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Retention of Organic Contaminants by Soils and

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RETENTION OF ORGANIC CONTAMINANTS BY SOILS AND CLAYS EXCHANGED WITH ORGANIC CATIONS

by

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ABSTRACT

RETENTION OF ORGANIC CONTAMINANTS BY SOILS AND CLAYS EXCHANGED WITH ORGANIC CATIONS

by

Jiunn-Fwu Lee

When organic cations of the form $[(CH_3)_3NR]^+$ were exchanged for natural metal ions such as Ca^{2+} and Na^+ in soil (clay), the sorptive properties of the soil (clay), were greatly modified. When modified with cations containing large organic moieties (R groups), the surface properties of soil (clay) changed from hydrophilic to hydrophobic. Soils (clays) exchanged with hexadecyltrimethylammonium (HDTMA) ions ($R = C_{16}H_{33}$) had significantly higher organic matter contents, and greatly enhanced sorptive capacities for removing nonionic organic chemicals (NOCs) from water. In aqueous solution, the uptake of NOCs by HDTMA treated soil (clay) was primarily by solute partitioning into the organic medium formed by conglomeration of large alkyl chains of organic cations. The organic phase derived from exchanged HDTMA was 10 to 30 times more effective than natural organic matter for removing NOCs from water.

In organo-clay complexes containing smaller organic cations, such as tetramethylammonium (TMA), the organic matter consisted of separate

small organic moieties. This phase did not act as an effective partition medium for removing NOCs from water, and the sorptive behavior of TMA-smectite were distinctly different from that of HDTMA-smectite. In the presence of water, TMA-smectite showed a high degree of shape selectivity resulting in high uptake of benzene and progressively lower uptake of larger aromatics. The dry TMA-smectite showed comparatively low selectivity in the uptake of aromatic chemicals. The shape-selectivity of TMA-smectite could be increased by the presence of water which appeared to shirnk the interlamellar cavities. Increased shape selectivity was also manifest in a high-charged smectite (from Arizona) due to the closer parking of TMA ions. Overall, the main factor affecting the degree of sorption of aromatic compounds by TMA-smectite was found to be the lateral free distances between the exchanged cations.

The modification of soils and clays with organic cations might be used to improved the retardation capabilities of low organic matter soils for NOCs, and to enhance the containment capabilities of clay landfill liners and slurry walls.

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INTRODUCTION

The sorption and desorption behaviors of soils, sediments and suspended particles are important factors affecting the environmental fates and effects of xenobiotic chemicals. Chemicals that are sorbed tightly are less available for processes such as leaching, volatization (Kay and Elrick, 1967; Spencer et al., 1988), transformation (Bartha, 1971; Bordeleau and Bartha, 1972) and degradation (Hsu and Bartha, 1974; Stevenson, 1982). The factors that may affect the extent to which chemicals sorb to the sorbents are : (1) physical and chemical properties of chemicals (Briggs, 1969; Chiou et al., 1979); (2) soil environmental factors : temperature, pH, water content, etc. (Harris and Warren, 1964; Bailey, 1968; Yaron and Saltzman, 1972); (3) soils characteristics: type of clay, content of clay, silt, sand, and soil organic matter (Moreale and Bladel, 1976; Chiou et al., 1983; Garbarini and Lion, 1986). For nonionic organic compounds (NOCs), which are by far the most important class of organic pollutants, the organic matter content of soil appears to be the most important soil factor in controlling their sorptive behavior. In studying the sorption of simazine by soil, Burnside et al. (1961) indicated that both clay and organic matter were involved in adsorption of simazine. Upchurch et al. (1962) reported that the percentage of monuron retained against leaching increased from 35% to 95% as the soil organic matter content increased from 0.87% to 1.14%. Similar studies done by Lambert et al.(1965, 1967, 1968) have shown that the organic fraction of soil was single factor most highly related to herbicide activity. Lambert further suggested that the role of soil organic matter was similar to that of an organic solvent in solvent extraction and that the partitioning of a neutral organic compound between soil organic matter and water correlated well with its partitioning between water and an immisible organic solvent. The works of Chiou et al (1979, 1983, 1985a) are of special interest when attempting to resolve the role of soil organic matter on the sorption of nonionic, nonpolar organic chemicals from water. These authors interpreted the uptake of nonionic organic compounds from aqueous system by soils in terms of a partitioning of the solutes between the solution and a hydrophobic phase consisting of the soil organic matter. They also suggested that a wide range of sorption behavior can be accounted for by considering the soil to be a dual sorbent, in which the mineral fraction of the soil functions as a conventional solid adsorbent and the organic matter functions as a partition medium. They further pointed out that in soil water systems, water is preferentially adsorbed by the mineral surfaces, and the uptake by soil consists primarily of solute partitioning into the organic matter. Thus water acts to deactivate the mineral surfaces for the adsorption of nonionic organic compounds which cannot compete with water for binding sites in the mineral surfaces. This concept of partitioning allows accurate estimation of soil-water distribution coefficient from octanol-water partition coefficients (K_{ow}) (Karickhoff, 1979; CHiou et al., 1982; Means et al., 1982), water solubilities (Freed et al., 1979; Chiou et al., 1983), and bioconcentration factor (BCF) (Chiou, 1985b). Recently, Boyd et al. (1988a) demonstrated that when large organic cations are exchanged for metal cations in soil, the sorptive capacity for nonionic compounds and the organic matter content of soil are greatly enchanced. The exchanged organic cations were shown to form an organic phase that behaved as a powerful partition medium for the removal of organic compounds from water. Therefore, it wound be of interest to study the sorption behavior of soil after treated with various organic cations.

In clay minerals, much effort has been focused on smectite for the sorption of xenobiotics because of its high cation exchange capacity (CEC) and surface area. Many authors (Hilton and Yuen, 1963; Shin et al., 1970; Pionke and Chesters, 1973; Hassett et al., 1980) have shown that clays have the ability to reduce drastically the effect of pesticides. For examples, Yuen et al. (1962) showed that the adsorption of monuron was highest in those soils in which smectite was the major clay constituent. Hill et al. (1955) found that more monuron was adsorbed by bentonite than by kaolinite. Coggins et al. (1959) suggested that the reason for the differential influence of substituted-ureas was due to the amount of bentonite present in soil. Although clays have been recognized as powerful adsorbents for the adsorption of polar, ionic organic compounds from water (Hance, 1969), few studies have been carried out on clays to serve as practical adsorbent for the removal nonpolar, nonionic organic chemicals from aqueous systems. This can be attributed to strong polar interaction of water with mineral surfaces (Mortland, 1970) which are thus no longer available for the sorption of relatively nonpolar organic solutes. However, this limited sorption character of clays toward nonionic chemicals can be remedied by replacing natural inorganic exchange cations by large organic cations through ion exchange reations (Barrer et al., 1955, 1957; Wolfe et al., 1985; Boyd et al., 1988b). As organic cations exchange for metal ions on clay surfaces, these organic cations act as "pillars" which hold the aluminosilicate sheets permanently apart and greatly increase the available sorbing surface. Also, in the modified form, the surface properties of clay will change from hydrophilicity to hydrophobicity because organic cations are not strongly hydrated and decrease the free mineral surface area. Several workers have indicated that exchanging quaternary ammonium cations for the metal ions on the clay surface could considerably modify the hydratic and swelling properties of clays (Stul et al., 1978, 1979). The properties and structure of alkyl and aryl ammonium complexes of smectite have been extensively studied with more attention being given to the alkyl ammonium complexes. The literature dealing with alkyl ammonium complexes has emphasised organic vapor uptake. Barrer et al. (1955, 1957) showed that tetramethyl ammonium (TMA) and methylammonium-montmorillonite are useful sorbents for the separations of organic vapors by selective intercalation. White and Cowan (1958) have successfully separated aliphatic from aromatic compounds using dimethyldioctadecyl ammonium (DMDOA) as the stationary phase in gas chromatography (GC). These authors also pointed out that DMDOA ions form pillars when adhered on the interlamellae creating large free intersheet volumes. The same results were obtained by Barrer et al. (1961).

Until recently, the uptake of organic chemicals by organo-clay derivates from aqueous systems has received little attention. McBride et al. (1977) has reported the uptake of aromatics from water by TMA- and

HDTMA-smetite. Slabaugh et al. (1968) reported adsorption of methanol on DMDOA-montmorillonite from aqueous phase. Stul et al. (1978, 1979) were able to adsorb a series of alcohols on dodecylammonium montmorillonite in studies conducted over a wide range of alcohol concentration. Recently, Mortland et al. (1986) and Boyd et al. (1988c) studied the uptake of phenol and chlorophenols from aqueous solution by smectite whose cations were exchanged by quaternary ammonium ions. These authors showed that the sorptive capacity of modified clays is greatly improved in comparison with unmodified clays.

To obtained additional perspective of the influence of exchanged organic cations on the mechanistic function of modified clay, Boyd et al. (1988a) studied the sorption of nonionic, nonpolar organic compounds on hexadecyltrimethylammonium (HDTMA)-smectite from water. They found that the exchanged HDTMA ions functions as a partition medium and the uptake of organic solutes by HDTMA-smectite is mainly by solute partitioning into the organic medium that is formed by conglomeration of large C_{16} alkyl groups associated with HDTMA. Improvement of the sorptive capacity of soils with low organic matter contents was similarly achieved by cation exchange reactions with HDTMA ions.

It has been known that by a simple ion-exchange process, clays can be activated to give a greatly enhanced sorbing surface toward organic compounds in aqueous system. However, interesting as these observations are, the amount of quantitative information is still limited regarding the sorptive behavior of clay complexes with different organic cations. The effects of the structure of the exchanged organic cations on the sorptive properties of the organo-clay (sorbent), as well as the physical/chemical properties of nonionic organic compounds (sorbates) that determine their sorptive uptake by organo-clays, are elucidated in this work. In addition, the effects of water on the sorptive phenomena are established. To accomplish this, the sorptive behavior of various organic compounds by different modified clays from both aqueous and vapor phase were studied. In order to further clarify the sorptive properties of modified clays for NOCs, the competitive effects of organic chemicals in multi-solute systems, and the effect of the charge density (or CEC) of the clay, were evaluated. In addition, for the sake of environmental interest, the stability and affinity of exchanged organic cations on modified clays are shown in this research.

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CHAPTER 1

ATTENUATING ORGANIC CONTAMINANT MOBILITY BY SOIL MODIFICATION

ABSTRACT

Low organic matter clays, soils and aquifer materials have very little sorptive capability for common groundwater contaminants. Here we use organic cations of the form $[(CH_3)_3NR]^+$ to displace naturally occurring exchange ions resulting in significantly higher organic matter content, and greatly enhanced sorptive properties for nonionic organic solutes. The organic phase derived from exchanged hexadecyltrimethylammonium, where R is a C-16 hydrocarbon, behaved as a powerful partition medium that was 10 to 30 times more effective on a unit weight basis than natural soil organic matter for removing benzene, dichlorobenzene and perchloroethene from water. This simple soil modification might be used to improve the retardation capabilities of low organic matter soils and aquifer materials, and to enhance the containment capabilities of clay landfill liners and bentonite slurry walls.

Low organic matter clays, soils and aquifer materials have very little sorptive capability for common groundwater contaminants. We have used organic cations of the form $[(CH_3)_3NR]^+$ to displace naturally occurring exchange ions (e.g. Na^+ or Ca^{2+}) from soil resulting in significantly higher organic matter contents, and greatly enhanced sorptive properties for nonionic organic solutes. The organic phase derived from exchanged hexadecyltrimethylammonium, where R is a C-16 hydrocarbon, behaved as a powerful partitioning medium that was 10 to 30x more effective on a unit weight basis than natural soil organic matter for removing benzene, dichlorobenzene and perchloroethene from water. This simple soil modification may be used to improve the retardation capabilities of low organic matter soils and aquifer materials, and to enhance the containment capabilities of clay landfill liners and bentonite slurry walls.

The sorption of nonionic organic contaminants from water by soil is controlled by the soil organic matter content. There is strong evidence that the mechanism of uptake is primarily partitioning into the soil organic phase (Chiou et al., 1979,1983) which acts as a solubilizing medium for nonionic organic solutes. In contrast, the soil mineral fraction (e.g. oxides and clays) is generally not important in the uptake of nonionic organic solutes in soil water systems. Dipole interactions between the mineral surfaces and water prohibit nonionic organic solutes from interacting with this fraction of soil (Chiou et al., 1985). One practical result of the strong interaction of water with clays is the lack of sorptive capability of clay containment barriers (e.g. bentonite slurry walls or clay landfill liners) whose sole function is to retard the movement of water. Similarly, low organic matter surface soils and aquifer materials have very little retardation capability for nonionic organic pollutants. As a result, many anthropogenic organic compounds are found as groundwater contaminants and represent a serious threat to human health.

Soil materials contain significant cation exchange capacity (CEC) derived primarily from clay minerals such as smectite and kaolinite. Clays possess a net negative electrical charge which is compensated for by exchange cations on their surfaces. In nature, these exchange cations are mainly alkali metal and alkaline earth metal cations like Na^+ or Ca^{2+}. Hydration of these metal cations imparts a hydrophilic nature to the mineral surfaces and, as described above, these surfaces are not good sorbents for nonionic organic species which cannot displace the tightly held water. Organic cations may enter into ion exchange with metal cations on the exchange sites of clays. When metal ions are exchanged with certain organic cations which contain sizable organic moieties, the surface of the clay may be greatly modified to become strongly organophilic.

Boyd et al. (1988a) have performed such ion exchange reactions using purified smectite clays and actual soil materials, and organic cations of the form $[(CH_3)_3NR]^+$. The R group imparts the desired organophilic properties needed for sorption of organic solutes, and may be a C-1 to C-20 hydrocarbon (Boyd et al., 1988b). In this report we present data showing the enhanced uptake of several mobile organic contaminants from water by soil materials exchanged with hexadecyltrimethylammonium $[(CH_3)_3N(CH_2)_{15}CH_3]$(HDTMA) cations.

Adsorption isotherms of ^{14}C-HDTMA on (a) Ca^{2+}-smectite, (b) Marlette soil A horizon, and (c) Marlette soil B_t horizon are shown in Figure 1. The adsorption of HDTMA by all three materials is very strong as expected, with nearly quantitative displacement of Ca^{2+}, in the case of Ca^{2+}-smectite or the naturally occurring inorganic ions present in the Marlette A and B_t horizons. These are type I isotherms characteristic of ion exchange reactions in which the added ion, in this case HDTMA, is strongly preferred. Figure 1 shows that HDTMA is very strongly sorbed from solution until the CEC of the clay or soil material (Table I) is exceeded. The strong preference for HDTMA is due to its high mass relative to inorganic exchange ions like Na^+ and Ca^{2+}. The large alkyl ammonium ions

Figure 1. Adsorption of hexadecyltrimethylammonium (HDTMA) iodide (methyl-^{14}C American Radiolabeled chemicals, Inc., specific activity 52 mci/mmole) by Ca-smectite (right scale) and Marlette soil A and B_t horizons (left scale). Either 0.2 g Ca-smectite or 1 g soil and 10 ml water were placed in glass centrifuge tubes. Portions (50 to 400µl of an ethanol solution containing 1:1000 ^{14}C-HDTMA:HDTMA were added in an amount equal to 0.25, 0.5, 0.75, 1, 1.5 and 2X the cation exchange capacity (CEC) of the clay or soil. The samples were shaken 24h at 25°C. The aqueous phas was separated by centrifugation and 1 ml assayed for ^{14}C by liquid scintillation counting.

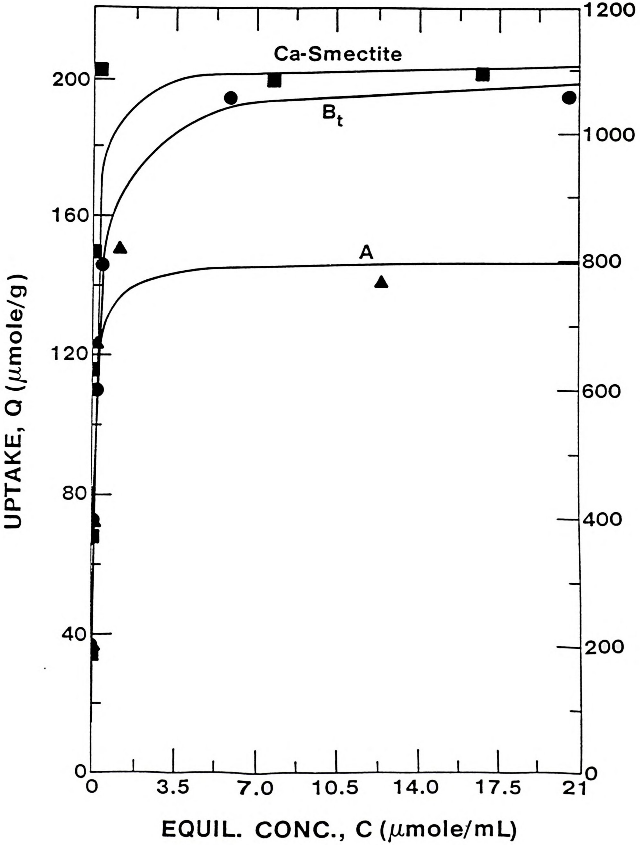

Ca-Smectite
B_t
A
UPTAKE, Q (μmole/g)
EQUIL. CONC., C (μmole/mL)
0
40
80
120
160
200
0
200
400
600
800
1000
1200
0
3.5
7.0
10.5
14.0
17.5
21

Table I. Properties of the untreated and HDTMA-treated clay and soil.

Property[a]	Ca-Smectite		B_t-horizon		A-horizon	
	Untreated	HDTMA-Treated	Untreated	HDTMA-Treated	Untreated	HDTMA-Treated
CEC (meq/100g)	91		14.6		16.4	
Particle size (%)						
Sand	0		42.6		56.6	
Silt	0		16.7		22.0	
Clay	100		40.7		21.4	
Organic Carbon (%)	0.91	17.3	0.3	3.7	2.6	6.5
Organic Matter (%)						
Soil O.M.	1.8	1.8	0.6	0.6	5.2	5.2
HDTMA O.M.	0	20.5	0	4.25	0	4.9
Total O.M.	1.8	22.3	0.6	4.85	5.2	10.1

[a] Cation exchange capacity (CEC) is sum of extractable cations: Al + Ca + Mg + K + Na[7]. Particle size analysis was performed by the Michigan State University Soil Testing Laboratory. Organic carbon analysis was performed by Huffman Laboratories, Inc., Golden, Colorado. Factors used to convert soil and HDTMA organic carbon to organic matter were 2 and 1.2, respectively.

once bound are also very difficult for smaller inorganic ions to displace due again to their high mass and because of van der Waals interactions between the alkyl chains themselves (Theng, 1979). As a result, large organic cations like HDTMA bind almost irreversibly to the clay surface.

Table I shows properties of the untreated and HDTMA-treated clay and soil materials. The treated materials were prepared by adding HDTMA in an amount equivalent to the CEC of the clay or soil. It is obvious from Table I that the organic matter contents have increased significantly. The amount of HDTMA organic matter expected in the treated samples can be calculated from the CEC. For example, the B_t soil should contain 4% HDTMA derived organic matter after the ion exchange reaction. Thus, the measured organic matter contents agree well with the expected (calculated) amount, again showing the stoichiometric displacement of inorganic ions by HDTMA. Depending on the particular organic cation and the CEC, organic matter contents in excess of 20 percent by weight can be achieved (Boyd et al., 1988b).

