherms of benzene, toluene, and o-xylene on TMA-smectite were not linear. In addition, the more-water-soluble benzene showed considerably greater affinities than the less-soluble trichlorobenzene for the TMA-smectite. These authors also reported that the TMA-smectite exhibited a greater uptake of benzene from aqueous solution than the HDTMA-smectite, despite the fact that the HDTMA-smectite had a much greater organic carbon content.

Lee *et al.* (1989) also demonstrated shape selectivity by TMA-smectite in the adsorption of aromatic compounds from water, as evidenced by a progressive reduction in uptake in going from benzene to larger aromatic compounds. This selectivity was only noted for the uptake of aromatic compounds from aqueous solution and not for the corresponding vapors on the dry clay. This unique selective property of TMA-smectite was attributed to water molecules modifying its sorptive behavior by shrinking the interlamellar cavities, in which adsorption of the aromatic molecules occurred.

In the present paper, two smectites of different charge densities were used to prepare TMA-clay complexes. Having observed that the Wyoming TMA-smectite adsorbed large quantities of benzene from water and displayed shape-selective adsorption in the uptake of aromatic compounds from water (Lee *et al.,* 1989), it was of interest to evaluate the sorptive characteristics of a high-charge TMA-smectite, in which the shape selective properties and porosity would be different because of increased density of exchanged TMA ions. The removal of aromatic molecules, such as benzene, toluene, and xylene, from water by modified clays was of further interest because these compounds are important ground-water contaminants.

EXPERIMENTAL

Samples for these investigations were prepared in the manner previously described by Lee *et al.* (1989). The organo-clay complexes were prepared by exchanging the TMA for Na^+ ions on Wyoming smectite and Arizona smectite having cation-exchange capacities (CEC) of 90 and 120 meq/100 g, respectively (Table 1) (van Olphen and Fripiat, 1979). The 0.2-μm fractions of the original clays were obtained by standard dispersion and sedimentation methods. The Na-clays were dispersed by mixing with water, and the impurities in these clays were allowed to settle out overnight. The clay suspension was then removed and mixed with an aqueous solution of TMA chloride salt in the amount of 3–5 meq TMA per 1 meq of CEC of the clay and stirred for 2–4 hr. The TMA-smectite complexes were then dialyzed to remove excess salts, freeze-dried, and stored at room temperature.

