

## CLAY-ORGANIC COMPLEXES AS ADSORBENTS FOR PHENOL AND CHLOROPHENOLS<sup>1</sup>

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**Abstract**—Several clay-organic complexes were synthesized by placing quaternary ammonium cations on smectite by cation exchange. They were then examined for their ability to adsorb phenol and several of its chlorinated congeners. The organic cations used were: hexadecylpyridinium (HDPY<sup>+</sup>), hexadecyltrimethyl ammonium (HDTMA<sup>+</sup>), trimethylphenyl ammonium (TMPA<sup>+</sup>), and tetramethylammonium (TMA<sup>+</sup>). The complexes containing long-chain alkyl (hexadecyl) groups were the most hydrophobic and adsorbed the phenols from water in proportion to their hydrophobicities, which increase with chlorine addition (phenol < chlorophenol < dichlorophenol < trichlorophenol). With n-hexane as the solvent, different adsorption was found which depended on the type and degree of solvent interactions with the compound and the clay-organic complex. Thus, the amount of adsorption of these phenols on clay-organic complexes was dependent on the relative energies of adsorbent-adsorbate and adsorbate-solvent interactions.

**Key Words**—Adsorption, Chlorophenols, Hydrophobicity, Organo clays, Phenol, Smectite.

### INTRODUCTION

The mechanisms of clay-organic interactions have been well documented in the literature (Mortland, 1970; Theng, 1974; Solomon and Hawthorne, 1983; Mortland, 1986). By placing organic cations or metal cations with strongly bound organic ligands on the cation-exchange sites of clays, the surface properties may be significantly altered. Long-chain alkyl ammonium cations adsorbed on the clay, for example, change the nature of the surface from hydrophilic to hydrophobic. Consequently, whereas enzyme (protein) adsorption on smectite is ordinarily pH dependent (coulombic effects), the enzyme may be strongly bound by clay-organic complexes such as hexadecyltrimethyl-ammonium-smectite (HDTMA<sup>+</sup>-smectite) by hydrophobic binding which is completely independent of pH (Garwood *et al.*, 1983; Boyd and Mortland, 1985a, 1985b, 1986). Such interaction involves hydrophobic portions of the enzyme interacting with the hydrophobic alkyl group on the mineral surface.

McBride *et al.* (1977) showed that different kinds of clay-organic complexes have widely varying adsorption properties for benzene, phenol, and chlorobenzenes. The present work is an extension of that study in that adsorption isotherms of phenol and a series of its chlorinated analogs were obtained for several clay-organic complexes of varying hydrophobicities. The particular microenvironment provided by each organic

cation on the clay surface should be reflected in different adsorption properties for the series of phenols.

### METHODS

The clay used was smectite from a Wyoming bentonite furnished by American Colloid Company. Ten grams of the Na-saturated clay was dispersed in 1 liter of distilled water and allowed to stand several hours to allow quartz sand and heavy minerals (5% of the whole) to settle out. The suspension was decanted and treated with the bromide or chloride salt of the appropriate organic cation in an amount just equal to the cation-exchange capacity of the clay (90 meq/100 g). A summary of the names, abbreviations, and structural formulae of the organic cations appear in Table 1. Because these organic cations are strongly preferred by the exchange sites over the Na<sup>+</sup> ions, most of the organic cation was taken up by the exchange complex. Excess organic salt was not added because these organic salts may be adsorbed by the clay in large excess of the exchange capacity. After the treated clay was washed on filter paper with distilled water, the clay was frozen, freeze dried, and stored in bottles for use.

Adsorption isotherms were obtained by weighing duplicate 50-mg quantities of the clay-organic complex into 125-ml Erlenmeyer flasks and adding the appropriate compound in amounts equal to 0.2, 0.4, 0.6, 1.0, 1.5, and 2.0 mmole/g of clay. Total volume of solution was 100 ml. The flasks were shaken overnight at 20°C on a rotary shaker and then either allowed to settle or were filtered the next morning. Analyses for the appropriate compound in the solution phase were made by using a Perkin-Elmer 320 spectrophotometer utilizing an appropriate absorption band in the ultraviolet

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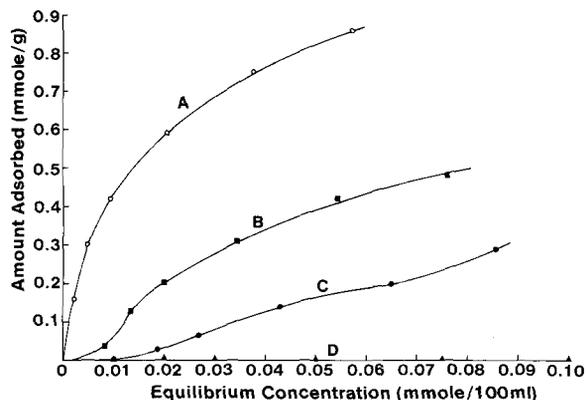


Figure 1. Adsorption isotherms (20°C) for phenols from water on HDTMA<sup>+</sup>-smectite. A = 3,4,5-trichlorophenol; B = 3,5-dichlorophenol; C = 3-chlorophenol; D = phenol (on abscissa).