The presence of HDTMA as an exchange ion dramatically alters the sorptive capabilities of the clay and soil materials. Benzene, dichlorobenzene, and perchloroethene uptake by the Marlette A and B_t horizons is shown in Figures 2 and 3. Typical soil sorption behavior was observed for the untreated soil materials. For benzene and perchloroethene, uptake from water was very low by the untreated B_t horizon, due to its low organic matter content (0.6%), and could not be distinguished from the blank (no soil) samples. Uptake from water by the untreated A horizon was higher owing to the higher A horizon organic matter content (5.2%). The sorption isotherms for benzene,

Figure 2. Sorption of benzene, perchloroethene (PCE) and 1,2-dichlorobenzene (DCB) by untreated and HDTMA-treated Marlette soil A horizon. Treated soil was prepared by mixing 200 g soil and 1800 ml water, and then adding 50 ml H_2O containing HDTMA in an amount equal to the CEC of the soil. After thorough mixing, the mixture was filtered, washed with water and freeze dried. For the isotherms, 3 g treated soil or 15 g untreated soil, and 25 ml water were placed in glass centrifuge tubes. Three to 45 ul of benzene (neat), or of 0.1 g/ml methanol solutions containing PCE or DCB, were added. The tubes were closed immediately and shaken 24 h at 25°C. The aqueous phase was separated by centrifugation and either analyzed directly for benzene by HPLC with uv-detection or extracted with hexane and this extract analyzed for PCE or DCB by GC with electron capture detection.

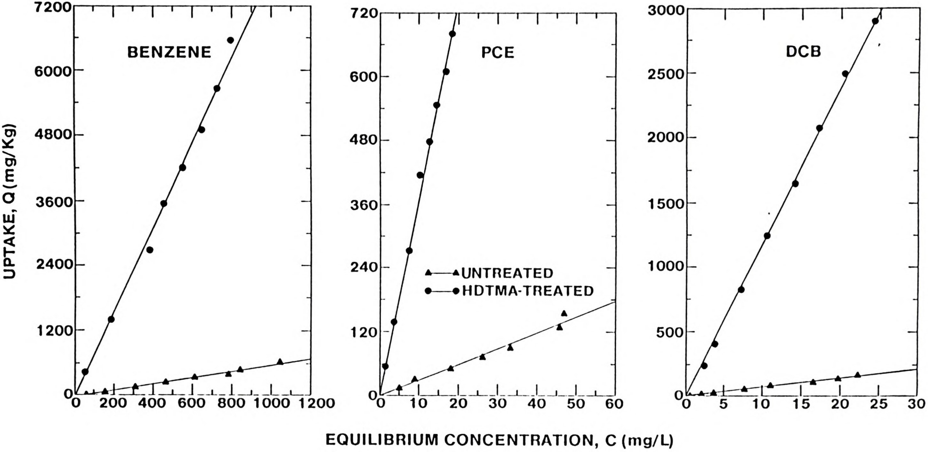
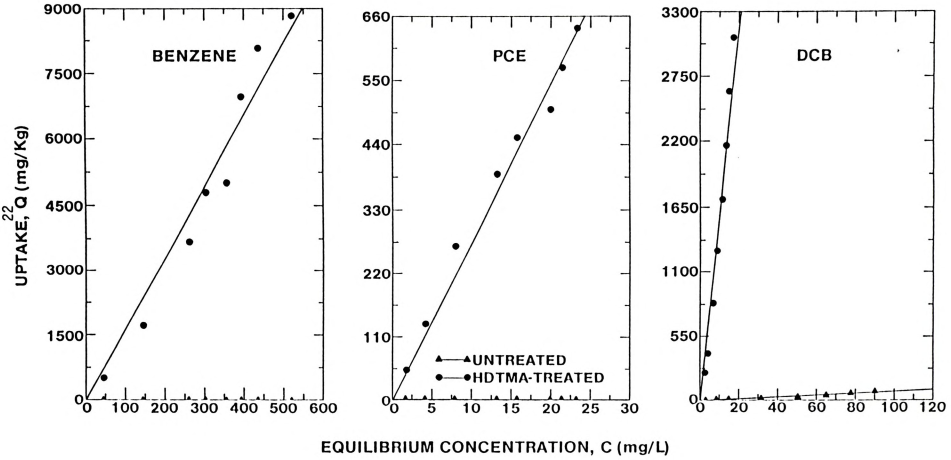

UPTAKE, Q (mg/Kg)
EQUILIBRIUM CONCENTRATION, C (mg/L)
BENZENE
0
1200
2400
3600
4800
6000
7200
0
200
400
600
800
1000
1200
PCE
0
120
240
360
480
600
720
0
10
20
30
40
50
60
UNTREATED
HDTMA-TREATED
DCB
0
500
1000
1500
2000
2500
3000
0
5
10
15
20
25
30

Figure 3. Sorption isotherms of benzene, perchloroethene (PCE) and 1 ,2-dichlorobenzene (DCB) by untreated and HDTMA- treated Marlette soil B_t horizon. The treated soil and isotherms were obtained as described in Figure 2.


UPTAKE, Q (mg/Kg)
BENZENE
9000
7500
6000
4500
3000
1500
0
0
100
200
300
400
500
600
PCE
660
550
440
330
220
110
0
0
5
10
15
20
25
30
▲—▲UNTREATED
●—●HDTMA-TREATED
DCB
3300
2750
2200
1650
1100
550
0
0
20
40
60
80
100
120
EQUILIBRIUM CONCENTRATION, C (mg/L)

dichlorobenzene and perchloroethene by the untreated A horizon were highly linear, as observed in previous studies on the sorption of these solutes by soils and sediments (Chiou et al., 1979, 1983). Uptake of these solutes is commonly expressed as

$$Q = KC$$

where Q is the amount sorbed per unit weight of soil and C is the equilibrium solute concentration in water. The sorption (partition) coefficient K corresponds to the slope of the line. The K values normalized for the soil organic matter contents (K_{om} = 100K/%O.M.) tend to converge on a single value for each solute (Chiou et al., 1979, 1983). The log K_{om} values obtained here are very close to those reported for other surface soils. For example, the log K_{om} values reported by Chiou et al. (1983) for benzene and dichlorobenzene were 1.26 and 2.27, respectively, as compared to our values of 1.04 and 2.14 (Table II). The log K_{om} values obtained for dichlorobenzene from the untreated Marlette A and B_t horizon are also in good agreement (2.14 and 2.12).

After treating the same soil materials with HDTMA in an amount equivalent to the CEC, the sorption of benzene, dichlorobenzene, and perchloroethene increased dramatically. This effect can be seen clearly in Figures 2 and 3 which shows the sorptive capability of the untreated and HDTMA-treated soils. For the A horizon the K values increased by a factor of 12 to 16X in the HDTMA treated material (Table II). The corresponding Kom values increased by about 6.5 to 8.5X. The increase in K was even greater for the B_t horizon which, in the untreated form, contains very little natural organic matter. For dichlorobenzene, K was about 200X greater in the modified B_t soil.

Table II. Sorption coefficients of benzene, perchloroethene (PCE) and 1,2-dichlorobenzene (DCB) on untreated and HDTMA-treated soil.

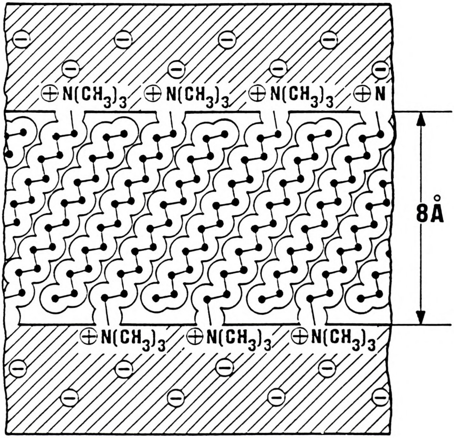
Sorption Coefficient	A-horizon		B_t-horizon		log K_{ow}[a]
	untreated	HDTMA-treated	untreated	HDTMA-treated	
K					
Benzene	0.57	7.8	0	16.5	
PCE	2.95	37.0	0	27.3	
DCB	7.25	120.0	0.80	162.6	
log K_{om}					
Benzene	1.04	1.89	-	2.53	2.3[b]
PCE	1.75	2.56	-	2.75	2.6
DCB	2.14	3.07	2.12	3.52	3.38

[a] Octanol-water partition coefficients (Ref. 2).
[b] Hexane-water partition coefficient (Ref. 8).

An estimate of the relative effectiveness of organic matter derived from HDTMA versus natural organic matter can be made by comparing the log K_{om} values from the untreated A horizon and from the HDTMA-treated B_t horizon. In the former case, organic matter is entirely natural, and in the latter organic matter is derived primarily from HDTMA (Table I). This comparison reveals that the organic matter composed of HDTMA is about 10 to 30 times more effective than natural soil organic matter for removing the organic solutes from water (Table II). Thus, not only can the organic matter content of soil be increased through modification with HDTMA, but the added organic matter is highly effective for immobilizing common mobile pollutants like benzene. The results reported here for actual soil materials are in good agreement with the sorption characteristics on HDTMA-smectite for benzene and trichloroethene (Boyd et al., 1988a).

The type of organic phase formed by HDTMA is depicted in Figure 4. Interaction of the non-polar C-16 hydrocarbon tails of HDTMA present on the exchange sites apparently forms an organic phase that acts as solubilizing (partitioning) medium for removing organic solutes from water. This would be functionally and conceptually similar to a bulk organic solvent like hexane or octanol. This concept is supported by the linearity of the isotherms (Chiou et al., 1979, 1983) and by the similarity of the log K_{om} values (from the HDTMA-treated B_t) for benzene, dichlorobenzene, and perchloroethene to the corresponding octanol-water or hexane water-partition coefficients, i.e. log K_{ow} or log K_{hw} (Table II). That the organic phase derived from exchanged HDTMA is more effective than soil organic matter for removing nonionic organic solutes from water is not surprising. The organic phase of HDTMA is derived

Figure 4. Schematic representing smectite clay intercalated with hexadecyltrimethylammonium cations. Gallery region resembles a bulk phase solvent like hexane or octanol, and functions as a highly effective partitioning medium for removing organic contaminants from water.


⊕N(CH$_3$)$_3$
⊕N(CH$_3$)$_3$
⊕N(CH$_3$)$_3$
⊕N
8Å
⊕N(CH$_3$)$_3$
⊕N(CH$_3$)$_3$
⊕N(CH$_3$)$_3$

entirely from the low polarity C-16 hydrocarbon tails (Fig. 4). Soil organic matter contains a high polar group content and is, therefore, a less effective medium solubilizing nonpolar compounds.

Our results demonstrate that HDTMA exchanged soil materials and clays are effective sorbents for removing common organic groundwater pollutants like benzene and perchloroethene from water. The soil modification is accomplished by simple ion exchange of highly preferred large organic cations like HDTMA for small inorganic cations like Na^+ or Ca^{2+}. Quaternary organic cations like HDTMA are common cationic surfactants and available commercially. Such modified soils and clays may be used: (1) to increase the sorptive capacity of low organic matter soils; (2) to increase the sorptive properties of subsurface materials under existing waste disposal sites via underground injection of the organic cation; and (3) as components of bentonite (smectite) slurry walls and clay landfill liners to enhance the containment capabilities of such waste disposal reservoirs.

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CHAPTER 2

RETENTION OF ORGANIC CONTAMINANTS BY SOILS EXCHANGED WITH ORGANIC CATIONS

INTRODUCATION

The interactions of organic contaminants and pesticides with soils, sediments, and aquifer materials are important in determing the environmental fates and effects of these toxic chemicals. Knowledge of the sorptive behaviors of such chemicals is necessary to better understand their fates and the potential biological effects in the soil environment. Chemical that are sorbed tightly on soils are less available for important processes such as leaching, volatization, biodegradation, and bioaccumulation. Two mechanisms, in general, have been involved the sorption of organic species on soil-water system. First, the sorption of organic chemicals may be related to highly specific interactions with soil components such as ion exchange, protonation, hydrogen bindings, coordination/ion dipole reactions with clays (Mortland, 1970; Theng, 1974) and nucleophilic addition reactions with soil organic matter (Parris, 1980). These sorptive mechanisms account for the uptake of organic cations and some polar organic molecules (e.g. amines) on soil. The second major mechanism of organic chemical-soil interaction involves nonionic organic compounds (NOCs), which are by far the largest and most problematic group of organic contaminants. This mechanism has been described by Chiou et al. (1979, 1983) as a partition process involving non-polar interactions between soil organic matter and NOCs. Sorption of this type is characterized by a linear isotherms, low equilibrium heats, noncompetitive sorption in multisolute systems, and dependence of sorption on the solute water solubility (Chiou et al., 1979, 1983) and the properties of soil (Briggs, 1969; Karickhoff et al., 1979; Garbarini et al., 1986). The sorption of important groundwater pollutants such as benzene and trichloroethylene by soil are examples of this type of interaction.

Many researchers have showed that the uptake of NOCs from water onto a great variety of soils is related primarily to the soil organic matter contents (Bowman et al., 1965; Boucher et al., 1972; Means et al., 1982; Dzombak et al., 1984; Chiou et al., 1983, 1985a) and this relationship between uptake of NOCs and soil organic matter has greatly simplified the prediction of NOCs by soil. However, until recently there was no clear mechanistic understanding of the association of NOCs with soil organic matter. Lambert et al. (1965, 1967, 1968) did recognize that, in the sorption of neutral organic pesticides on soils, the role of soil organic matter was similar to that of an organic solvent extraction. These authors further suggested that sorption could be attributed to an active fraction of soil organic matter and considered soil to be analogous to a chromatographic column with a stationary phase of organic matter. Recently, Chiou et al. (1979, 1983) in studies of sorption of NOCs from water on soil showed that: (1) the sorption isotherms of NOCs were linear over a wide range of aqueous concentrations, (2) soil uptake of NOCs exhibited a small heat effect, (3) no apparent solute competition occurred in multisolute systems, and (4) a dependence of sorption on the solute water solubility. Based on these observations of sorptive characteristics in soil-water equilibria, Chiou et al. (1979, 1983) suggested that sorption of NOCs from water on soil is primarily due to the partitioning of NOCs into the soil organic phase. Adsorption onto the soil mineral phase is suppressed in the presence of water because the poorly water soluble organic species cannot compete with strongly held water for adsorption sites (Chiou et al., 1985a).

It is now apparent that low organic matter soils, clays, and aquifer materials have little sorptive capacity for removing of NOCs from soil-water systems, and are therefore ineffective in attenuating organic contaminant mobility. However, this limited sorptive capacity of low organic carbon soils can be greatly improved by replacing natural metal cations with large organic cations through a ion exchange reaction. This simple modification for improvement of the retardation capacity of low organic matter soils has been examined by Boyd and his co-workers (1988a). These authors used hexadecyltrimethylammonium (HDTMA) ions to replace naturally occuring metal ions and found that in HDTMA-exchanged soil, not only had the organic matter content been increased, but the sorptive capacity for NOCs was greatly enhanced. The organic phase derived from HDTMA exchanged on both soils (Boyd et al., 1988a) and smectite clays (Boyd et al., 1988b) was shown to be a powerful partition medium for the removal of NOCs from water. It was suggested that such modified soils and clays may be used to improve the retardation capabilities of low organic matter soils and aquifer materials, and to enhance the containment capabilities of clay landfill liners and slurry walls. In the present communication, the studies of soil modification for attenuating organic contaminant mobility have been expanded to include seven NOCs with water solubilities ranging over approximately two orders of magnitude. Many of these have relatively high water solubilities and are common groundwater contaminants. In addition, the structural effects of different exchanged organic cations of the general from $[(CH_3)_3NR]^+$ in relation to the sorption of NOCs from water is established. Three organic cations, HDTMA (R =

$C_{16}H_{33}$), dodecyltrimethylammonium (DDTMA) (R = $C_{12}H_{25}$), and nonyltrimethylammonium (NTMA) (R = C_9H_{19}), have been used for the preparation of soil-organic complexes from which different sorptive behaviors derived from different organic cations can be elucidated. Finally, soils having different textural composition (clay contents) are used to assess the influence of cation exchange capacity (CEC) on the sorptive properties of HDTMA-exchanged soils.

EXPERIMENTAL

Soils

The following soils were used in this study: Marlette soil A and B_t horizon (fine-loamy, mixed, mesic Glossoboric Hapludalfs), Oshtemo soil B_t horizon (coarse-loamy, mixed, mesic Typic Hapludalfs), and St. Clair soil B_t horizon (fine, illitic, mesic Typic Hapludalfs). Organo-soil complexes were prepared by reacting 200g of soils with HDTMA, DDTMA, or NTMA chloride salts. The organic cation salts were dissolved in water (1800ml) and added in an amount equal to CEC of soils. After thorough mixing, the organo-soil complexes were dialyzed against distilled water until a negative chloride test was obtained. Then, the exchanged soils were freeze-dried and stored at room temperature.

Chemicals

The organic chemicals used in this work were: benzene, toluene, ethylbenzene, perchloroethene (PCE), trichloroethene (TCE), o-dichlorobenzene (o-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB). All reagents used in this study were analytical grade or better and purchased from Aldrich Chemical Co., Milwaukee, Wis. Benzene and toluene were added to the soils as the neat liquids, whereas the others were prepared in methanol stock solutions, using a Hamilton microliter syringe.

Soil properties:

The cation exchange capacity (CEC) of soils was taken to be the sum of extractable cations: Al + Ca + Mg + K + Na. Exchangeable Ca, Mg, K, and Na were extracted with 1N NH_4OAC at pH 7 and determined by atomic absorption spectrophotometry. Exchangeable Al from each soil was determined by displacement with 1N KCl. The quantity of Al in the extract was analyzed by titrating with standardized base. Organic carbon analysis was performed by Huffman Laboratories, Inc., Golden, Colorado. Factotrs used to convert soil, HDTMA, DDTMA, and NTMA organic carbon to organic matter were 2, 1.24, 1.27, and 1.29, respectively.

Batch equilibrium experiments:

(1) Asdorption isotherms of organic cations on soils: 1g of St. Clair, Marlette, or Oshtemo soils B_t horizon and 10ml of water were placed in Corex glass tubes. Portions of an ethanol solution containing 1:1000 ^{14}C-HDTMA: HDTMA were added in an amount equal to 0.25, 0.5, 0.75, 1, 1.5, and 2 times the CEC of soils. The mixed suspension were shaken for 24h at 20°C in a reciprocating shaker. THe aqueous phase were separated by centrifugation and 1ml assayed for ^{14}C by liquid scintillation counting.

(2) Adsorption isotherms of organic chemicals on soil-organic complexes: Adsorption isotherms were obtained by adding varying quantities of test organic chemicals (Lee et al., 1988) to Corex glass tubes which contained either 25ml of water and 3g of organo-soil complexes or 20ml of water and 15g of untreated soils. To obtain equilibrium, mixed solutions were placed on a reciprocating shaker for 24h at 20°C. Preliminary

kinetic investigations indicated that the sorption equilibrium was reached in 20h. Phases were separated by centrifugation at 8000 rpm for 30 min. using a Sorvall RC5-C centrifuge equipped with an SS-34 rotor. Aliquots of the equilibrium supernatant (1ml) were then transferred into a glass vial containing 10ml of hexane (for o-DCB, 1,2,4-TCB, TCE, and PCE) or carbon disulfide (for benzene, toluene, and ethylbenzene). The vials were closed with foil-lined screw caps and shaken vigorously for 1h on a reciprocating shaker.

Analytical procedures:

The hexane and carbon disulfide extracts were analyzed for the organic compounds by gas chromatography (GC). GC was performed on a Hewlett Packard model 5890A equipped with both electron capture and flame ionization detectors. The mass of organic compounds in the extracts was determined by measurement of peak areas by a Hewlett Packard 3392A integrator. For 1,2,4-TCB and o-DCB, a 1.5% SP-2250/1.95% SP-2401 on 100/120 supelcoport packed glass column (2.4m x 6.4mm ID). For TCE and PCE, the separation was performed on 1% SP-1000 coated on 60/80 carbopack B packed steel column (1.8m x 3.2 mm ID). Finally, the column packed with 5% SP-1200/1.75% Bentonite 34 coated on 100-120 mesh supelcoport support was used for separation of benzene, toluene, and ethylbenzene. Carrier gas was high-purity N_2 at flow of 40ml/min. Operating temperature for injection port and detector were 270°C and 300°C, respectively. Each run was isothermal: Oven temperature were 80°C for benzene and toluene, 100°C for ethylbenzene, 150°C for TCE, o-DCB, and 1,2,4-TCB, and 180°C for PCE. All samples were run in duplicates and the recovery of these test chemicals ranged from 90% to 98%. The equilibrium concentration measured were not adjusted for the recovery.