Adsorption isotherms were determined using the batch equilibration technique. Eight initial concentrations were prepared in the range 100 to 1500 ppm for benzene, 20 to 550 ppm for toluene, and 12 to 190 ppm for o-xylene. Corex glass tubes (25 ml) containing 100 mg of TMA-smectite and 25 ml of the aqueous solutions containing the organic compounds were closed with foil-lined screw tops and shaken for 24 hr at room temperature in a reciprocating shaker. Preliminary kinetic investigations indicated that sorption equilibrium was reached in less than 20 hr. The aqueous phase was separated by centrifugation at 8000 rpm for 30 min at 20°C using a Sorvall refrigerated RC 5C centrifuge equipped with a SS-34 rotor. A 1-ml portion of the supernatant was then transferred into a glass vial containing 10 ml of carbon disulfide, closed with foil-
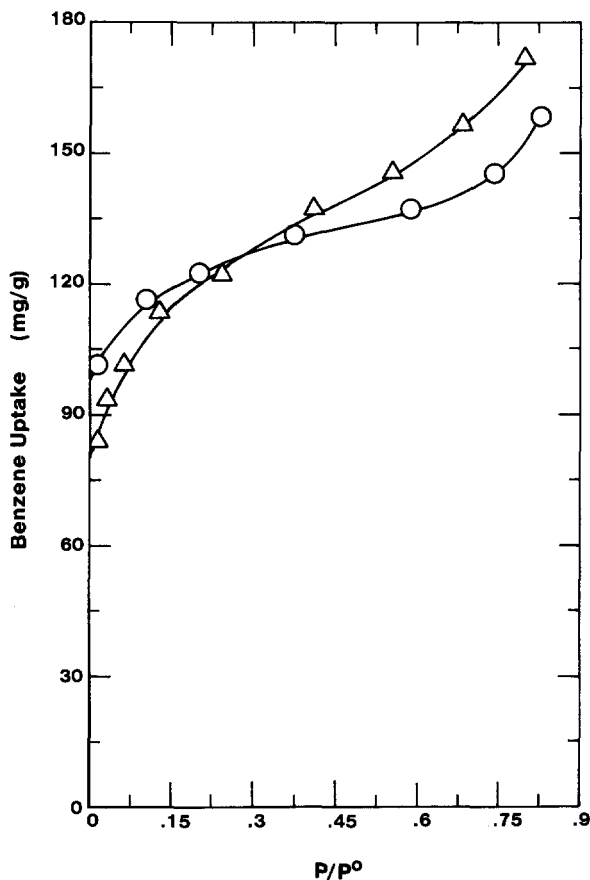
Figure 1. Adsorption of benzene vapor by dry high-charge Arizona (triangles) and low-charge Wyoming (circles) tetramethylammonium-smectite.
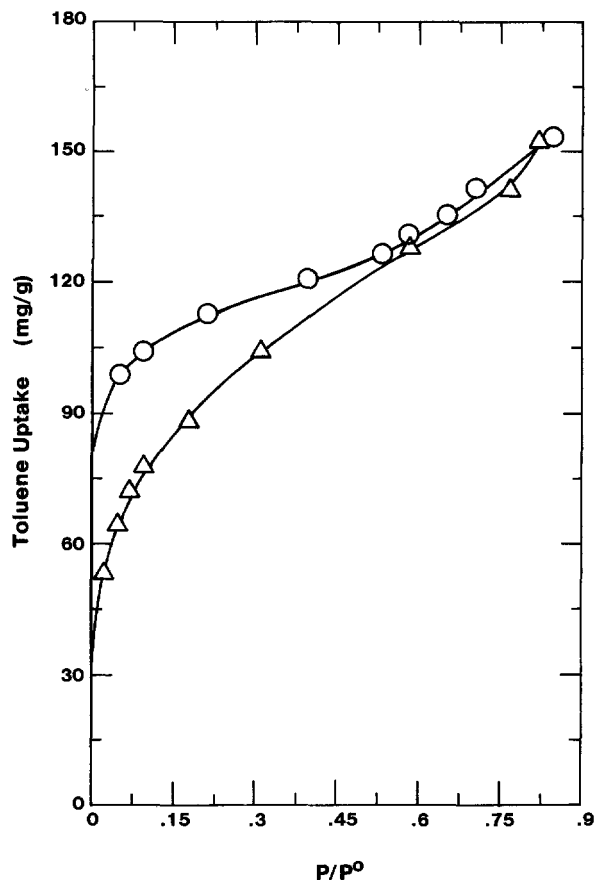
Figure 2. Adsorption of toluene vapor by dry high-charge Arizona (triangles) and low-charge Wyoming (circles) tetramethylammonium-smectite.

lined screw caps, and shaken vigorously for 1 hr on a reciprocating shaker. A portion of the carbon disulfide layer was then removed for gas chromatographic (GC) analysis.

To measure the competitive effects of benzene and toluene adsorption by the TMA-smectite, the iso-

Table 1. Properties of the low-charge and high-charge tetramethylammonium-smectite complexes.

Property	Wyoming[1]	Arizona[2]
Cation-exchange capacity (meq/100 g)	90.0	120.0
Organic carbon (g/100 g)	4.0	5.0
d(001) (Å)	13.8	13.8
N_2 surface area (m²/g)	206	187
Formulae (half unit cell)		
Wyoming $(Al_{1.53}Fe^{3+}_{0.16}Mg_{0.33})(Si_{3.95}Al_{0.05})O_{10}(OH)_2$		
Arizona $(Al_{1.4}Fe^{3+}_{0.17}Mg_{0.43})(Si_{3.8}Al_{0.12})O_{10}(OH)_2$		

[1] Supplied by American Colloid Company as Wyoming bentonite.