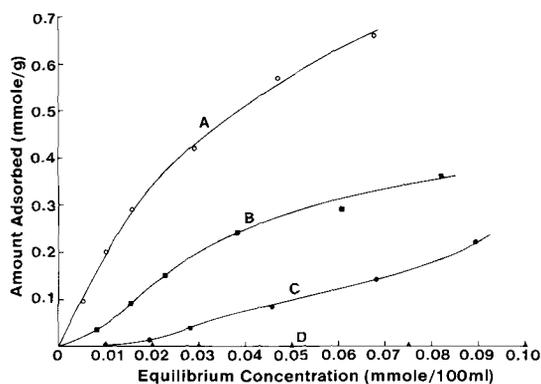


Figure 2. Adsorption isotherms (20°C) for phenols from water on HDPY<sup>+</sup>-smectite. A = 3,4,5-trichlorophenol; B = 3,5-dichlorophenol; C = 3-chlorophenol; D = phenol (on abscissa).

region (Table 2). X-ray powder diffraction data were obtained utilizing a Philips diffraction unit with a copper target. Samples were oriented on glass microscope slides.

## RESULTS

Figures 1–3 display adsorption isotherms of phenol, 3-chlorophenol, 3,5-dichlorophenol, and 3,4,5-trichlorophenol from water onto hexadecyltrimethylammonium (HDTMA<sup>+</sup>)-, hexadecylpyridinium (HDPY<sup>+</sup>)-, and trimethylphenylammonium (TMPA<sup>+</sup>)-smectite. The isotherms in Figures 1 and 2 for HDTMA<sup>+</sup>- and HDPY<sup>+</sup>-smectites exhibit marked differences for the various phenols. As the number of chlorines on the phenol structure was increased, the greater was the adsorption on these two hydrophobic matrices. Phenol,

the most hydrophilic of these molecules, was not adsorbed at all by either matrix. A good index of the hydrophilic properties of these molecules should be their solubilities in water which appear in Table 2. An inverse relationship is demonstrated between that property and the adsorption on the two hydrophobic surfaces, thus suggesting that as hydrophilic properties of molecules decrease (or hydrophobic properties increase), adsorption increases via hydrophobic interaction. The monochlorophenol gave a type V isotherm (classification of Gregg and Sing, 1982) which was characterized by an initial convexity followed by a slight plateau and then the beginning of a final upsweep. The dichlorophenol isotherms also exhibited type V characteristics, but lacked the final upsweep. Such isotherms are characteristic of weak adsorbate-adsorbent interactions, causing adsorption at low concentrations to be small. Once a molecule is adsorbed, however, adsorbate-adsorbate forces promote the adsorption of more molecules in a cooperative fashion (Gregg and Sing, 1982). The trichlorophenol isotherms exhibited classical type I characteristics and, as such, obeyed the Langmuir equation. Here, adsorbate-adsorbent interaction was relatively strong, probably due to hydrophobic interaction. Calculation of the maximum adsorption capacity from the Langmuir plots gave 1.05

Table 1. Name and structural formula of organic cations on exchange complex of the smectite.

Name	Abbreviation	Structure
Hexadecyltrimethylammonium	HDTMA <sup>+</sup>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{N}^+-\text{(CH}_2\text{)}_{15}\text{-CH}_3 \\   \\ \text{CH}_3 \end{array}$
Hexadecylpyridinium	HDPY <sup>+</sup>	$\text{C}_5\text{H}_5\text{N}^+-\text{(CH}_2\text{)}_{15}\text{-CH}_3$
Trimethylphenylammonium	TMPA <sup>+</sup>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{N}^+-\text{C}_6\text{H}_5 \\   \\ \text{CH}_3 \end{array}$
Tetramethylammonium	TMA <sup>+</sup>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{N}^+-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$

Table 2. Ultraviolet absorption bands and water solubilities of the phenols used in this study.

Compound	Wavelength of absorption band (nm)	Water solubility (20°C) (mg/kg) <sup>1</sup>
Phenol	269	$7.75 \times 10^4$
3-chlorophenol	274	$2.5 \times 10^4$
3,5-dichlorophenol	277	$4.5 \times 10^3$
3,4,5-trichlorophenol	292	not found
2,4,6-trichlorophenol	293	$0.8 \times 10^3$

<sup>1</sup> Freier (1976).