RESULTS

The physical and chemical properties of untreated Marlette soil and the Marlette soil treated with three different organic cations are shown in Table 1. The three organic cations used were all of the form $[(CH_3)_3NR]^+$ and R varied in size from a C_{16} (HDTMA) to a C_{12} (DDTMA) to a C_9 (NTMA) hydrocarbon. When the Marlette A and B_t horizon soils were treated with HDTMA, DDTMA, and NTMA ions (in an amount equivalent to the CEC of the soil), the organic carbon (OC) contents increased significantly. The organic matter (OM) content of treated soils is the sum of indigenous soil organic matter (SOM) plus OM derived from the exchanged organic cations. For example, The tolal OM content of HDTMA-treated Marlette soil B_t horizon (4.85%) was obtained by adding the indigenous SOM (0.6%) plus OM derived from HDTMA ions (4.25%). As expected, larger organic cations (e.g. HDTMA ions) were more effective for the contribution of OM than small organic cation (e.g. NTMA ion). The relative increase in organic matter contents was much greated for the B_t horizon soil, which as a subsurface soil, has low indigenous SOM valves. Thus, in the treated B_t soils most of the total organic matter is dervied from the exchanged organic cations. In contrast, in the treated A horizon soil, natural organic matter exceed the added synthetic organic matter.

The properties of three different soils either untreated or treated with HDTMA are shown in Table 2. The soils were selected to give a range of textural classes, CECs and clay contents. Of these, the Oshtemo (sandy loam) has the lowest clay content and the lowest CEC, and the St. Clair

Table 1. Properties of the untreated Marlette soils and the Marlette soil treated with three different organic cations.

	B_t Horizon				A Horizon		
Property	Untreated	Treated			Untreated	Treated	
		HDTMA	DDTMA	NTMA		HDTMA	DDTMA
CEC (meq/100g)	14.6				16.4		
Particle Size (%)							
Sand	42.6				56.6		
Silt	16.7				22.0		
Clay	40.7				21.4		
pH	5.4				6.4		
Organic Carbon (%)	0.30	3.71	1.98	1.18	2.59	6.48	4.37
Organic Matter (%)							
Soil Organic Matter	0.60	0.60	0.60	0.60	5.18	5.18	5.18
Organic Matter Derived from Organic Cations	0	4.25	2.13	1.14	0	4.85	2.25
Total Organic matter	0.60	4.85	2.73	1.74	5.18	10.03	7.43

Table 2. Properties of three different soils (B_t-horizons) either untreated or treated with HDTMA.

	Untreated			HDTMA-treated		
Property	St. Clair	Marlette	Oshtemo	St. Clair	Marlette	Oshtemo
CEC (meq/100g)	18.3	14.6	4.5			
Particle Size (%)						
Sand		42.6				
Silt		16.7				
Clay		40.7				
pH	6.72	5.40	5.84			
Organic Carbon (%)	0.44	0.30	0.11	3.25	3.71	0.83
Organic Matter (%)						
Soil Organic Matter	0.88	0.60	0.22	0.88	0.60	0.22
HDTMA Organic Matter	0	0	0	3.50	4.25	0.90
Total Organic Matter	0.88	0.60	0.22	4.38	4.85	1.12

(clay) the highest. Table 2 shows that the OM content of the treated soils is depentent on the CEC of the soils. Thus, the treated-Oshtemo soil, with the lowest CEC, had the lowest total OM content. As mentioned above, the soil-organic complexes were prepared by adding organic cations in an amount equal to the CEC of soils.

The adsorption of HDTMA ions by the three soils (B_t horizons) is shown in Figure 1. HDTMA was added in varying amount up to twice the CEC of the soil. Adsorption isotherms of HDTMA ions on soils were typical for high-affinity ion exchange reactions. The isotherm shape is Type I in Brunauer's classification (1944) showing a high of preference of the soil for the added HDTMA exchange ions. As illustrated in Figure 1, the HDTMA ions are very strongly sorbed from solution by the soils. The isotherms show a very little HDTMA in solution at dosages close to the CEC of soils, and some continued sorption of HDTMA ions in excess of CEC. However, when HDTMA ions were added at 1.5 and 2 times the CEC of the soil, the solution equilibrium concentrations increased significantly.

The release of exchanged ^{14}C-HDTMA from the Marlette B_t horizon soil after mixing with aqueous solutions of $CaCl_2$ was also measured (data not shown). Calcium chloride was added in amount equal to 10, 50, and 100 times the amount of exchanged HDTMA. Sorption isotherms of benzene, toluene, and ethylbenzene on the untreated and HDTMA-treated St. Clair and Oshtemo soil B_t horizon are shown in Figure 2. As expected, the untreated soils display very low uptake of these organic chemicals from water, presumably due to their low OC contents; the isotherms of benzene and toluene could not be distinguished from the blank (no soil) samples. In contrast to the lack of sorption by the untreated soils, very high uptake

Figure 1. Adsorption isotherms of hexadecyltrimethyl ammonium (HDTMA) on untreated soils B_t horizon.

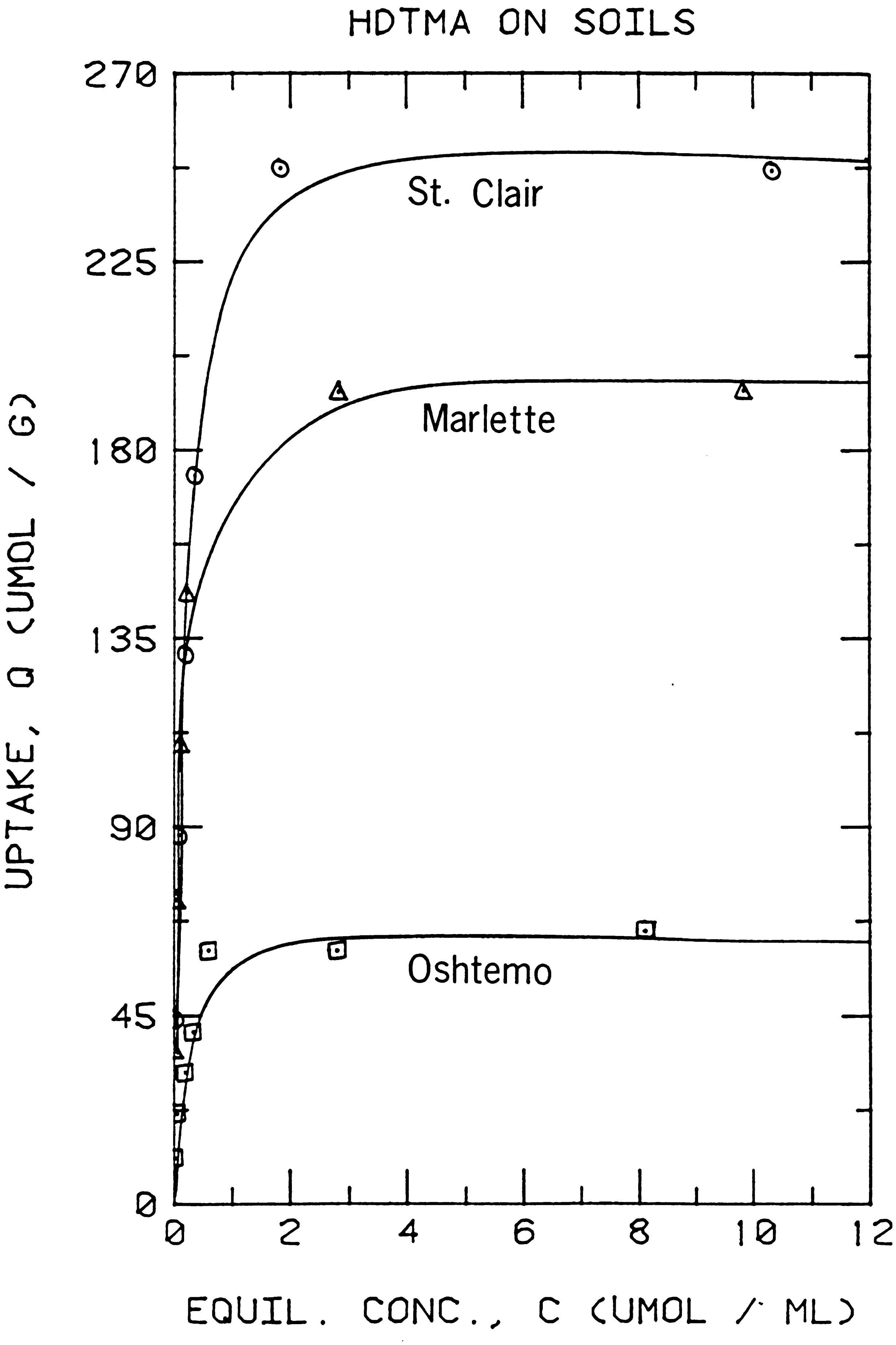
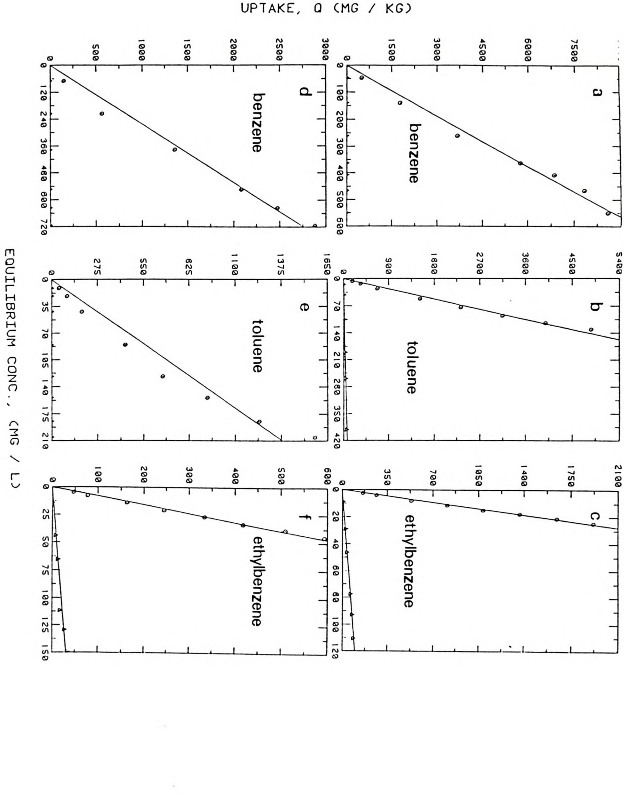

HDTMA ON SOILS
St. Clair
Marlette
Oshtemo
UPTAKE, Q (UMOL / G)
0
45
90
135
180
225
270
EQUIL. CONC., C (UMOL / ML)
0
2
4
6
8
10
12

Figure 2. Sorption of benzene, toluene, and ethylbenzene on untreated (triangles) and HDTMA-treated (circles) B_t-horizon St. Clair (a - c) and Oshtemo (d - f) soils.


UPTAKE, Q (MG / KG)
EQUILIBRIUM CONC., (MG / L)
a
benzene
b
toluene
c
ethylbenzene
d
benzene
e
toluene
f
ethylbenzene
0
1500
3000
4500
6000
7500
100
200
300
400
500
600
900
1800
2700
3600
4500
5400
70
140
210
280
350
420
350
700
1050
1400
1750
2100
20
40
60
80
100
120
500
1000
2000
2500
240
360
480
720
275
550
825
1100
1375
1650
35
105
175
25
50
75
125
150

of benzene, toluene, and ethylbenzene was found on the HDTMA-treated soils. This is reflected in the dramatic increase in the slopes of isotherms shown in Figure 2. All isotherms were linear over a broad range of aqueous phase concentrations.

Figure 3 shows sorption isotherms for benzene, toluene, and ethylbenzene on the untreated and HDTMA-treated A and B_t horizons. Again, uptake by the B_t horizon of all chemicals tested was greatly enhanced in the HDTMA-treated soil. For the treated A-horizon, uptake was also enhanced significantly, but the relative increase was lower than for the B_t horizon because of the highest indigenous SOM content in the A horizon. Although the HDTMA-treated Marlette A-horizon soil is about 50% natural SOM and 50% HDTMA organic matter (Table 1) sorption was more than doubled in the treated soil.

The influence of soil properties on the sorptive behaviors of the HDTMA-treated St. Clair, Marlette, and Oshtemo soils for benzene, toluene and ethylbenzene can be seen by comparing the isotherms shown in Figure 4. Increasing the CEC of soils (Oshtemo < Marlette < St. Clair) resulted in steeper isotherms (high slopes). Further inspection of Figure 4 shows that in overall sorptive behavior, much larger differences in the slopes of the isotherms were found between HDTMA-treated Oshtemo and St. Clair soils as compared to the differences between the treated-Marlette and St. Clair soils. This trend follows the same trend in total OM contents of the HDTMA-treated soils that decrease in the order: Marlette ≈ St. Clair > Oshtemo.

Figure 5 shows the isotherms of benzene, toluene, and ethylbenzene uptake by Marlette soil B_t horizon having HDTMA, DDTMA, and NTMA as the

Figure 3. Sorption of benzene, toluene, and ethylbenzene on untreated (triangles) and HDTMA-treated (circles) Marlette soil A (a - c) and B_t (d - f) horizons.

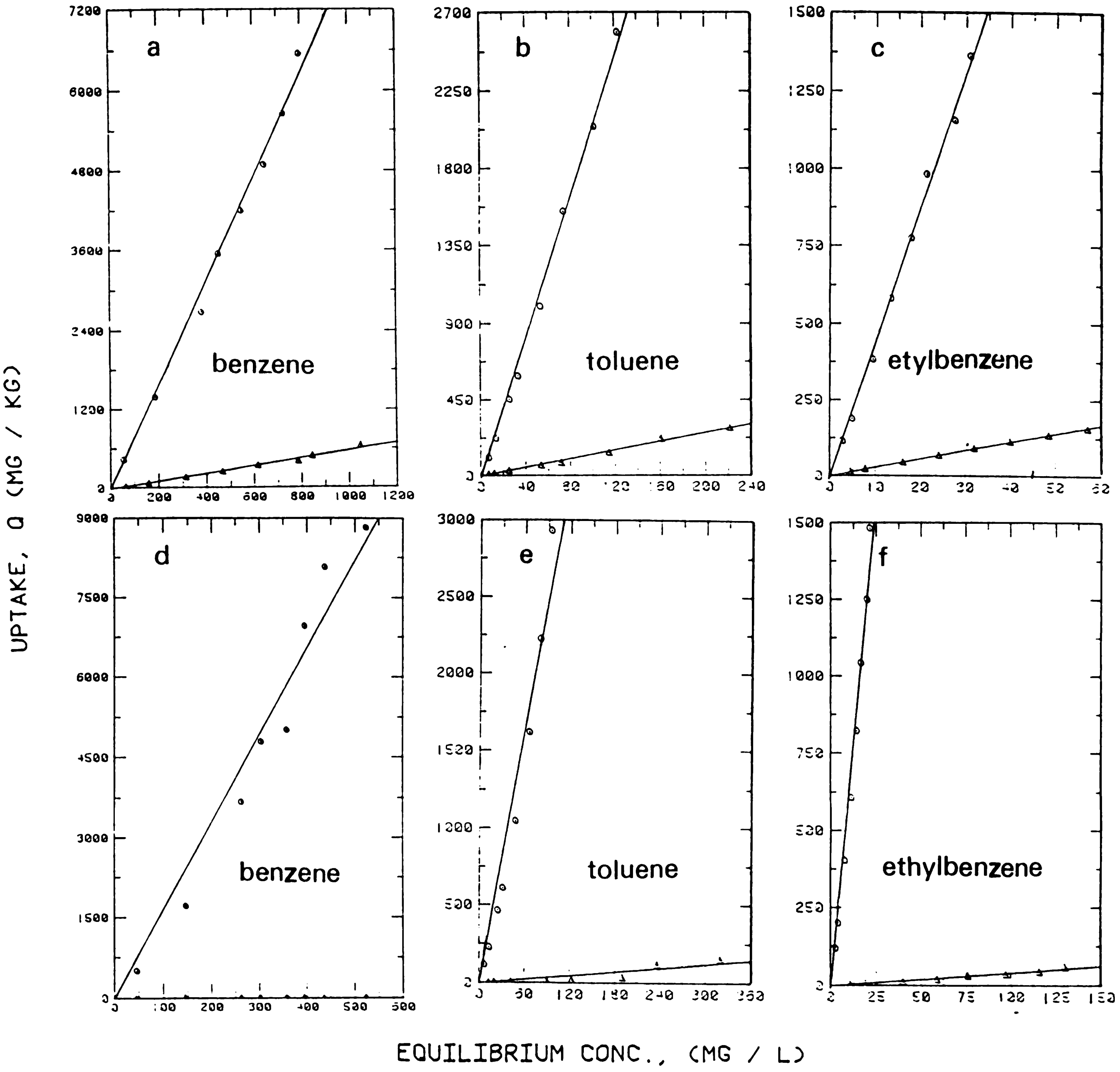

UPTAKE, Q (MG / KG)
EQUILIBRIUM CONC., (MG / L)
a
benzene
b
toluene
c
etylbenzene
d
benzene
e
toluene
f
ethylbenzene
0
1200
2400
3600
4800
6000
7200
200
400
600
800
1000
1200
450
900
1350
1800
2250
2700
40
80
120
160
200
240
250
500
750
1000
1250
1500
10
20
30
40
50
60
1500
3000
4500
6000
7500
9000
100
300
500
600
60
180
300
360
25
75
100
125
150

Figure 4. Sorption of benzene (a), toluene (b), and ethylbenzene (c) on HDTMA-treated St. Clair (circles), Marlette (squares), and Oshtemo (triangles) soils B_t horizon.