[2] Reference clay sample SAz-1 from the Clay Minerals Repository of The Clay Minerals Society.

therms of binary mixtures were obtained as follows: aqueous solutions (25 ml) at eight initial concentrations of benzene in the range of 100 to 1500 ppm and of toluene in the range of 20 to 550 ppm were added simultaneously to the Corex glass tubes, that contained 100 mg of the TMA-smectite. The added amounts of benzene and toluene corresponded to about the same relative concentrations (aqueous concentration/water solubility) for each solute. The binary solutions were then shaken and treated as described above.

Gas chromatography was carried out on a model 5890A Hewlett Packard gas chromatograph equipped with a flame ionization detector. Peak areas were quantitated using a Hewlett Packard 3392A integrator. The concentration of the organic compound(s) in the carbon disulfide extract was determined by using a series of external standards. The column used was packed with 5% sp-1200/1.75% bentonite 34 coated on 100–120-mesh Supelcoport. Carrier gas was high-purity nitrogen at a flow of 40 ml/min. The oven temperature was 65°C for benzene, 80°C for toluene, and 100°C for
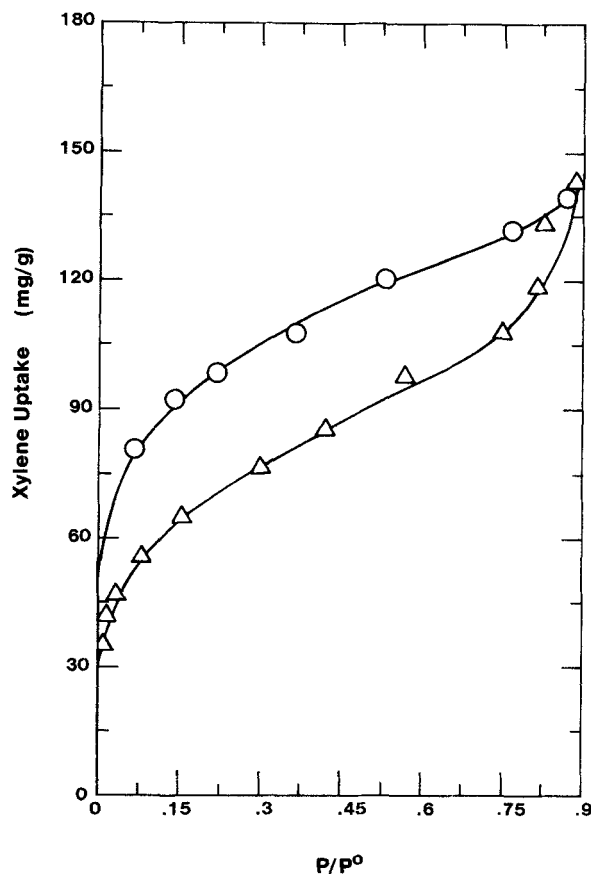
Figure 3.   Adsorption of o-xylene vapor by dry high-charge Arizona (triangles) and low-charge Wyoming (circles) tetramethylammonium-smectite.
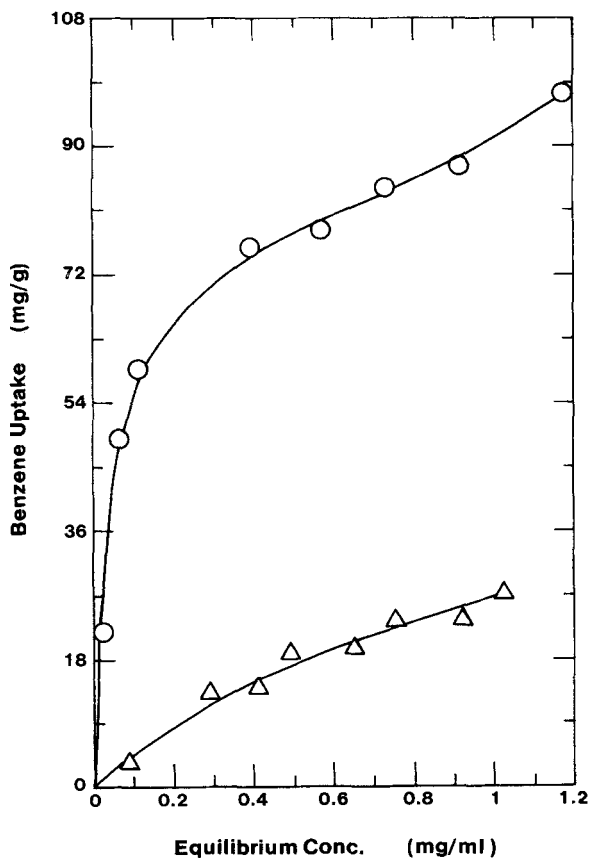