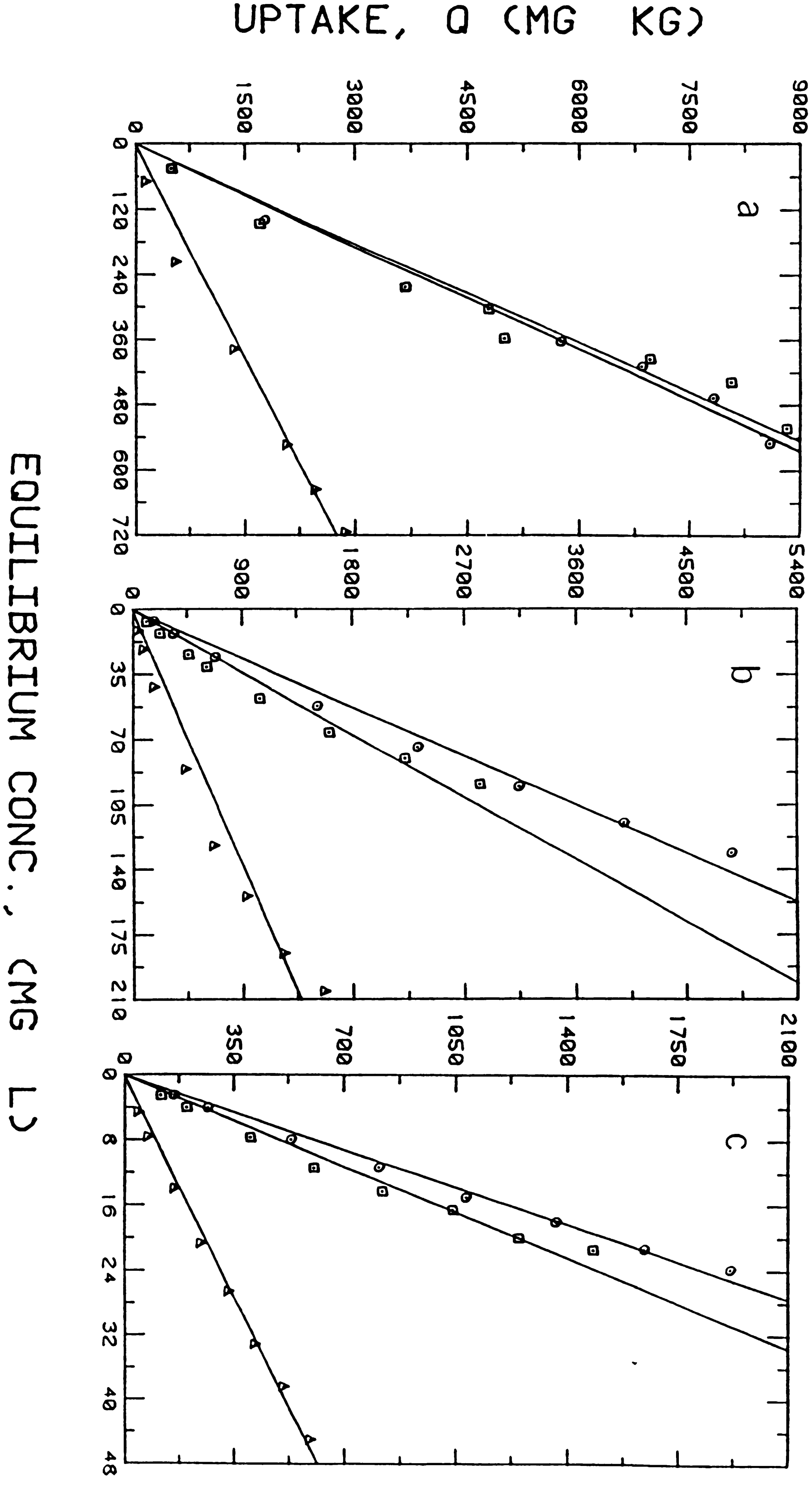
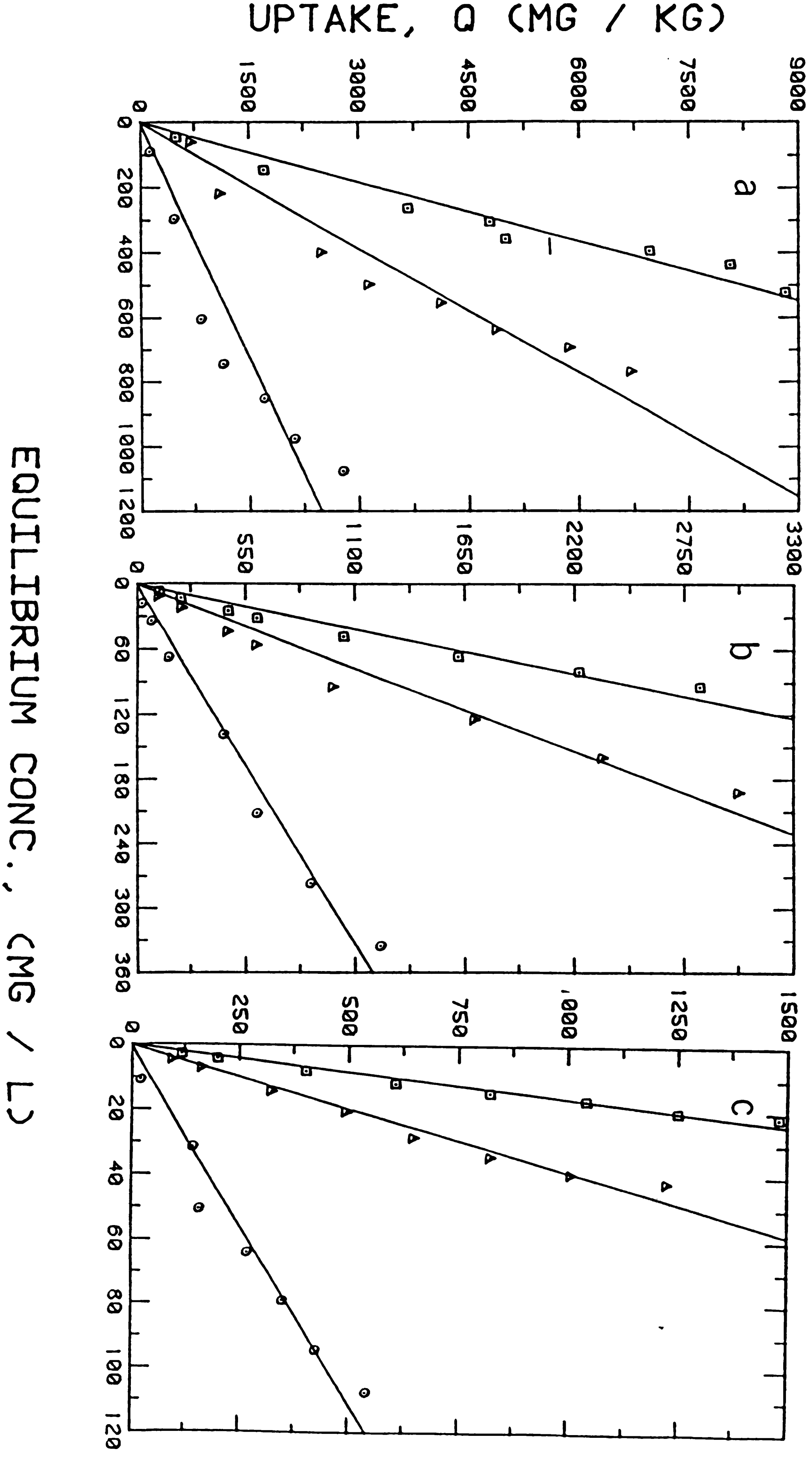

UPTAKE, Q (MG KG)
EQUILIBRIUM CONC., (MG L)
a
b
c
0
1500
3000
4500
6000
7500
9000
0
120
240
360
480
600
720
0
900
1800
2700
3600
4500
5400
0
35
70
105
140
175
210
0
350
700
1050
1400
1750
2100
0
8
16
24
32
40
48

Figure 5. Sorption of benzene (a), toluene (b), and ethylbenzene (c) on treated Marlette soil B_t horizon: NTMA-treated (circles), DDTMA-treated (triangles), HDTMA-treated (squares).


UPTAKE, Q (MG / KG)
EQUILIBRIUM CONC., (MG / L)
a
b
c
0
1500
3000
4500
6000
7500
9000
0
200
400
600
800
1000
1200
0
550
1100
1650
2200
2750
3300
0
60
120
180
240
300
360
0
250
500
750
1000
1250
1500
0
20
40
60
80
100
120

exchanged cations. A positive relation is apparent between the amount of sorbed chemicals and alkyl chain length of exchanged organic cations. As the chain length decreases in going from HDTMA (C_{16}) to DDTMA (C_{12}) to NTMA (C_9), the degree of uptake of organic species from water is decreased. The decrease in sorption follows the total OM contents which decrease in the same order: HDTMA > DDTMA > NTMA. Again, sorption isotherms were linear over a wide range of aqueous phase concentration. Except for the uptake of benzene by NTMA-treated Oshtemo soil, the linear correlation coefficient (r^2) for all isotherms are greater than 0.95.

Table 3 and 4 show the water solubilities, partition coefficients, K, and the OM normalized K_{om} values (K/fraction OM) of the organic chemicals used in present work. Table 3 shows the effect of three different exchange cations on the sorptive properties of the Marlette soil. Table 4 shows the effect of HDTMA treatment on the sorptive properties of three different soils. The organic compounds tested in this study span a range of approximately 2 orders of magnitude of water solubilities, and were selected to represent major organic ground water contaminants. The sorption coefficients (K values) of the linear isotherms correspond to the ratio of the concentration of the sorbed chemical in the soil to its equilibrium solution concentration in water. These values are obtained by dividing the solute uptake, Q (mg/kg), by the equilibrium concentration, C (mg/l) or simply from the slopes of the linear isotherms.

Examination the K values listed in Table 3 and 4 reveals that the K values increase with the OC content of soil and were higher for compounds with lower water solubilities. This relation between sorption

Table 3. Sorption coefficients of organic chemicals on the untreated Marlette soil and on the Marlette soil treated with three different organic cations.

Sorption Coefficients	Water Solubility (ppm)	B_t Horizon				A Horizon		
		Untreated	Treated			Untreated	Treated	
			HDTMA	DDTMA	NTMA		HDTMA	DDTMA
K								
Benzene	1780	0	16.50	7.78	2.08	0.57	7.80	4.75
TCE	1100	0	29.20	6.32	ND	0.88	26.70	5.82
Toluene	520	0	26.90	14.36	3.32	1.29	20.38	10.76
PCE	400	0.17	27.30	11.93	ND	2.60	37.03	14.93
Ethylbenzene	155	0.41	62.51	25.94	4.53	2.79	43.53	17.94
o-DCB	150	0.80	162.59	65.52	ND	7.25	119.50	47.37
1,2,4-TCB	20	5.60	ND	86.33	ND	40.25	ND	109.90
log K_{om}								
Benzene		--	2.53	2.46	2.08	1.04	1.89	1.81
TCE		--	2.78	2.36	ND	1.23	2.42	1.89
Toluene		--	2.74	2.72	2.28	1.39	2.30	2.16
PCE		1.64	2.75	2.64	ND	1.70	2.56	2.30
Ethylbenzene		1.83	3.11	2.98	2.42	1.73	2.63	2.37
o-DCB		2.14	3.52	3.38	ND	2.14	3.07	2.80
1,2,4-TCB		2.97	ND	3.50	ND	2.89	ND	3.17

Table 4. Sorption coefficients of three different soils (B_t-Horizons) either untreated or treated with HDTMA.

Sorption Coefficient	Untreated			HDTMA-treated		
	St. Clair	Marlette	Oshtemo	St. Clair	Marlette	Oshtemo
K						
Benzene	0	0	0	15.96	16.50	3.83
Toluene	0.170	0	0	34.47	26.90	6.59
Ethylbenzene	0.805	0.41	0.206	75.54	62.51	12.84
log K_{om}						
Benzene	--	--	--	2.56	2.53	2.53
Toluene	1.29	--	--	2.89	2.74	2.76
Ethylbenzene	1.96	1.83	1.97	3.23	3.11	3.06

and OM content can be seen by comparing the K values from the treated and untreated soils or from soils which have been treated with various organic cations. For example, the K values obtained from the uptake of PCE on untreated (0.6% OM) and HDTMA-treated (4.85% OM) Marlette soil B_t horizon are 0.17 and 27.3, respectively (Table 3). Similarly, the K values obtained from treated soils decrease in the order: HDTMA-treated > DDTMA-treated > NTMA-treated soils. For example, the K values of ethylbenzene on the treated Marlette B_t horizon soils were 62.51, 25.94 and 4.53 for HDTMA-, DDTMA-, and NTMA-treated soil, respectively (Table 3). In all cases, K_{om} values for the treated soils were higher than the soil K_{om} values for the untreated soils. The K values of organic chemicals were also affected profoundly by their chemical properties. As the water solubilities decrease in going from benzene (1780 ppm) to 1,2,4-TCB (20 ppm), the K values for sorption by the untreated Marlette A-horizon soil increases from 0.57 to 40.25 (Table 3). In general, K values for the treated soils also increased with decreasing water solubilities of the organic solutes (Table 3 and 4). None of the other parameters examined (e.g. particle size and pH) were strongly correlated with K values.

The sorption coefficients K normalized for the OM content (K_{om} = 100K/%OM) are also given in Table 3 and 4. Some of K_{om} values could not be obtained from untreated soils B_t horizon because the measured partition coefficients were very small and K values could not be determined with sufficient accuracy. It can be seen from Table 3 that the log K_{om} values decreased in the order: HDTMA ≈ DDTMA > NTMA > untreated soil. In all cases, K_{om} values for treated soils were greater than soil K_{om} values for untreated soils.

Table 4 gives the calculated log K_{om} values of benzene, toluene, and ethylbenzene for three untreated and HDTMA-treated soils. For all three soils, the log K_{om} values tended to converge on a single value for each organic chemical. For example, all three HDTMA-treated soils give log K_{om} values of 2.5 for benzene and three untreated soils give approximately log K_{om} values of 1.9. Overall, for the same solute, the log K_{om} values are higher for treated soils than those for untreated soils.

DISCUSSION

The results presented here clearly demonstrate that the sorptive properties of surface and subsurface soils for NOCs can be greatly enhanced by simple ion exchange reactions of large organic cations for naturally occurring inorganic exchange ions. The ion exchange reaction results in the nearly stoichiometric displacement of the small inorganic exchange ions. This can be seen clearly in the adsorption isotherm of ^{14}C-HDTMA by the three subsurface soils which rise very sharply. Addition of HDTMA to soil in amounts less than or equal to the CEC of the soil, resulted in very low equilibrium solution concentrations of ^{14}C-HDTMA. It is apparent from these isotherms that HDTMA is highly preferred as an exchange ion and will easily displace inorganic ions. The organic exchange ions once bound are held essentially irreversibly on the clay surface. This is shown by the inability of high ionic strength $CaCl_2$ solution to displace exchanged ^{14}C-HDTMA.

In this work we confirm and expand our previous results (Boyd et al., 1988a) on the increased sorptive capabilities of HDTMA-exchanged soil by examining several additional organic compounds which are representative of common ground water contaminants. Treatment of surface or subsurface soil with HDTMA dramatically increased the uptake from water of all compounds tested. For example, the sorption coefficients of the treated subsurface soil increased by about 200 fold for toluene, PCE, ethylbenzene and dichlorobenzene. The more water soluble compounds (e.g. benzene and TCE) were not measurably removed from water by the untreated subsurface soils but comparatively high uptake was observed in the treated soils. For the surface soils, sorption coefficients of the untreated samples were higher than for the untreated subsurface soil because of the high indigenous SOM content of the A-horizon soil. However, the HDTMA-exchanged A-horizon soil also displayed enhanced uptake of all NOCs tested. For HDTMA-treated surface soil the increase in K was about 15 times. Although the organic matter content of the Marlette A horizon soil was approximately doubled by exchange with HDTMA, the K values for the treated soil increased to a much large extent (~15x) suggesting that the HDTMA-derived organic matter is a much more effective sorbent for NOCs than natural SOM.

A more accurate evaluation of the sorptive capabilities of natural SOM and synthetic OM derived from exchanged cations can be obtained by comparing the corresponding K_{om} values which indicate the effectiveness of different organic phases on a unit weight basis. For the untreated A horizon soil, all OM is natural SOM; whereas, for the treated B_t horizon soils, OM is derived primarily from the exchanged organic cations. The K_{om} values of benzene, TCE, toluene, PCE, ethylbenzene and o-DCB on the HDTMA-treated Marlette B_t soil are 10 to 30 times higher than the corresponding K_{om} values on the untreated Marlette A horizon soil. It can be therefore concluded that OM derived from added HDTMA is approximately 10 to 30 times more effective on a unit weight basis than natural SOM for removing NOCs from water. Thus, not only can the OM content of soil be increased significantly by this simple soil modification technique, but the added OM is highly effective and can be expected to enhance the retention of NOCs by soil.

The data presented here strongly suggest that the organic matter derived from the exchanged quaternary ammonium ions behave as a partition medium in the uptake of NOCs from water. This is a process of solubilization of NOCs on the synthetic organic phase formed by the conglomeration of the alkyl tails of exchanged organic cations. This process is essentially identical to the partitioning of solutes from water into an immisible bulk organic solvent phase such as hexane or octanol. The similarity of the $\log K_{om}$ values of the HDTMA-treated Marlette B_t horizon soil to the corresponding $\log K_{ow}$ values (octanol water partition coefficient) strongly supports this mechanism.

The concept of solute partitioning has previously been used to describe soil water equilibria of NOCs (Chiou et al., 1979, 1983). The characteristic of solute partitioning developed for natural soils are also observed for the treated soils. These include: highly linear isotherms, dependence of the sorption coefficients on the water solubility of the NOC and a close correspondence between $\log K_{om}$ and $\log K_{ow}$ values.

Although natural SOM and the synthetic organic matter phases are mechanistically similar in uptake of NOCs from water, the effectiveness of the latter is 10 to 30 times greater than the former, as mentioned previously. These results obtained from the composition of the two OM phases with HDTMA-derived OM being a better nonpolar solvent than natural SOM which has a high polar functional group content.

An additional objective of the work was to examine the sorptive behavior of soil exchanged with these different organic cations, containing alkyl moieties of different size, ranging from C_9 to C_{16}. Obviously, in the size of the organic cation decreases, the increase in OM after cation exchange is less. However, the effectiveness of the organic phases derived from the different cations can be compared on an equal weight basis by comparing the K_{om} values. This comparison of the treated Marlette B_t horizon soils reveals that the organic phases composed of HDTMA and DDTMA were similar with HDTMA being slightly more effective. When the C_9 quaternary ammonium ion was used (NTMA) a large decrease in the K_{om} value occurred, although these values were still considerably higher than K_{om} values for natural SOM. Apparently, as the alkyl chain length decreases below C_{12}, the hydrocarbon moieties become more isolated and form a less effective partion medium than with the larger cations, i.e., HDTMA and DDTMA.

These results appear to be consisted with earlier work on the interlayer arrangement of exchanged n-alkylammonium ions on smectite clays. When smectite is exchanged with n-alkylammonium ions, the increases in basal spacing of the clay occurs in a stepwise fashion as the number of carbon atoms in the alkyl chain increases. A spacing of about 1.1nm is observed for C_2 - C_{10} alkyl chains, which jumps to 1.8nm for C_{12} - C_{20} alkyl chains (Theng, 1974). For the small alkyl chain, planer surface coverage is low enough to allow a "keying in" of organic cation on opposing clay layers. However, with the larger alkyl ion (C_{12} and greater) surface coverage is greater than 50% and they cannot fit into the unoccupied mineral surfaces of the opposing clay surfaces. As a result, they are forced to interact with one another instead of with the free mineral surfaces.

The sorptive capabilities for NOCs of three different soils exchanged with HDTMA were also compared. These subsurface soils differed primarily in their CECs which were relatively high for the St. Clair and Marlette soils and low for the Oshtemo soil. As expected, the OM contents of the HDTMA-exchanged Marlette and St. Clair soils were higher than the Oshtemo soils, and as a result the K values for Benzene, toluene and ethylbenzene decreased in the order: St. Clair = Marlette > Oshtemo (Table 4). However, the K_{om} values for these three HDTMA-treated soils (Table 4) were nearly identical indicating that the HDTMA-organic phases formed on were equally effective.

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CHAPTER 3

SHAPE SELECTIVE ADSORPTION OF AROMATIC MOLECULES FROM WATER BY TETRAMETHYLAMMONIUM-SMECTITE

ABSTRACT

The adsorption of aromatic compounds by smectite exchanged with tetramethylammonium (TMA) was studied. Aromatic compounds adsorbed by TMA-smectite appeared to adopt a tilted orientation in a face-to-face arrangement with the TMA-tetrahedra. The sorptive characteristics of TMA-smectite were influenced strongly by the presence of water. The dry TMA-smectite showed little selectivety in the uptake of benzene, toluene and xylene. In the presence of water, TMA-smectite showed a high degree of selectivety based on molecular size/shape, resulting in high uptake of benzene and progressively lower uptake of larger aromatic molecules. Water appeared to shrink the interlamellar cavities resulting in this selectivety.