Figure 4.   Adsorption of benzene from aqueous solution by high-charge Ariziona (triangles) and low-charge Wyoming (circles) tetramethylammonium-smectite.

xylene. Operating temperatures for the injection port and detector were 270° and 300°C, respectively. All adsorption measurements were carried out in duplicate. Blank determinations of organic compounds in absence of clays were conducted; the recoveries ranged from 92 to 98%. The equilibrium concentrations measured were not adjusted for these recoveries. The uptake of benzene, toluene, and o-xylene vapor by dry TMA-smectite was measured by using a static-equilibrium sorption apparatus described by Chiou *et al.* (1988). The N_2 BET surface areas (Table 1) were determined using a Quantasorb Jr. sorption meter described by Lee *et al.* (1989). Samples were dehydrated under vacuum at 150°C for 12 hr.

A Philips X-ray diffractometer model XRG 3100 equipped with a Cu tube was used for X-ray powder diffraction (XRD) examination. Samples were prepared by placing clay-water suspensions onto glass microscope slides and drying them at room temperature (Table 1). Organic carbon analyses were performed in duplicate by Huffman Laboratories, Golden, Colorado (Table 1).

RESULTS

Adsorption isotherms for the uptake of benzene, toluene, and o-xylene vapors by the dry TMA-smectite samples are shown in Figures 1–3. The isotherms for both the low-charge and high-charge TMA-smectite samples were sigmoid shaped approaching Type II in Brunauer's classification (Brunauer, 1944). For both smectite samples, the amount of organic vapor taken up by dry TMA-smectite decreased in the order: benzene > toluene > o-xylene. The magnitude of this decrease was much greater for the high-charge TMA-smectite compared with the low-charge TMA-smectite, for which differences in the uptake of benzene, toluene, and xylene vapors were relatively small. Although the amount of benzene taken up was nearly identical for the low-charge and high-charge TMA-smectite samples, the amount of toluene vapor adsorbed by the low-charge TMA-smectite exceeded that adsorbed by the high-charge TMA-smectite, especially at lower P/P⁰. For o-xylene, the largest of the three compounds tested, uptake by the low-charge TMA-
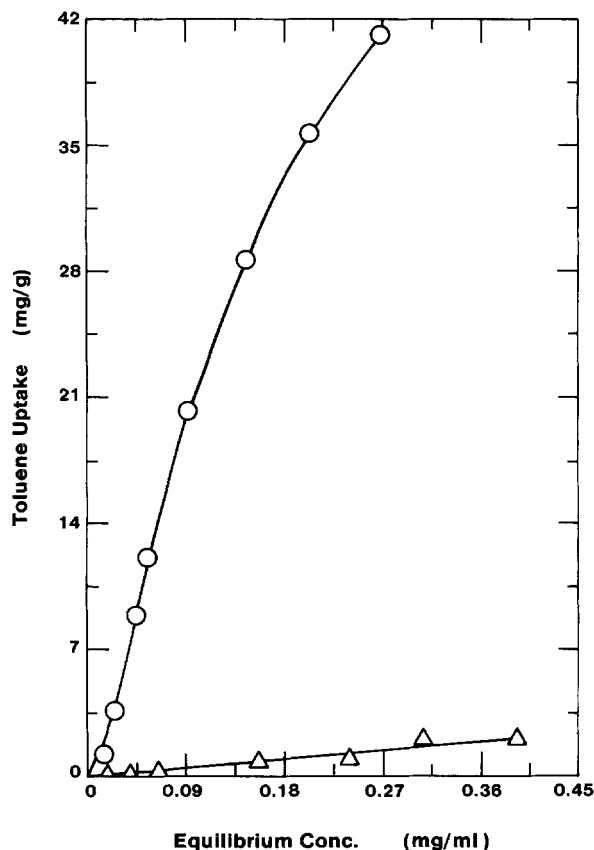
Figure 5.   Adsorption of toluene from aqueous solution by high-charge Arizona (triangles) and low-charge Wyoming (circles) tetramethylammonium-smectite.
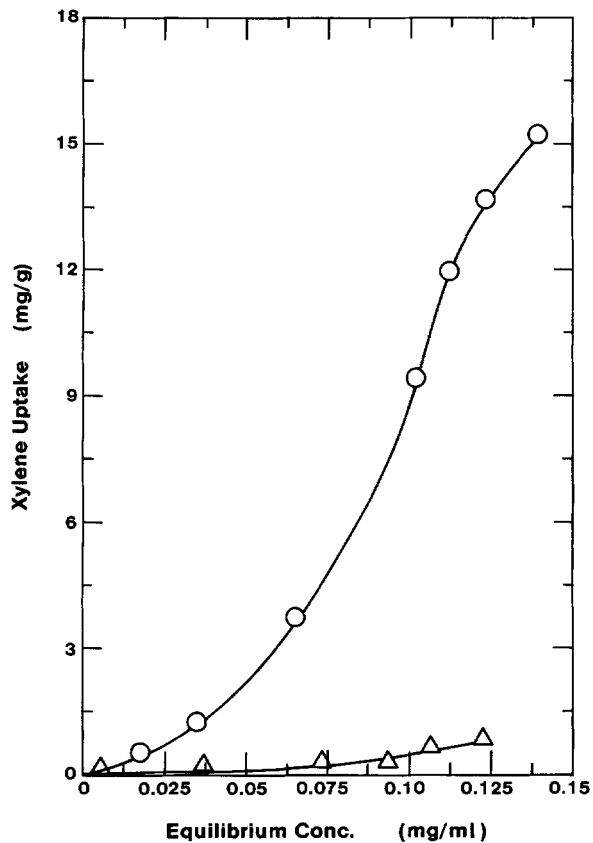
Figure 6.   Adsorption of o-xylene from aqueous solution by high-charge Arizona (triangles) and low-charge Wyoming (circles) tetramethylammonium-smectite.

smectite was considerably more than by the high-charge TMA-smectite, and this difference extended to relatively high P/P^0. The extent of organic vapor uptake for all three organic compounds suggested that adsorption occurred in the interlamellar regions as well as on the external surfaces of the TMA-smectites. For example, the amount of benzene adsorbed at $P/P^0 = .2$ was about 120 mg/g, corresponding to a total benzene-monolayer surface area of about 230 m²/g (the area of a benzene molecule is 25 Å). The adsorptive behavior of both TMA-smectite samples showed no threshold pressure.