INTRODUCTION

The net negative electrical charge of clays is balanced by exchanged cations. In nature these are usually alkali metal and alkaline earth ions such as Na^+ and Ca^{2+} which are strongly hydrated by the presence of water. The hydration of inorganic exchange ions present on clays, and the polar nature of Si-O groups imparts a hydrophilic nature to the mineral surfaces. As a result, water is preferentially adsorbed by these surfaces and nonpolar organic compounds cannot compete with strongly held water for adsorption sites on the clay surfaces.

It is possible to greatly modify the surface properties of clays by replacing natural inorganic exchange cations by larger alkylammonium ions (Barrer et al., 1955, 1957). These ions act as "pillars" which hold the aluminosilicate sheets permanently apart. In the modified form, the clay surface may become organophilic and interact strongly with organic vapors and with organic compounds dissolved in water. These organo-clays are now able to sorb paraffins (Barrer et al., 1955) and aliphatic alcohols (Stul et al., 1978, 1979), to remove organic contaminants from water (Boyd et al., 1988a, b, c), and to serve as chromatographic stationary phases (White et al., 1958; McAtee et al., 1977).

Until recently, the literature on the sorptive behavior of organo-clays has been concerned almost exclusively with the organic vapor uptake by dry modified-clay samples. Mortland et al. (1986) and Boyd et al. (1988a) studied the uptake of phenol and chlorophenols from aqueous solution by smectites whose cations were exchanged by quarterary ammonium ions of the form $[(CH_3)_3\text{-NR}]^+$, where R is an alkyl group. These authors showed that in general when R was a large nonpolar alkyl group (e.g., R = $C_{16}H_{33}$) the modified clay samples exhibited greatly improved sorption capacities in comparison with unmodified clays or modified clays in which the exchanged organic ions were small in size. McBride et al. (1977) and Mortland et al. (1986) found however that the smectite exchanged with small tetramethylammonium ion (here referred to as TMA-smectite) exhibited much higher affinity for benzene from water than for less water-soluble and large sized 1,2,4-trichlorobenzene (1,2,4-TCB). The extent of benzene uptake by the TMA-smectite was also much greater than by clays exchanged with tetraethylammonium ion (TEA), or with hexadecyltrimethyl ammonium ion (HDTMA), in the sequence of TMA-smectite > HDTMA-smectite > TEA-smectite. These studies indicated that the exchanged organic ions affected the sorptive behavior of clay in some manner that appeared to be related to the size and molecular arrangement of the exchanged ion in the clay.

To obtain a more perspective view of the influence of the exchanged organic ion on the mechanistic function of the modified clay, Boyd et al. (1988b) studied the sorption characteristics of benzene and trichloroethylene (TCE) on HDTMA-smectite from both aqueous solution and vapor phase. They found that the dry HDTMA-smectite behaved as a dual sorbent, in much the same fashion as dry soil (Chiou et al., 1985), in which the bare mineral surfaces function as a solid adsorbent and the exchanged HDTMA organic ions function as a partition medium. In aqueous solution, adsorption of nonionic organic compounds by free mineral surfaces is minimized by the strong competitive adsorption of water, and the uptake of organic solutes by the modified clay is effected mainly by solute partitioning in the organic medium that is formed by conglomeration of large C_{16} alkyl groups associated with HDTMA. The presumed partition effect with the HDTMA-smectite is supported by the linear sorption isotherm, lack of a competitive effect between organic solutes, and the dependence of the sorption capacity on the amount of HDTMA in clay. The uptake of organic vapors by dry HDTMA-smectite was greater than by water-saturated HDTMA-smectite because of concurrent adsorption on mineral surfaces, and consequently, vapor uptake isotherm were not linear. The improved sorption of benzene and TCE from water by HDTMA-smectite over that by pure clays was attributed to partition into the highly nonpolar hydrocarbon medium. Improvement of the sorption capacity of soils with low organic matter contents was similarly achieved by cation exchange reactions with HDTMA ions (Boyd et al., 1988c). This study also demonstrated that HDTMA-derived organic matter added to soil was 10 to 30 times more effective on a unit weight basis than natural soil organic matter for removing organic contaminants from water.

Considering the benzene sorption data with TMA-smectite and HDTMA-smectite in aqueous systems as mentioned above, one may speculate that the greater uptake by TMA-smectite than by HDTMA-smectite is effected by some unique mechanism other than partition associated with TMA-modified clay surfaces, since it is questionable that small TMA ions can function as an effective partition medium. The research described here was designed to elucidate that impact of exchanged TMA ions on the mechanistic function of the modified clay. Sorption isotherm for a series of organic compounds of varying sizes and water solubilities were performed both from aqueous solution and from vapor phase in order to evaluate the influence of water as well as the molecular properties of the compounds on sorption.

EXPERIMENTAL

The sorbents used in these experiments were TMA-smectite and TMA-illite which were prepared by reacting < 2μm fraction of Wyoming bentonite or Clarence till with TMA chloride salts in the amount of 3-5 fold meq. per meq. of CEC (0.9 meq. x g^{-1} and 0.3 meq. x g^{-1} respectively for smectite and illite). After reacting for 2 to 4 h, the clay-organic complexes were dialyzed against distilled water until no chloride appeared in the dialysate.

The mixed TMA/Ca-smectites were made by reacting aqueous solution containing both $CaCl_2$ and TMA ions with Na-saturated Wyoming bentonite in 3-5 fold excess of the CEC. The mixed TMA/Ca-smectites were prepared at three different saturated levels (100, 50 and 25 percent) corresponding to the different amounts of CEC occupied by TMA ions. For example, the 25 percent saturated TMA-smectite was prepared by adding $CaCl_2$ and TMA ions simultaneously at a 3 : 1 ratio of Ca:TMA. Additional details for the preparation of modified clays have been published previously (Boyd et al., 1988b).

Adsorption isotherms were determined for aqueous solutions of eight organic pollutants by using a batch equilibration technique. Benzene, toluene, ethylbenzene, o-xylene, p-xylene, o-dichlorobenzene (o-DCB), 1,2,3-trichlorobenzene (1,2,3-TCB), and hexachlorocyclohexane (r-isomer) (lindane) were purchased from Aldrich Chemical Co. All reagents used in this study were analytical grade or better and used without further purification. Experiments were conducted at ambient temperatures (20 ± 1 °C).

To determine the sorptive capacity of TMA-smectite, samples of clay (0.1-0.3 g) were weighed into 25 ml Corex glass centrifuge tubes with Teflon-lined screw caps, and 25 ml distilled water added leaving a minimum headspace to avoid the loss of solutes from evaporation. The initial concentration ranges for the aqueous solution of eight organic pollutants were: benzene, 100 to 1500 mg l^{-1}; toluene, 20 to 550 mg l^{-1}. o-xylene and p-xylene, 12 to 190 mg l^{-1}; o-DCB and ethylbenzene 12 to 150 mg l^{-1}; 1,2,3-TCB, 0.8 to 10 mg l^{-1}; and lindane, 0.4 to 8 mg l^{-1}. Benzene and toluene were added directly as the neat liquid using a Hamilton microliter syringe; whereas, the others were prepared in methanol as a stock solution. The concentration of organic pollutants did not exceed their water solubility values. After appropriate volumes of eight chemicals were added, the centrifuge tubes were immediately closed with foil-lined screw caps then shaken for 24 h on a reciprocating shaker. Preliminary kinetic investigations indicated that sorption equilibrium was reached in 20 h or less and so an equilibration time of 24 h was chosen for all experiments. After shaking, the tubes were centrifuged for 30 min. at 8000 rpm to separate the liquid and solid phases. The supernatant liquid (1 ml) was then transferred into a glass vial containing 10 mf of hexane (for o-DCB, 1,2,3-TCB, and lindane) or carbon disulfide (for benzene, ethylbenzene, toluene, and xylene). The vials were closed with foil-lined screw caps and shaken vigorously for 1 h on a reciprocating shaker. An aliqout of hexane or carbon disulfide layer was then removed for gas chromatography (GC) analysis.

The GC was performed on a Hewlett Packard model 5890A GC using either an electron capture (o-DCB, 1,2,3-TCB and lindane) or a flame ionization detector (benzene, ethylbenzene, toluene and xylene). For 1, 2, 3-TCB, o-DCB and lindane, a 1.5% sp-2250/1.95% sp-2401 on 100/120 Supelcoport packed glass column (2.4m x 6.4mm ID) was used. For benzene, ethylbenzene, toluene and xylene, a 5% sp-1200/1.75% Bentonite 34 on 100/120 Supelcoport packed steel column (1.8m x 3.2mm ID) was used. The carrier gas was N_2 applied at a linear velocity of 40 ml min^{-1}. The injector temperature was 250°C and the detector 300°C. Each run was isothermal: 80°C for benzene and toluene, 100°C for ethylbenzene and xylene and 150°C for 1,2,3-TCB, o-DCB and lindane. For a quantitative measurement of peak areas, a Hewlett Packard 3392A integrator was employed. All samples were run in duplicates and the recovery of these tested chemicals ranged from 92 to 98%. The equilibrium concentration measured were not adjusted for the recovery.

A Quantasorb Jr. sorption meter was used for surface area measurement. The fully to partially saturated TMA-smectites were dehydrated at 150°C for 12 hours under vacuum. The surface areas were then determined at liquid N_2 temperatures using N_2 as the adsorbate and He as the carrier gas. The adsorption data were plotted according to the BET equation. Approximately 100 mg of sorbents were used for each determination.

The uptake of benzene, toluene, and o-xylene vapors by dry smectite fully to partially saturated with TMA was measured by using a static equilibrium sorption apparatus. The test compounds were purified by vacuum distillation before their vapors were introduced into the sorption chamber containing a Cahn electrical microbalance. After vacuum distillation, the vapor pressures of the test compounds were monitored by the Baratron pressure gauge of the apparatus. Additional details of the procedure and equipment have been given elsewhere (Chiou et al., 1988).

RESULTS

The clay samples used in this study were smectite and illite. The illite was fully exchanged with TMA. Smectite was fully to partially saturated with TMA; Ca^{2+} occupied the remaining exchange sites. The organic carbon contents and surface areas of these clays are given in Table I. The TMA-smectite with 4.0, 2.5 and 1.7 percent organic carbon corresponds to approximately 100, 50 and 25 percent saturation of the exchange complex with TMA ions. A plot of surface area against fraction of TMA ions on the exchange complex (0, 0.25, 0.5 and 1) reveals that the mixed TMA/Ca-smectites were above the line connecting homoionic

Table 1. Organic carbon contents and surface areas of the clay adsorbents.

Sample	Organic carbon	TMA:Ca	Surface area
	(g/100g)		(m^2/g)
TMA-smectite	4.0	1:0	172.4
TMA/Ca-smectite	2.5	1:1	135.9
TMA/Ca-smectite	1.7	1:3	84.7
Ca-smectite	0.9	0:1	24.8
TMA-illite	1.2	1:0	n.d.*

*n.d. is not determined.

Ca-smectite and TMA-smectite (Fig. 1). The fact that the surface areas are not linearly related to the extent of exchange of TMA for Ca^{2+} clearly demonstrates a degree of randomness in distribution of calcium and TMA ions on the clay surface. If the calcium and TMA ions were segregated into different interlamellar regions of smectite, then the points would lie on the dashed line in Figure 1.

The sorption isotherms of benzene, toluene, o-xylene, p-xylene, ethylbenzene, o-DCB, 1,2,3-TCB and lindane from aqueous solution by homoionic TMA-smectite and TMA-illite are presented in figure 2a-h. Figure 2a also shows the benzene sorption isotherm for TMA/Ca-smectite where TMA ions occupy approximately 25 percent of the cation exchange sites. TMA-smectite showed the highest affinity for benzene; toluene, ethylbenzene, xylene were intermediate, and lindane and 1,2,3-TCB were the lowest. The uptake of benzene from water was lower for the mixed TMA:Ca(1:3)-smectite as compared to smectite fully saturated with TMA (Figure 2a). For the 1:1 TMA:Ca-smectite, benzene uptake was intermediate (data not shown). There is also a noticeable difference in the type of sorption isotherms represented in the graphs. The benzene isotherm is Type I (Brunauer, 1944). As uptake decreases in going from benzene to toluene to ethylbenzene and xylene, the isotherm shape changes to Type V. Lindane and 1,2,3-TCB have linear sorption isotherms. The uptake of 1,2,3-TCB was higher than for lindane, which is the only non-planar molecule studied. With the exception of lindane, all the organic compound used in this study show less uptake by TMA-illite as compared to the TMA-smectite (Fig. 2). For lindane, TMA-illite gave slightly higher uptake than TMA-smectite.

Figure 1. Surface area of TMA/Ca-smectites as a function of the fraction of cation exchange capacity occupied by TMA.

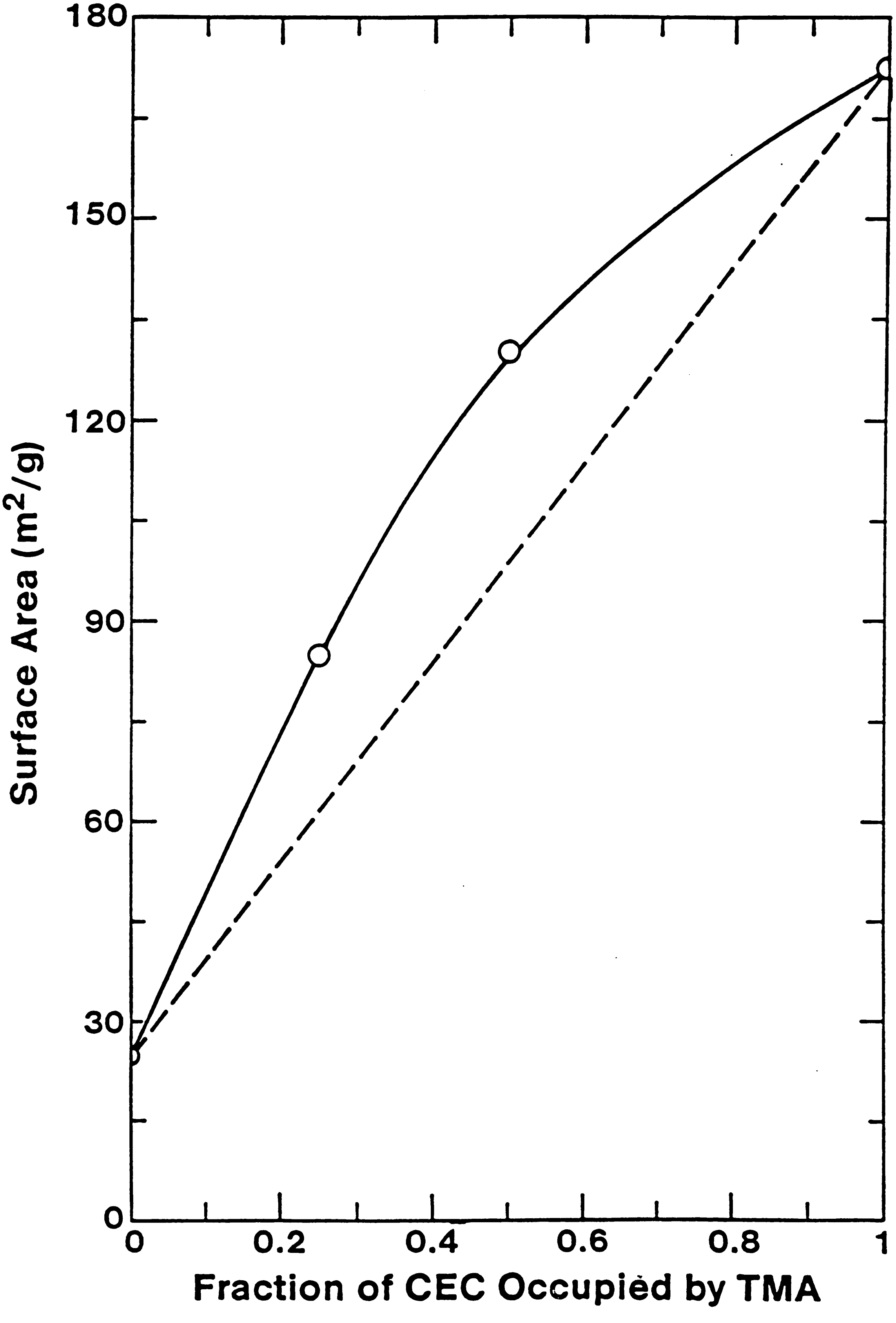

Surface Area (m²/g)
180
150
120
90
60
30
0
0
0.2
0.4
0.6
0.8
1
Fraction of CEC Occupied by TMA

Figure 2. Adsorption of organic compounds from water by TMA-smectite (triangles), mixed TMA:Ca(1:3)-smectite (squares), and TMA-illite (circles). Plot (a) is benzene, (b) is toluene, (c) is p-xylene, (d) is ethylbenzene, (e) is o-xylene, (f) is o-dichlorobenzene, (g) is 1,2,3-trichlorobenzene and (h) is lindane.

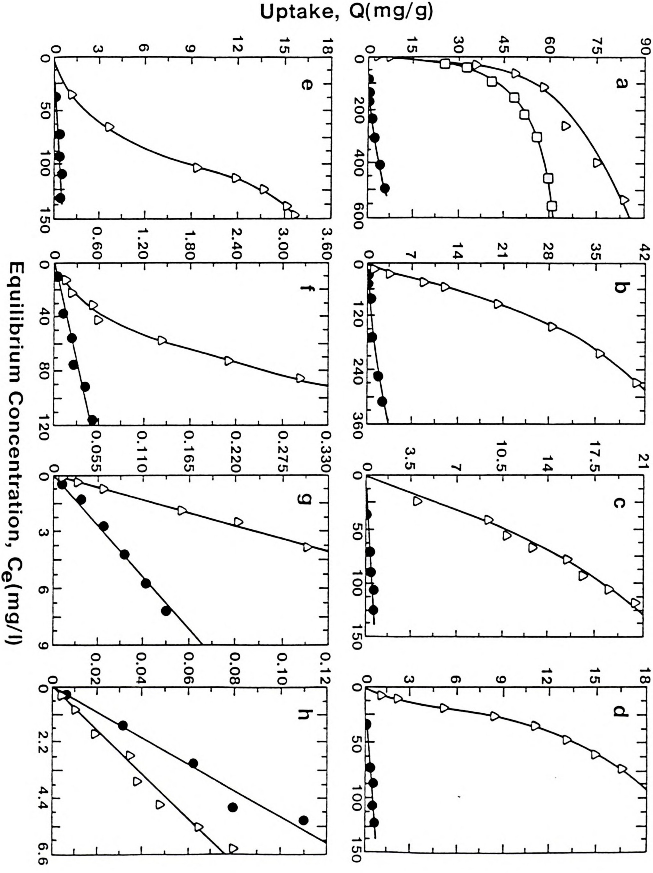

Uptake, Q(mg/g)
Equilibrium Concentration, C_e(mg/l)
a
0 15 30 45 60 75 90
0 200 400 600
b
0 7 14 21 28 35 42
0 120 240 360
c
0 3.5 7 10.5 14 17.5 21
0 50 100 150
d
0 3 6 9 12 15 18
0 50 100 150
e
0 3 6 9 12 15 18
0 50 100 150
f
0 0.60 1.20 1.80 2.40 3.00 3.60
0 40 80 120
g
0 0.055 0.110 0.165 0.220 0.275 0.330
0 3 6 9
h
0 0.02 0.04 0.06 0.08 0.10 0.12
0 2.2 4.4 6.6

Figure 3 shows the uptake of benzene vapors by dry TMA-smectite and mixed TMA/Ca-smectite. Figure 4 shows the uptake of toluene and o-xylene. vapors by dry TMA- smectite. The amounts of benzene, toluene and o-xylene uptake by TMA-smectite decreased in the order benzene > toluene > o-xylene, but overall the differences were relatively small. The uptake of benzene, toluene, and o-xylene vapors at $P/P° = 0.75$ were 145, 140, and 132 mg/g, respectively. When there was partial exchange of Ca^{2+} by TMA ions, the sorptive capacity of TMA-smectite rose in proportion to the fraction of TMA ions present. The uptake of benzene vapor by TMA-smectite was approximately twice that of TMA:Ca(1:3)-smectite.