Figures 4–6 show adsorption isotherms for the uptake of benzene, toluene, and o-xylene from water by the low- and high-charge TMA-smectite samples. The uptake of each compound from water was less than the uptake of the corresponding vapors by the dry samples. A noticeable difference in the amount of these organic chemicals taken up by the low-charge and high-charge TMA-smectite samples can be seen in the isotherms. For each sample, the amount of uptake decreased in the order: benzene > toluene > xylene; however the

uptake of benzene from water was much lower for the high-charge TMA-smectite than for the low-charge TMA-smectite. This obvious difference contrasts with the uptake of benzene vapor by both dry samples, which was nearly identical. The uptake of toluene and o-xylene by the high-charge TMA-smectite was very low, and the differences between the uptake by the low-charge and high-charge TMA-smectite samples were magnified as the molecular size increased from benzene to toluene to o-xylene.

A pronounced difference was also noted in the shape of the adsorption isotherms shown in Figures 4–6, indicating progressively weaker interactions with the TMA-smectite in the order: benzene > toluene > o-xylene. From both the shape of the isotherms and the degree of uptake, the aromatic molecules clearly showed weaker interactions in an aqueous environment with the high-charge TMA-smectite than with the low-charge TMA-smectite. The adsorption isotherms of toluene and o-xylene suggest that these two chemicals were not significantly intercalated by the high-charge TMA-smectite. On the other hand, the uptake
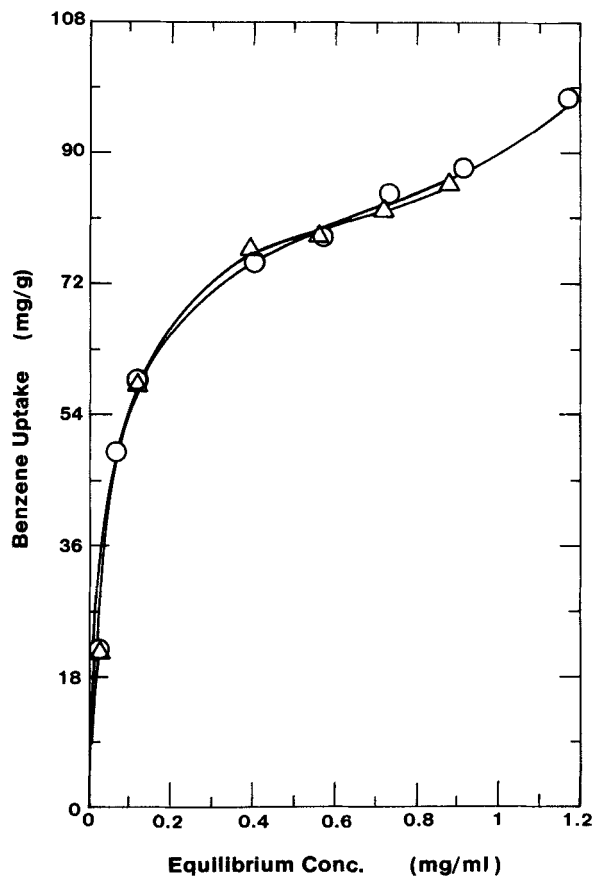
Figure 7. Adsorption of benzene from water by low-charge Wyoming tetramethylammonium-smectite in the presence (triangles) and absence (circles) of toluene.
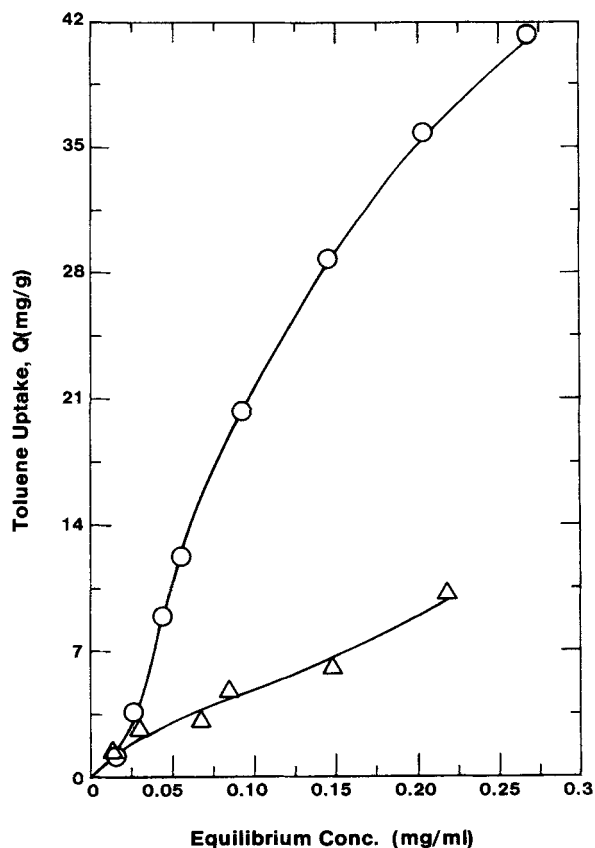