In order to evaluate differences in uptake from water by solutes of different water solubilities, and to compare the uptake of organic chemicals from vapor phase to that from aqueous phase, the aqueous-phase isotherms are expressed in terms of reduced concentration (Kilpling et al., 1965). Figure 5 is obtained by plotting the amount of uptake by the clay sample (Q) against Ce/Cs, where Ce and Cs are equilibrium concentration and water solubility respectively, rather than against Ce as in the standard isotherm plot. The vapor sorption isotherms are similarly expressed in the form of Q versus $P/P°$, where P is the equilibrium partial pressure and P° is the saturation vapor pressure of the compound at system temperature. The reduced plot provides a theoretical basis for the order of preference of TMA-smectite for various solutes and vapors tested under the same chemical activities.

By comparison of the reduced isotherms, uptake of benzene, toluene, and o-xylene as vapors by dry TMA-smectite is found to be greater than that of the solutes from aqueous system by the water-saturated TMA-

Figure 3. Adsorption of benzene vapor by dry TMA-smectite. The organic carbon (OC) contents refer to the amount of carbon in TMA ions. Additional exchange ions were Ca^{2+}.

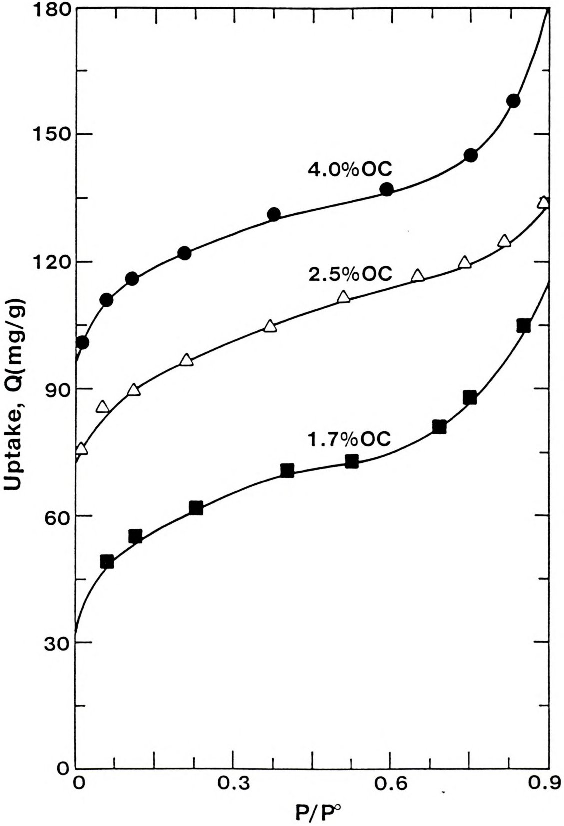

180
150
120
90
60
30
0
0
0.3
0.6
0.9
Uptake, Q(mg/g)
P/P°
4.0%OC
2.5%OC
1.7%OC

Figure **4**. Adsorption of toluene (triangles) and o-xylene (circles) vapors by dry TMA-smectite.

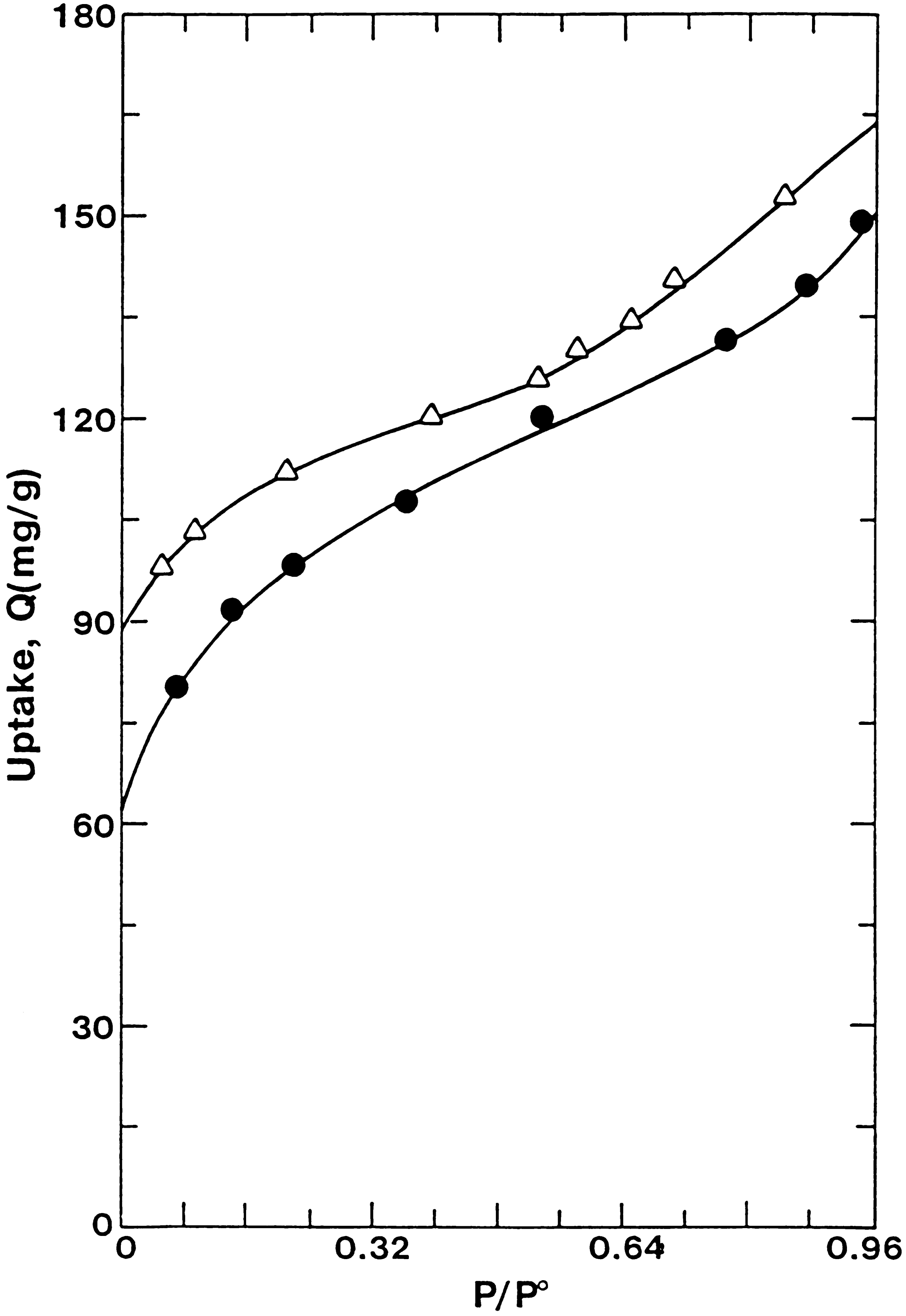
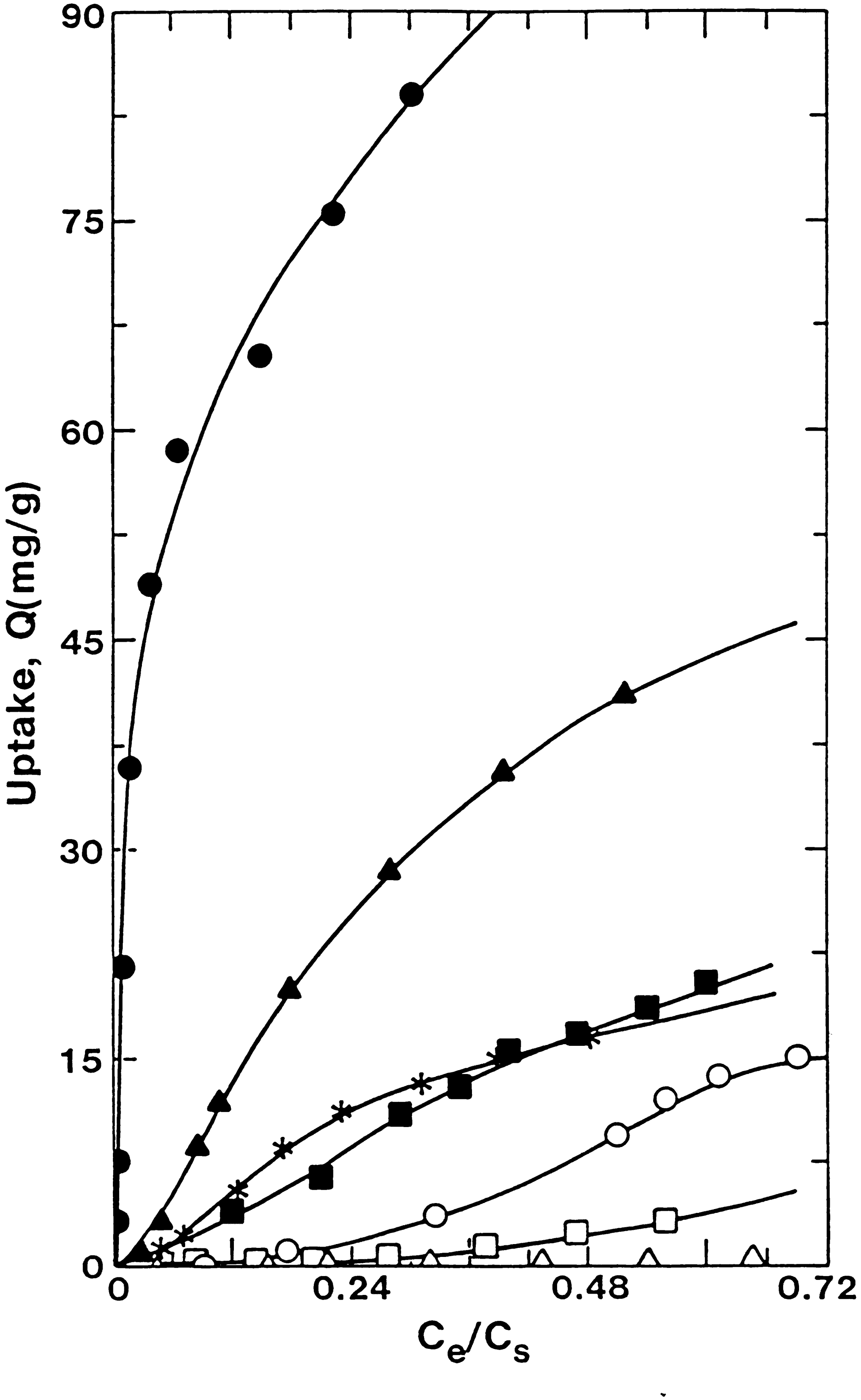

180
150
120
90
60
30
0
0
0.32
0.64
0.96
Uptake, Q(mg/g)
P/P°

Figure 5. Reduced plot showing adsorption of organic compounds from water by TMA-smectite (Q) versus relative concentration (Ce/Cs): benzene (closed circles), toluene (closed triangles), ethylbenzene (asterisks), p-xylene (closed squares), o-xylene (open circles), o-dichlorobenzene (open squares), 1,2,3-trichlorobenzene and lindane (open triangles).


Uptake, Q(mg/g)
0
15
30
45
60
75
90
0
0.24
0.48
0.72
C_e/C_s

smectite, based on the results given in Figures 3-5. For instance, when P/P° and Ce/Cs = 0.3, the amount of benzene sorbed as a vapor and from water was 130 and 84 mg/g, respectively.

DISCUSSION

When adhered to the interlamellar surfaces of smectite, TMA ions because of their small size are isolated from each other. When larger organic cations are used, such as HDTMA, the hydrophobic tails interact with each other producing an organic phase which acts as a partition medium (Boyd et al., 1988b). Nonionic organic molecules partition from water into this organic phase which acts as a solubilizing medium similar to a bulk solvent phase such as octanol or hexane. The mechanism of uptake of nonionic organic compounds from water by TMA-smectite (i.e. , adsorption) is distinctly different from that by HDTMA-smectite (i.e. partitioning). A curvilinear Type I isotherm is observed for the sorption of benzene by TMA-smectite; whereas, a linear isotherm is observed for the sorption of benzene by HDTMA-smectite (Boyd et al., 1988b). Other sorption characteristics of TMA-smectite contrast with the partition behavior of HDTMA-smectite. For example, compounds such as benzene and toluene that have high water solubilities show strong affinities for TMA-smectite. In a partition mechanism, the higher the water solubility, the lower the partition coefficient. The uptake of benzene from aqueous solution is also higher for TMA-smectite than for HDTMA-smectite despite the fact that TMA-smectite has a much lower organic carbon content (4%) than HDTMA-smectite (17%). For solute partitioning, it is expected that a higher carbon content of sorbent should result in greater solute uptake.

However, at Ce/Cs = 0.3, the uptake of benzene from aqueous solution is 84 mg/g for TMA-smectite and 25 mg/g for HDTMA-smectite (Boyd et al., 1988b).

For the adsorption of organic vapors by dry TMA-smectite, results from this study were similar to those obtained by Barrer et al. (1957). Isotherms of benzene, toluene, and o-xylene were all of the same form, composed of an initial sharp rise followed by a slow increase over a fairly wide range of P/P°. The very high affinity of TMA-smectite shown toward aromatic compounds in this paper, compared with aliphatic hydrocarbon sorption from the vapor phase (Barrer et al., 1955), suggests that there are some particularly favorable factors promoting the adsorption of aromatic compounds. The juxtaposition of alternate tetrahedral TMA ions adhering to the upper and the lower aluminosilica sheets appears to provide modified "organic-coated" clay surfaces that are not strongly wetted by water. Benzene may therefore be adsorbed onto these modified surfaces possibly in a tilted orientation of its planar aromatic ring onto the triangular faces of the TMA tetrahedra. In estimating the surface areas of TMA ions and the free interlamellar cation distances of TMA-clay, Barrer et al. (1961) concluded that the tilted orientation is necessary for the intercalation of benzene in alkylammonium montmorillonites. The higher uptake of aromatic hydrocarbons than of aliphatic hydrocarbons by TMA-smectite could be a result of the more compact and sheet-like aromatic structure for intercalation and some interaction of the π-electron system of the aromatic molecules with positively charged nitrogen of TMA.

Although the greatest uptake of aromatic compounds has been found by dry TMA-smectite, TMA-smectite does not show any pronounced selectively in the adsorption of vapors of benzene, toluene or o-xylene (Figures 3 and 4). However, significant differences in selectivities were observed for the uptake of these aromatic compounds from aqueous solution by TMA-smectite. This is shown both by the amount of uptake and the shapes of the isotherms for the aromatic compounds studied. TMA-smectite shows a clear preference for benzene despite the fact that benzene has the highest water solubility and lowest molecular weight of the compounds tested. These factors would be expected to result in less partition uptake from water as by HDTMA-exchanged clays (Boyd et al., 1988b, c). Therefore, it appears that this selectivity is related to the shape and size of the benzene molecule and the free space between the TMA ions on the surface of water saturated clay. The importance of this shape/size requirement is further illustrated by the fact that the extent of uptake decreased as the size of the solute molecules is increased by adding substituents to the benzene ring. Thus, the degree of uptake from water by TMA-smectite decreases in the order: benzene > toluene> xylene ~ ethylbenzene > dichlorobenzene > trichlorobenzene > lindane. The isotherm shapes also change from Type I for benzene to Type V for toluene, xylene, ethylbenzene and dichlorobenzene, indicating progressively weaker interactions with the TMA-smectite. The linear isotherms of trichlorobenzene and lindane manifests very weak adsorptive interaction of these large molecules with the TMA-smectite in aqueous solution.

This disparate affinity of TMA-smectite for the adsorption of aromatic compounds from aqueous phase can be attributed to the molecular shape as well as the role of water molecules. In an aqueous system water molecules may associate with TMA ions and also solvate mineral sites of TMA-smectite resulting in insufficient interlamellar spaces to allow the accommodation of relatively larger molecules such as o-xylene and 1,2,3-TCB. Therefore, the main factor affecting the degree of adsorption of aromatic molecules by TMA-smectite was found to be the molecular shape/size. Organic molecules (e.g. benzene) whose critical dimensions are less than the lateral distance between interlamellar ions or intersheet spacing are adsorbed with greater ease and in substantial amounts. These reasons offered explanation to extremely high affinity of TMA-smectite for benzene, and the comparatively low affinity for larger di- and trichlorobenzenes.

The presence of water also decreases the overall uptake of the aromatic molecules tested. Benzene, toluene and xylene are adsorbed by TMA-smectite in greater extent from vapor phase than from aqueous solution. In the dry TMA/Ca-smectites, both free mineral surfaces and TMA-modified surfaces provide adsorption sites for the aromatic molecules. The decreased uptake by water-saturated TMA/Ca-smectite can be accounted for in part by the inability of free mineral surfaces to adsorb nonionic, nonpolar compounds from water because of the preferential adsorption of water by the mineral surfaces (Chiou et al., 1985); in this case water acts to deactivate the mineral surface. In addition, TMA ions may also be weakly hydrated resulting in less uptake.

As compared with TMA-smectite, TMA-illite shows lower uptake capacity for all the compounds used in this study except lindane. This behavior can be attributed to the fact that illite does not have the capability of interlamellar expansion to create additional surface for adsorption. That the adsorption of all aromatic compounds tested is greater for TMA-smectite than for TMA-illite indicates that these molecules are being intercalated to some extent by TMA-smectite. However, as the molecular size increases in going from benzene to trichlorobenzene, fewer adsorption sites of sufficient size are available, and the larger molecules have limited access to the interlamellar regions. Thus for trichlorobenzene, the difference in uptake by TMA-smectite and TMA-illite are relatively small as compared to benzene. Although both lindane and benzene possess a six carbon ring, the molecular structure of lindane is not planar; instead, the carbon ring assumes a "puckered" chair form. The nonplanar molecular configuration of lindane apparently does not allow it to be adsorbed on the interlamellar surfaces by TMA-smectite and in this case the uptake of lindane is actually slightly higher for TMA-illite as compared to TMA-smectite.

As the amount of TMA in TMA-smectite decreases, the amount of benzene uptake also decreases. For uptake of vapors by dry TMA-smectite, this decrease probably results from a concominant decrease in surface area (Table I) as TMA is replaced by calcium, and a decrease in number of TMA-ions as adsorption sites for benzene. For benzene uptake from aqueous solution, the decreased adsorption likely results from having fewer TMA ions and thus fewer sites for benzene. Here the mineral surface is preferentially occupied by water so that surface area per se is not a proper indicator.

The work reported here emphasizes very striking differences in the adsorptive properties of dry and wet TMA-smectites as evaluated from their uptakes of organic compounds from aqueous and vapor systems. Sieving effects of TMA-smectite can only be seen from aqueous solution in which water molecules shrink the interlamellar cavities resulting in a strongly selective uptake of aromatic compounds. It is suggested that TMA-smectite could be used for the selective removal of benzene-like compounds from aqueous system.

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CHAPTER 4

SELECTIVE ADSORPTION OF AROMATIC MOLECULES BY TMA-SMECTITES OF DIFFERENT CHARGE DENSITY

INTRODUCTION

The type of exchangeable cations on clays directly influences the surface properties of clays, and the resulting sorptive characteristics of clays for the uptake of nonionic organic compounds (NOCs). In nature, the net negative electrical 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 polar nature of Si-O groups of clays impart a hydrophilic nature to the mineral surfaces. As a result, the adsorption of NOCs by clays is suppressed in the presence of water because the relatively lower polar organic chemicals cannot compete with strongly held water for adsorption sites on the clay surface. In the absences of water, the clay acts as a conventional solid adsorbent, and shows high sorptive capacity related to total surface area (Chiou and Shoup, 1985; Call, 1957; Jurinak, 1957).