Figure 8. Adsorption of toluene from water by low-charge Wyoming tetramethylammonium-smectite in the presence (triangles) and absence (circles) of benzene.

of benzene from aqueous solution appears to have involved the interlamellar surfaces of the TMA-clays.

Competitive effects in the adsorption of benzene-toluene mixtures from aqueous solution by the low-charge TMA-smectite are presented in Figures 7 and 8. If the adsorption isotherms of benzene as a single solute and as a binary solute from its mixture with toluene are plotted on the same diagram, they are nearly superimposable (Figure 7), demonstrating that toluene, at about an equal relative concentration (concentration in water/aqueous solubility) as benzene, was unable to compete effectively with benzene for adsorption sites on the low-charge TMA-smectite. Benzene, however, competed effectively with toluene for adsorption sites on the low-charge TMA-smectite, and the adsorption of toluene in the presence of benzene was greatly depressed (Figure 8).

DISCUSSION

The closer packing of TMA ions on the higher charge density Arizona smectite was demonstrated by a higher organic carbon content of 5% compared with 4% in the lower charge density Wyoming smectite (Table 1). The difference in organic carbon content of 20% was in agreement with the approximate difference in CEC of 25% for the two smectite samples. The high-charge TMA-smectite also had a lower N_2 BET surface area than the low-charge TMA-smectite indicating less mineral surface area due to the higher density of TMA ions in the high-charge sample.

Two types of binding interactions are potentially available in the dry TMA-smectite samples. Aromatic molecules may interact with the aluminosilicate mineral surfaces and with TMA exchange ions (referred to here as mineral-sites and TMA-sites). Depending on the interionic distances between nearest neighbor pairs of TMA exchange ions, an aromatic molecule could conceivably be adsorbed by either a mineral- or a TMA-site. Considering the surface areas of TMA ions and the free space between exchanged TMA ions on Wyoming smectite, Barrer and Perry (1961) concluded that the most efficient packing of benzene molecules in the interlamellar regions was a tilted orientation

relative to the aluminosilicate sheets. If, however, the TMA ions are considered to be non-rotating and adhere alternately to the upper and lower lamella, the interionic distances will accomodate a benzene molecule parallel to the clay layers. Thus, benzene and other aromatic molecules may interact with the TMA-tetrahedra in a tilted orientation, or with the mineral surfaces parallel to the clay layers, or simultaneously with both.

The degree to which benzene molecules (or other aromatic molecules) can adopt a more parallel orientation with the mineral surface depends on the available "free" area between TMA ions; a size distribution of such areas probably exists in TMA-smectite. The more spacious free-mineral sites should be occupied preferentially, followed by progressively smaller sites at which the aromatic molecule must assume a more tilted orientation with less energetic interactions. Similarly, as the molecular size increases (i.e., from benzene to toluene to xylene, etc.), the molecule is forced to adopt a more vertical orientation relative to the clay layers; these steric constraints lead to lower overall uptake.

The closer packing of TMA ions in the high-charge smectite apparently resulted in a decrease in the free-mineral surface area (not covered by TMA ions) in the interlamellae. This decrease is indicated by the N_2 BET surface areas of the two samples (Table 1). For the sample in dry state, adsorption at a free-mineral site was probably more energetically favored than adsorption at a TMA-site. This difference is expected to be more pronounced at low loading or at low P/P^0, where the vapor condensation requires a greater molar heat of adsorption. Because the low-charge smectite contains more free-mineral area than the high-charge smectite, the dry low-charge sample exhibited greater uptake and a sharper isotherm rise at low P/P^0. At high P/P^0, where the vapor condensation requires less attractive forces, the difference between the uptakes by the two samples was less.

To compare the uptake of organic chemicals by the dry and hydrated TMA-smectite samples, the isotherms from aqueous solution were normalized by use of relative concentration (equilibrium solution concentration/water solubility). This comparison indicated that the hydrated samples had lower adsorption capacities, which probably resulted from the adsorptive competition of water and a water-induced sieving effect. The adsorptive competition of water may account for the somewhat smaller uptake of benzene by the low-charge TMA-smectite, in which significant intercalation occurred in both the wet and dry samples. For example, at a partial pressure or relative concentration of .2 (at which point the isotherms began to flatten), benzene uptake by the dry and wet low-charge samples was about 120 and 75 mg/g, respectively (Figures 1 and 4). In the aqueous system, the ratio of ad-

sorbed benzene to exchanged TMA ions was about 1:1, whereas in the dry state this ratio was about 1.7:1. The lesser uptake of benzene and the observed 1:1 ratio of benzene to TMA ions in the presence of water may have resulted from the preferential adsorption of water by the free-mineral sites, leaving only the TMA-sites for the adsorption of benzene.

A water-induced sieving effect may account for the very low adsorption of benzene, toluene, and o-xylene by the high-charge TMA-smectite in the presence of water; it also may have contributed to the reduced adsorption of toluene and xylene by the low-charge TMA-smectite. Hydration of the free-mineral surfaces or the exchanged TMA ions, or both, apparently reduced accessibility of the aromatic molecules to the interlayers. In the high-charge TMA-smectite, not only did the average lateral distance between adjacent TMA exchange ions decrease due to its higher CEC, but hydration water may have further occluded the interlamellar regions resulting in more restricted passage of the solute. As a result, the adsorptive capacity of the high-charge TMA-smectite in an aqueous system was much reduced compared with that of low-charge TMA-smectite.

The proposed adsorption mechanism for the uptake of organic compounds from water should lead to adsorptive competition in multisolute systems. The competitive effect of two solutes was examined by studying adsorption of mixtures of benzene and toluene over a range of concentrations of each solute. In the binary solute system, benzene competed effectively with toluene for adsorption sites, as the uptake of toluene was greatly decreased by the presence of benzene. In comparison, the uptake of benzene was not significantly affected by toluene because of the much higher affinity of benzene for the water-saturated TMA-smectite. This competitive effect is consistent with the single-solute isotherms of benzene and toluene, as shown in Figures 4 and 5. These results suggest that the adsorption of toluene in the presence of benzene was restricted because benzene preferentially occupied the intralamellar regions of the low-charge TMA-smectite.

The work presented here demonstrates the potential versatility of modified clay minerals for the separation of organic compounds in aqueous systems. By ion-exchange reactions of TMA for inorganic exchange ions on smectite, adsorbents of widely different behavior may be prepared for shape-selective adsorption of aromatic compounds. The degree of shape-selectivity can be increased by using smectites of higher charge density. In these systems, an important factor affecting the degree of sorption of aromatic compounds from water by TMA-smectite was the interionic area between exchanged TMA ions. Although the high-charge Arizona TMA-smectite did not adsorb substantial quantities of benzene in the presence of bulk water, the low-charge Wyoming TMA-smectite was very effective in remov-

ing benzene from water and may be a useful material for purifying benzene-contaminated water.

ACKNOWLEDGMENTS

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