However, this limited sorptive capacity of clays toward NOCs from aqueous solution can be remedied by replacing natural metal cations with larger organic cations through ion exchange reactions (Barrer et al., 1955, 1957; McAtee et al., 1977). Several researchers have indicated that exchanging quaternary ammonium cations for the metal ions on the clay surface could considerably modify the sorptive characteristics of clays (White et al., 1958; Barrer et al., 1961; Wolfe et al., 1985). As organic cations exchange for metal ions on mineral surface, these organic cations act as "pillars" and increase the distance between the aluminosilicate sheets. Importantly, the organic cations are not strongly hydradated and, due to surface coverage, they also decrease the free mineral surface area. As a result, the surface properties of the clay may change from hydrophilic, when exchanged with naturally occurring inorganic ions, to organophilic when organic exchange ions are present.

Mortland et al. (1986) and Boyd et al. (1988a) used quaternary ammonium cations as exchange ions on smectite to enhance the uptake of phenol and chlorophenols from water. These authors showed that in general the sorptive capacity of modified clays exchanged with large quaternary ammonium ions was greatly improved as compared to unmodified clays or modified clays in which the exchanged organic cations were small in size.

To elucidate the role of exchanged hydrophobic organic cations on the sorptive behavior of modified clays, Boyd et al. (1988b) studied the sorption of NOCs on hexadecyltrimethylammonium $[(CH_3)_3N(CH_2)_{15}CH_3]^+$(HDTMA)-smectite from both aqueous and vapor phases. These authors found that in dry HDTMA-smectite, both the mineral and organic phase are effective sorbents for the uptake of NOCs, analogous to the behavior of mineral and organic matter in dry soil (Chiou et el., 1985). However, in aqueous solution adsorption on mineral surfaces was suppressed by water and the uptake of NOCs by HDTMA-smectite was primarily by solute partitioning into the organic medium formed by the conglomeration of large C_{16} alkyl groups of HDTMA ions. This partition behavior of HDTMA-smectite, as shown in the uptake of NOCs from aqueous solution, can be recognized in many aspects, including: (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 octonal-water partition coefficient (K_{ow}) of the NOC and the corresponding organic matter normalized partition coefficients (K_{om}) of the organo-clay, and (4) the related dependence of the sorption coefficient of HDTMA-smectite on the organic carbon content of the modifed clay, i.e. , the proportion of the CEC occupied by HDTMA ions (Boyd et al., 1988b).

Recently, Lee et al. (1988) in studies of the sorption of aromatic compounds on water-saturated tetramethylammonium (TMA)-smectite found that the sorptive characteristics of TMA-smectite contrasted with the partition behavior of HDTMA-smectite for the uptake of NOCs from water. For instance, the sorption isotherms of benzene, toluene and o-xylene on TMA-smectite were not linear. In addition, compounds with high water solubilities (e.g. benzene) showed strong affinities for TMA-smectite, whereas, lower water solubility compounds such as trichlorobenzene had very low affinities for TMA-smectite. It was also shown that the uptake of benzene from aqueous solution was significantly higher for TMA-smectite than for HDTMA-smectite, despite the fact that HDTMA-smectite had a much higher organic carbon content than TMA-smectite.

The work by Lee et al. (1988), also demonstrated that TMA-smectite showed shape selectivity in the sorption of aromatic compounds from water, with high uptake of benzene and progressively lower uptake of larger aromatic compounds. This selectivity could only be seen for the sorption of aromatic compounds from aqueous solution, and not for the sorption of the corresponding vapors by the dry clay. This unique selective property of TMA-smectite was attributed to water molecules modifying the sorptive behavior of TMA-smectite by shrinking the interlamellar cavities where adsorption of the aromatic molecules occurred.

In this paper, two smectites of differing charge densities were used for the preparation of TMA-clay complexes. One smectite, obtained from

Arizona, has a cation exchange capacity (CEC) of 120 meq per 100 g; the other, from Wyoming, has a CEC of 90 meq per 100g (Table 1). When fully exchanged with TMA ions, both modified clays possess considerable interlamellar porosity, however, on Arizona TMA-smectite, the surface density of TMA ions is increased because of its higher CEC. Therefore, these two materials were used to investigate the effect of layer charge density on the sorptive behavior of TMA-smectite.

EXPERIMENTAL

Samples for these investigations were prepared in a manner previously described (Lee et al., 1988). The organo-clay complexes were prepared by exchanging the TMA for Na ions on Wyoming smectite and Arizona smectite having CEC values of 90 meq/100g and 120 meq/100g, respectively (Table 1). The 0.2 μm fractions of the original clays were obtained by standard dispersion and sedimentation methods. After discarding the impurities of the original clays, the clays (primarily in the Na form) were treated with an excess of TMA chloride salt in the amount of 3-5 meq per meq of CEC of the clays for 2-4 h. The TMA-smectites were then dialyzed against distilled water until a negative chloride test with silver nitrate for the dialyzate was obtained. Then the TMA-smectites were freeze dried and stored at room temperature.

Adsorption isotherms were determined using the batch equilibration technique. Eight initial concentrations were prepared in the range of 100 to 1500 ppm for benzene; 20 to 550 ppm for toluene; 12 to 190 ppm for o-xylene; 12 to 150 ppm for o-dichlorobenzene (o-DCB) and ethylbenzene, and 0.8 to 10 ppm for 1,2,3-trichlorobenzene (1,2,3-TCB). 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 h at room temperature in a reciprocating shaker. Preliminary kinetic investigations indicated that the sorption equilibrium was reached in less than 20 h. Shaking was followed by centrifugation at room temperature in a high speed centrifuge at 8000 rpm for 30 min. A 1 ml portion of the supernatant was then transferred into a glass vial containing 10 ml of carbon disulfide, closed with foil-lined screw caps and shaken vigorously for 1 h on a reciprocating shaker. A portion of carbon disulfide layer was then removed for gas chromatographic (GC) analysis.

To measure the competitive effects of benzene and toluene adsorption on TMA-smectite, the isotherms of binary mixtures were performed as follows: 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 which contain 25 ml of 0.4% w/w clay-water suspension. The mixed solutions were then shaken and treated as described above.

The GC 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 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, 100°C for xylene and ethylbenzene, and 125°C for o-DCB. Operating temperature for injection port and detector were 270°C and 300°C, respectively. All adsorption measurements were carried out in duplicate. Blank determinations of organic compounds in absence of clays were conducted and 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 previously (Chiou et al., 1988).

A Philips diffractometer model XRG3100 equipped with a copper target x-ray tube was used for x-ray diffraction examination. Samples were prepared by placing clay aqueous suspension 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 organic vapors by dry TMA-smectites are shown in Figures 1-3. The adsorption isotherms on both Wyoming and Arizona TMA-smectites are sigmoid curves approaching Type IV in Brunauer's classification (Brunauer, 1944). For both clays, the amount of organic vapor uptake by dry TMA-smectites decreased in the order benzene > toluene > o-xylene. The magnitude of this decrease was much greater for Arizona TMA-smectite as compared to Wyoming TMA-smectite, where differences in the uptake of benzene, toluene and xylene vapors were relatively small. Further inspection of Figures

Figure 1. Adsorption of benzene vapor by dry Arizona and Wyoming TMA-smectites.

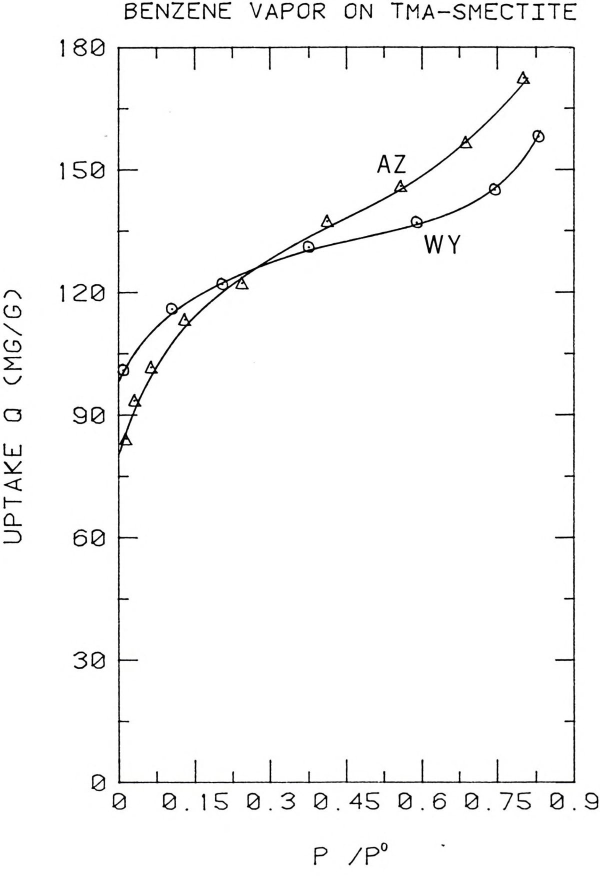

BENZENE VAPOR ON TMA-SMECTITE
UPTAKE Q (MG/G)
0
30
60
90
120
150
180
0
0.15
0.3
0.45
0.6
0.75
0.9
P /P⁰
AZ
WY

Figure 2. Adsorption of toluene vapor by dry Arizona and Wyoming TMA-smectites.

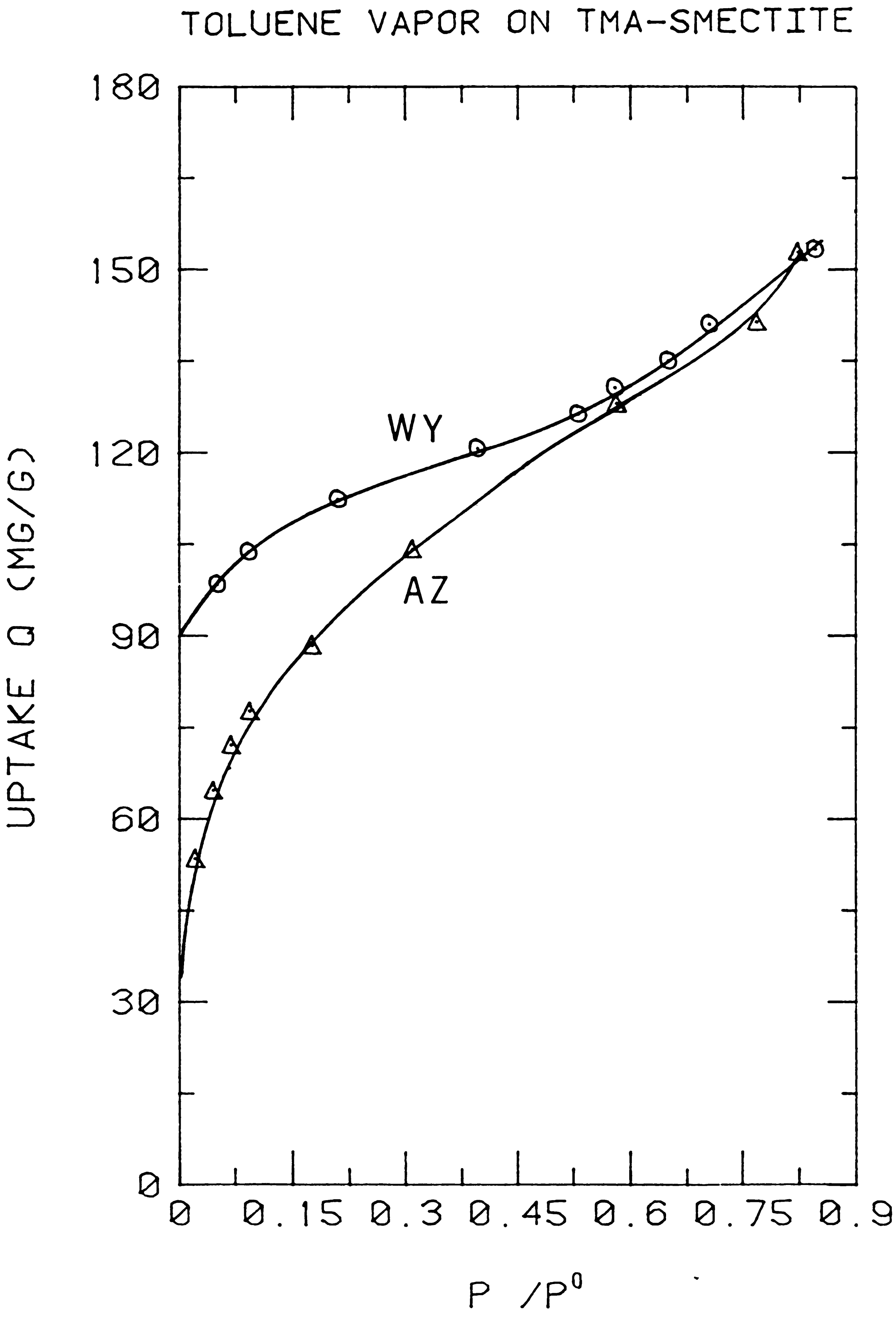
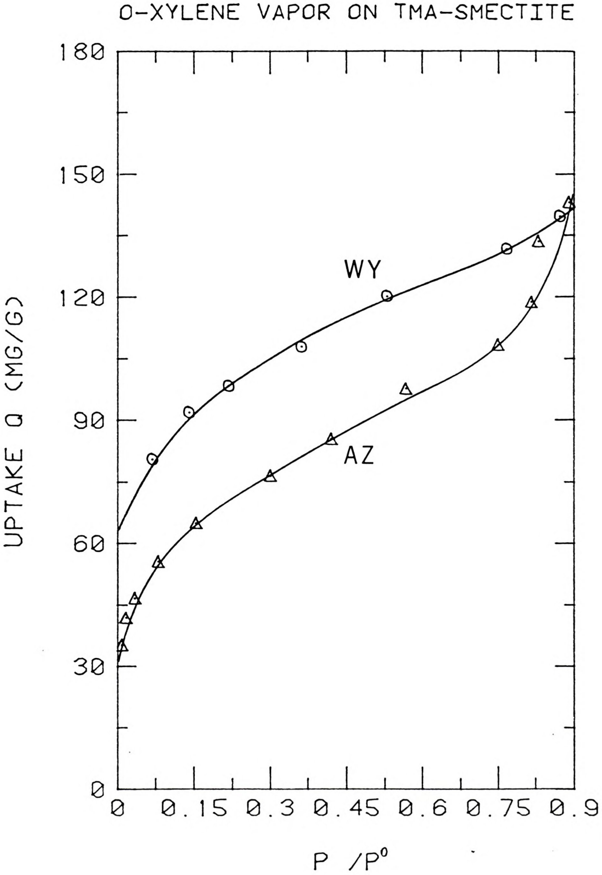

TOLUENE VAPOR ON TMA-SMECTITE
UPTAKE Q (MG/G)
P /P⁰
180
150
120
90
60
30
0
0
0.15
0.3
0.45
0.6
0.75
0.9
WY
AZ

Figure 3. Adsorption of o-xylene vapor by dry Arizona and Wyoming TMA-smectites.


O-XYLENE VAPOR ON TMA-SMECTITE
UPTAKE Q (MG/G)
180
150
120
90
60
30
0
0
0.15
0.3
0.45
0.6
0.75
0.9
P /P⁰
WY
AZ

1-3 shows that the amount of benzene uptake was nearly identical for the Wyoming and Arizona TMA-smectites, whereas the amounts of toluene vapor sorbed by Wyoming TMA-smectite exceed the amount taken up by Arizona TMA-smectite, especially at lower P/P°. For o-xylene, the largest of the three compounds tested, the uptake by Wyoming TMA-smectite was considerably higher than by Arizona TMA-smectite, and this difference extended to relatively high P/P°. The amount of organic vapor uptake of all three compounds tested indicated that adsorption occurred at both the internal and external surfaces of the TMA-smectites. In addition, the sorptive behavior of both TMA-smectites did not show threshold pressure.

Figures 4-6 show adsorption isotherms for the uptake of benzene, toluene and o-xylene from water by Wyoming and Arizona TMA-smectites. The uptake of each compound from water was lower than the uptake of the corresponding vapors by the dry samples. A noticeable difference in the degree of uptake of these organic chemicals by both Wyoming and Arizona TMA-smectites can be seen in the isotherms. In each case, the amount of uptake decreases in the order: benzene > toluene > xylene. However, the uptake of benzene from water was much lower for Arizona TMA-smectite than for Wyoming TMA-smectite. This obvious difference is in contrast with the uptake of benzene vapor by the dry samples which was nearly identical for both clays. The uptake of toluene and o-xylene by Arizona TMA-smectite was very low, and differences between the sorptive uptake by Wyoming and Arizona TMA-smectites were magnified in going from benzene to toluene to o-xylene. As expected from the results with o-xylene (Figure 2), o-DCB and ethylbenzene were entirely excluded from the Arizona TMA-smectite (data not shown) ; they were, however, sorbed slightly by Wyoming

Figure 4. Adsorption of benzene from aqueous solution by Arizona and Wyoming TMA-smectites.

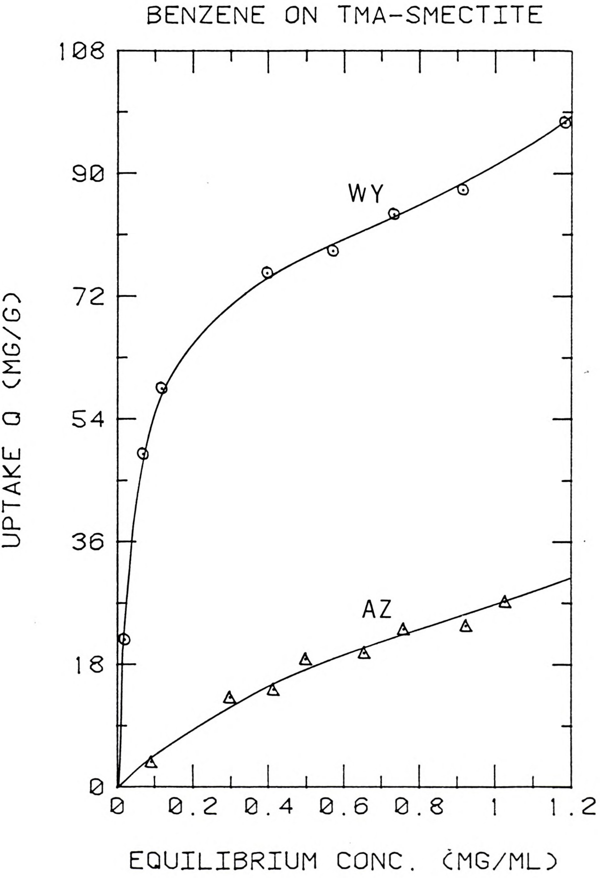

BENZENE ON TMA-SMECTITE
UPTAKE Q (MG/G)
EQUILIBRIUM CONC. (MG/ML)
WY
AZ
0
18
36
54
72
90
108
0
0.2
0.4
0.6
0.8
1
1.2

Figure 5. Adsorption of toluene from aqueous solution by Arizona and Wyoming TMA-smectites.

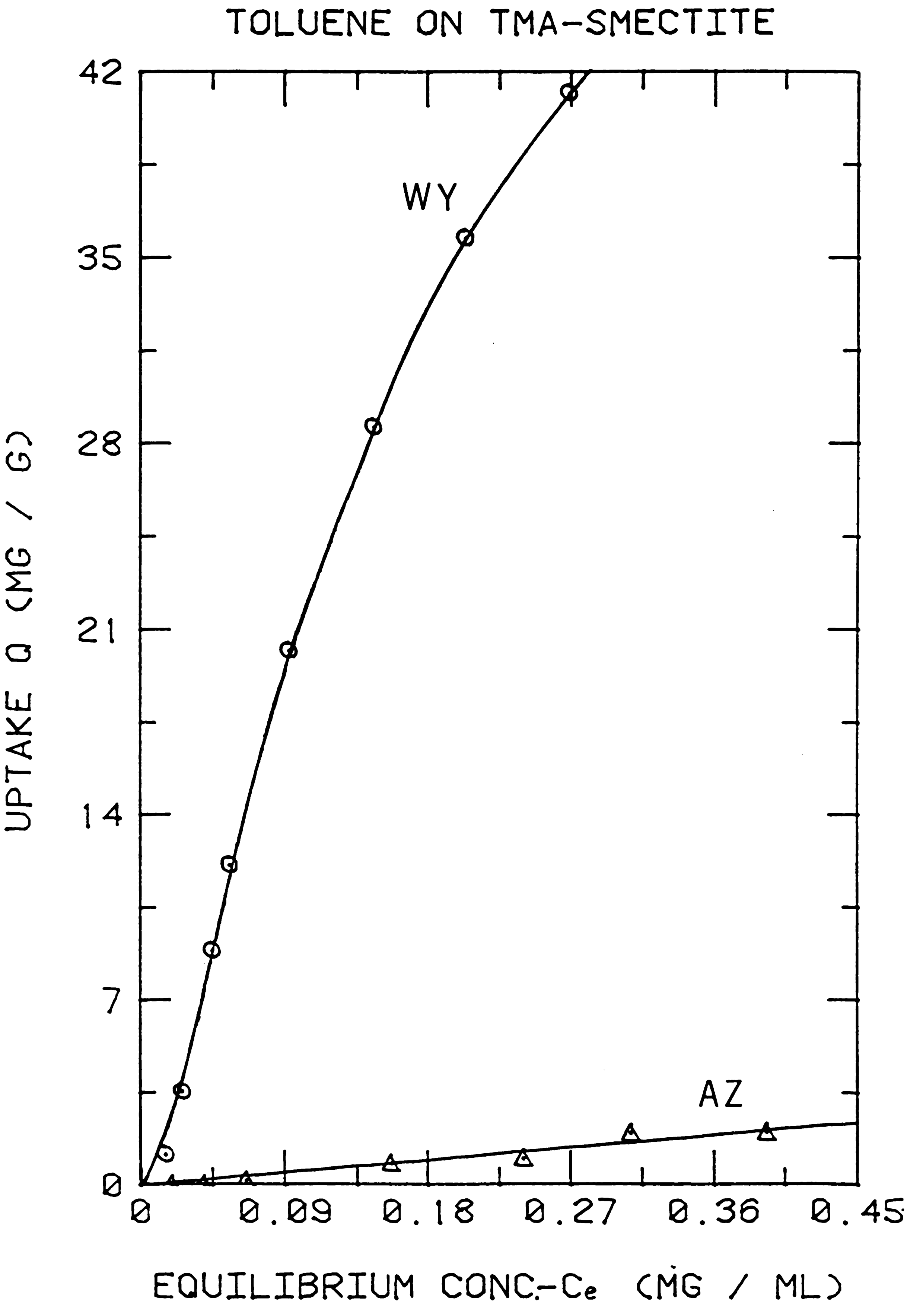
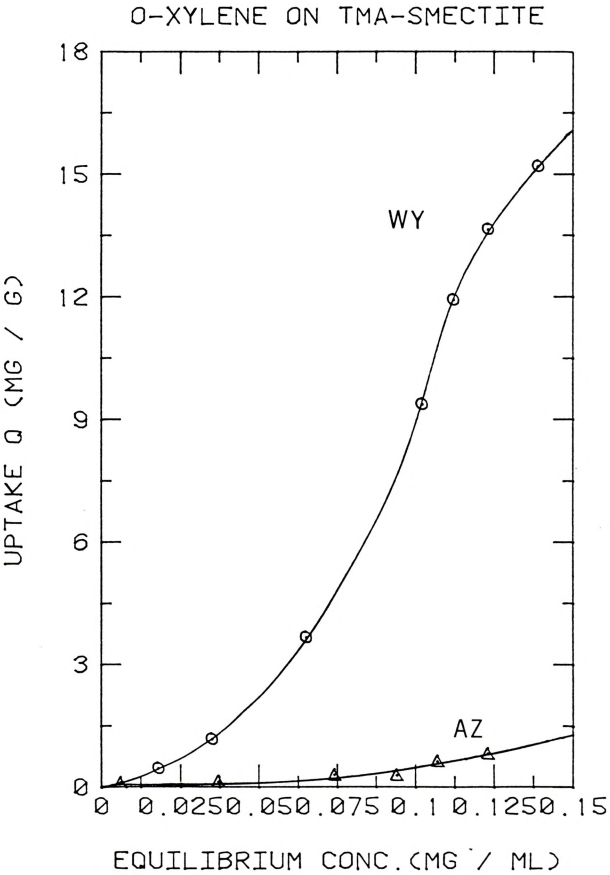

TOLUENE ON TMA-SMECTITE
UPTAKE Q (MG / G)
EQUILIBRIUM CONC.-Ce (MG / ML)
0
7
14
21
28
35
42
0
0.09
0.18
0.27
0.36
0.45
WY
AZ

Figure 6. Adsorption of o-xylene from aqueous solution by Arizona and Wyoming TMA-smectites.

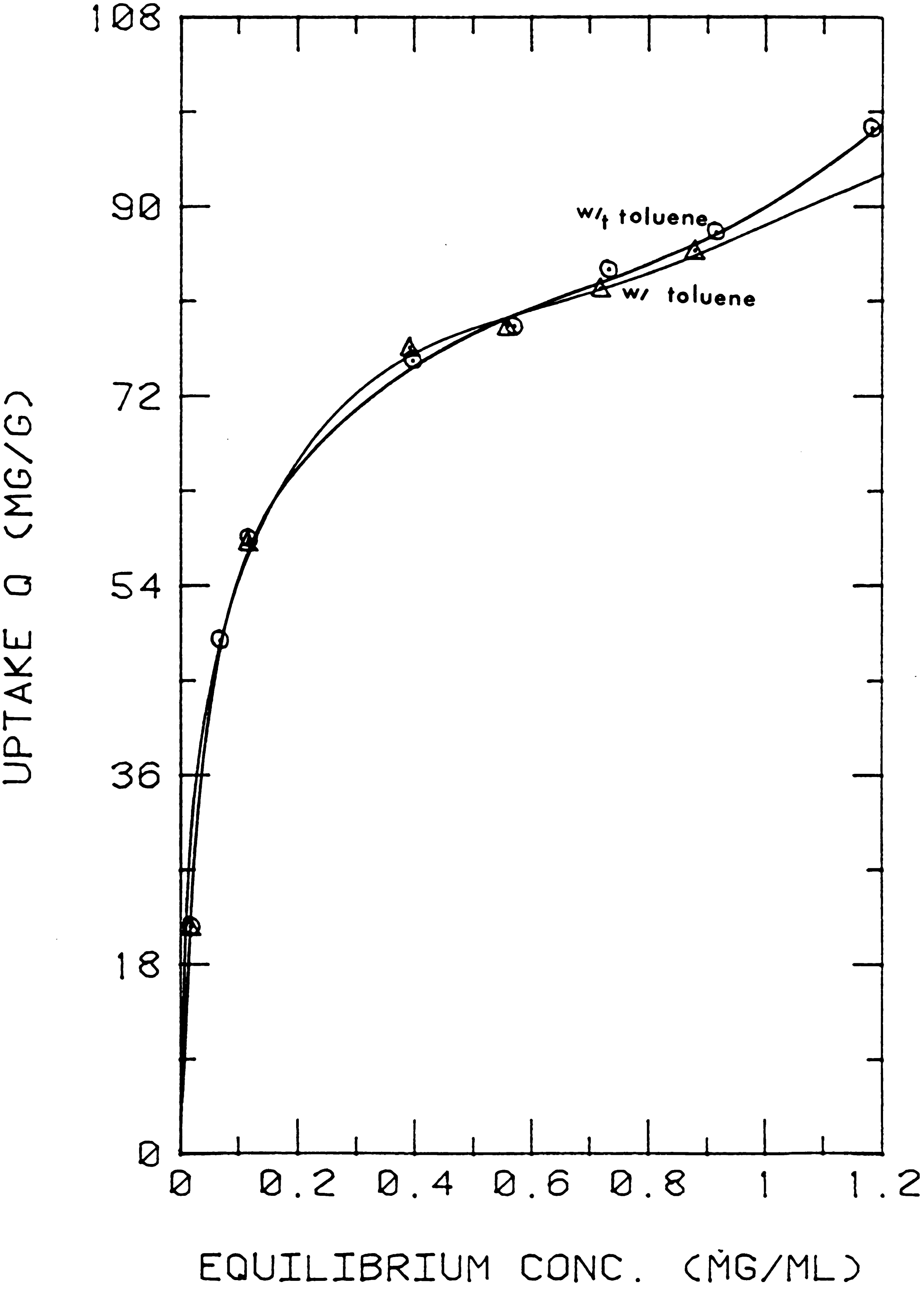

O-XYLENE ON TMA-SMECTITE
UPTAKE Q (MG / G)
EQUILIBRIUM CONC.(MG / ML)
0
3
6
9
12
15
18
0
0.025
0.05
0.075
0.1
0.125
0.15
WY
AZ

TMA-smectite (Lee et al., 1988).

There is also a pronounced difference in the shape of adsorption isotherms shown in Figure 4-6 indicating progressively weaker interactions with TMA-smectite in the order: benzene > toluene > o-xylene. It is clear from both the shape of the isotherms and the degree of uptake that, in the presence of water, the aromatic molecules have weaker interactions with Arizona TMA-smectite than with Wyoming TMA-smectite. The adsorption isotherms of toluene and o-xylene suggest that the uptake of these two chemicals from aqueous solution by Arizona TMA-smectite is restricted to external surfaces. On the other hand, the uptake of benzene from water appears to involve the interlamellar surfaces of the TMA-clays.

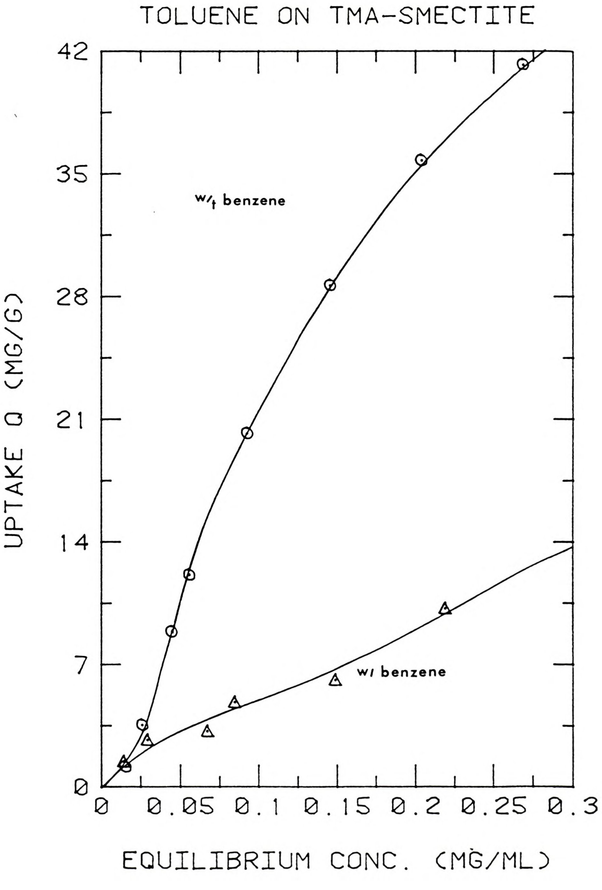
Competitive effects in the sorption of benzene-toluene mixtures from aqueous solution by Wyoming TMA-smectite are presented in Figures 7 and 8. When the adsorption isotherms for benzene alone and in a binary solute mixture with toluene are plotted on the same diagram, the isotherms are nearly superimposable (Figure 7). This demonstrates that toluene, at any concentration, is unable to compete with benzene for adsorption sites on Wyoming TMA-smectite. However, benzene shows very effective competition with toluene for the adsorption sites of Wyoming TMA-smectite, and in the presence of benzene, the adsorption of toluene is greatly depressed (Figure 8). As the initial concentration of benzene increased, the differences in uptake of toluene from water by Wyoming TMA-smectite are increased.

Figure 7. Adsorption of benzene from water in the presence (triangles) and absence (circles) of toluene by Wyoming TMA-smectite.



BENZENE ON TMA-SMECTITE

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


TOLUENE ON TMA-SMECTITE
UPTAKE Q (MG/G)
0
7
14
21
28
35
42
0
0.05
0.1
0.15
0.2
0.25
0.3
EQUILIBRIUM CONC. (MG/ML)
w/t benzene
w/ benzene

DISCUSSION

The relation between the sorptive behavior of TMA-smectites and the density of exchanged TMA ions was studied using two smectites of different charge densities. The closer packing of TMA ions on the higher charge density Arizona-smectite was demonstrated by an organic carbon content of 5 percent as compared to 4 percent in the lower charge density Wyoming-smectite (Table 1). The difference in organic carbon contents of 20 percent was in agreement with the approximate differences in cation exchange capacities of 25 percent for the two smectites.

Consideration of the surface areas of TMA ions, and the free space between exchanged TMA ions on Wyoming smectite, led Barrer et al (1961) to conclude that it was necessary for benzene to adopt a tilted orientation when adsorbed in the interlamellar regions of TMA-smectite. Thus, benzene and presumably other aromatic molecules appear to be oriented in a face-to-face arrangement with the planar faces of the TMA-tetrahedra. Size restrictions in the interlamellar regions were previously shown to result in high uptake of benzene and progressively lower uptake of larger (more substituted) aromatic molecules from water (Lee et al., 1988). This type of shape-selective adsorptive behavior of TMA-smectite is much different than the sorptive behavior of smectite exchanged with quaternary ammonium ions containing large hydrocarbon moieties, such as hexadecyltrimethylammonium $[(CH_3)_3N(CH_2)_{15}CH_3]^+$ (HDTMA). When absorbed on the surface of smectite, the hydrocarbon tails of such large organic cations (e.g. HDTMA) appear to form an organic phase that acts as a partition medium for the uptake of nonionic organic compounds (NOCs) (Boyd et al., 1988). This is a process of solubilization of NOCs

Table 1. Properties of Wyoming and Arizona TMA-smectites.

Property	Wyoming[a]	Arizona[b]
CEC (meq/100g)	90	120
Organic carbon (g/100g)[c]	4.0	5.0
d(001) (nm)	1.38	1.38
(nm)=d(001)-0.95	0.43	0.43

Formulae

Wyoming $(Al_{1.53}Fe_{0.16}Mg_{0.33})(Si_{3.95}Al_{0.05})O_{10}(OH)_2$

Arizona $(Al_{1.4}Fe_{0.17}Mg_{0.43})(Si_{3.88}Al_{0.12})O_{10}(OH)_2$

---

[a] Supplied by American Colloid Co.

[b] Regerence Clay sample SA_z-1 from C.M.S. repository.

[c] Organic carbon derived from TMA ions.

in the HDTMA-derived organic phase, and no shape selectivity is observed. Rather the degree of uptake is related exclusively to the water solubility of the NOC. The partitioning of NOCs also manifests highly linear isotherms as compared to the generally nonlinear isotherms observed for TMA-smectite.

The closer packing of TMA ions in the Arizona-smectite as compared to Wyoming-smectite resulted in a higher degree of shape selectivity in the adsorption of aromatic compounds. For the sorption of organic vapors, both dry TMA-smectites showed similar affinities for the sorption of benzene. However, as the size of sorbates increased in going from benzene to toluene to o-xylene, the uptake of organic vapors by Arizona TMA-smectite decreased; whereas, the amount of vapor uptake by Wyoming TMA-smectite remained relatively constant. Thus, Arizona TMA-smectite showed an obvious shape selectivity in the adsorption of aromatic vapors in the absence of water; whereas, dry Wyoming TMA smectite showed little selectivity among benzene, toluene, and xylene. As the values of TMA-smectites are 4.3Å (Table 1), both TMA-smectites have essentially identical interlayer distances to accommodate the benzene-like compounds. Therefore, the selectivity of Arizona TMA-smectite can be attributed to the effects of charge density on the clay surfaces.

The closer packing of TMA ions in the Arizona smectite apparently resulted in a significant change in the size distribution of cavities in the interlamellae. Arizona TMA-smectite appears to contain fewer sites (between TMA ions) of sufficient size to accommodate the larger aromatic molecules. Thus overall, the selectivity of Arizona TMA-smectite was greater than the more loosley packed Wyoming TMA-smectite. In the former case, shape selectivity was observed for the adsorption of organic vapors by the dry sample, and to a greater extent for the sorption of the aromatic compounds from water. However, for Wyoming TMA-smectite shape selectivity was only prominent in the aqueous system. Thus, in addition to size distribution of cavities resulting from the packing of TMA ions, water played a direct role in determining the shape selective adsorption of aromatic compounds.

The different affinity of both TMA-smectites for the sorption of aromatic compounds from water can be seen in Figures 4-6. In the aqueous system, aromatic compounds showed a clear preference for Wyoming TMA-smectite. This is demonstrated by both the amount of uptake and the shapes of isotherms. All aromatic compounds tested were sorbed by Wyoming TMA-smectite, however, toluene and o-xylene were nearly completely excluded from Arizona TMA-smectite. Since the vertical free distance between lamellae is 4.3Å in both TMA-smectites, it must be the lateral free distance between TMA ions which causes the difference. The higher charge density of Arizona smectite means a greater population of TMA ions fixed per unit area, with resulting lower amounts of free surface available for adsorption and smaller cavities on the interlamellae. Sieving effects of the TMA-smectite were either smaller or not demonstrated for the uptake of organic vapors because the internal surfaces and cavities of dry TMA-smectite were more available. However, as the adsorption is taking place in an aqueous system, the water molecules will associate with the free mineral surfaces and to some extent with the exchanged TMA ions. Not only does the average lateral distances between adjacent interlamellar cations decrease as the amount of TMA exchanged increases, but the lateral distance will further shrink due to hydration. Therefore, the free distances between nearest neighbor pairs of organic cations are not large enough in the Arizona TMA-smectite for significant uptake substituted aromatic molecules to occur. It is thus suggested that these aromatic compounds occupy only the largest few interlamellar gaps of Arizona TMA-smectite. In this event the sorptive capacity of the Arizona TMA-smectite in aqueous system will be much reduced as compared with that of Wyoming TMA-smectite. As expected from the results of o-xylene, o-DCB and ethylbenzene were also excluded from Arizona TMA-smectite, however, they were intercalated by Wyoming TMA-smectite.

The proposed adsorptive mechanism for the uptake of organic compounds from water should manifest competitive effects in multisolute systems. This was examined by studying adsorption of sorbate mixtures of benzene and toluene over a range of concentrations of each solute. The adsorption isotherms of the pure single sorbates show that more benzene than toluene is taken up by both TMA-smectites from water (Figure 3). Thus, in the binary solute system benzene should compete effectively with toluene for adsorption sites. This effect was observed as the uptake of toluene was greatly depressed by the presence of benzene. However, the uptake of benzene was not affected by toluene because the affinity of benzene for the water-saturated TMA-smectite is greater than that of toluene. These results suggest that the adsorption of toluene in the presence of benzene is restricted to the external surfaces with benzene preferentially occupying the intralamellar regions of Wyoming TMA.smectite. As a result, the adsorption isotherm of toluene in the presence of benzene by Wyoming TMA-smectite (Fig. 8) is similar to the adsorption isotherm of toluene by Arizona TMA-smectite (Fig. 5) where adsorption is also limited to external surfaces.

The work presented here, in conjunction with earlier studies, has demonstrated 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, molecular sieves of widely differing behavior may be prepared which demonstrate shape-selective adsorption of aromatic compounds. The degree of shape-selectivity can be increased by using smectites of higher charge density. In these experiments, the main factor affecting the degree of sorption of aromatic compounds from water by TMA-smectite was found to be the lateral distances between the interlamellar cations on water-saturated TMA-smectite.

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