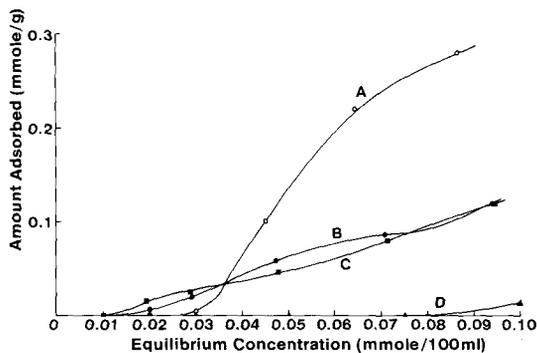


Figure 3. Adsorption isotherms (20°C) for phenols from water on  $\text{TMPA}^+$ -smectite. A = phenol; B = 3-chlorophenol; C = 3,4,5-trichlorophenol; D = 3,5-dichlorophenol.

and 1.16 mmole/g for the  $\text{HDTMA}^+$ - and  $\text{HDPY}^+$ -smectite, respectively. These high levels of adsorption indicate that the trichlorophenol must have penetrated into interlayer surfaces. This penetration was confirmed by X-ray powder diffraction which showed a 001 spacing at about 30 Å for  $\text{HDTMA}^+$ -smectite after it adsorbed large quantities of the trichlorophenol from water. The  $\text{HDTMA}^+$ -smectite ordinarily has a 001 spacing of 18 Å. These data indicate that as chlorines were added to the phenol structure, adsorbent-adsorbate interaction with  $\text{HDTMA}^+$ - and  $\text{HDPY}^+$ -smectite increased.

The adsorption of the phenols from water onto trimethylphenylammonium ( $\text{TMPA}^+$ ) smectite was quite different (Figure 3). More phenol was adsorbed than any of the chlorinated analogs. The phenol isotherm, even so, was a typical type V isotherm which indicates weak adsorbate-adsorbent interaction.

The type of solvent has a profound effect on the nature of the adsorption isotherms (see Figures 4–6 in which isotherms in water and n-hexane are compared).

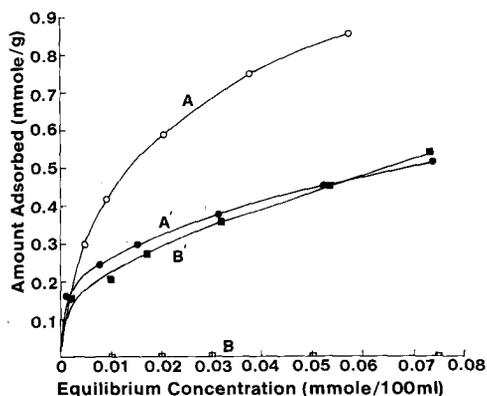


Figure 4. Adsorption isotherms for 3,4,5-trichlorophenol from water (A) and hexane (A'), and phenol from water (B) and hexane (B') onto  $\text{HDTMA}^+$ -smectite.

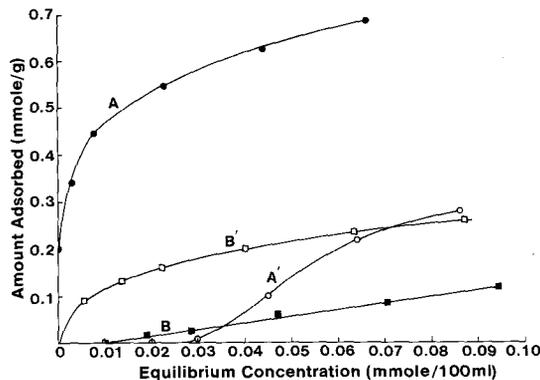


Figure 5. Adsorption isotherms for phenol from hexane (A) and water (A'), and 3,4,5-trichlorophenol from water (B) and hexane (B') onto  $\text{TMPA}^+$ -smectite.

Figure 4 shows the adsorption of 3,4,5-trichlorophenol and phenol on  $\text{HDTMA}^+$ -smectite from water and hexane. Whereas the former was strongly adsorbed from water, phenol was not adsorbed at all. Yet, if n-hexane was the solvent, the two species were adsorbed to similar degrees. These data demonstrate the relative importance of both adsorbate-solvent and adsorbate-surface interactions on the partitioning of adsorbate molecules between solvent and surface. The adsorption of these phenols from hexane may also be affected by swelling of some of these clay-organic complexes (Theng, 1974) in hexane, thus providing interlayer surface. Figure 5 shows similar data for the adsorption of the two molecules on  $\text{TMPA}^+$ -smectite. These data indicate a strong preference for phenol over the chlorinated species in both solvents, adsorption being greater from hexane. Figure 6 shows adsorption isotherms of the two phenols on tetramethylammonium ( $\text{TMA}^+$ ) smectite from the two solvents. Here, neither phenol was adsorbed to any greater extent from water, but large quantities were adsorbed from n-hexane, the amount of phenol being about twice as much as that of the chlorinated species.

Even isomers of the same compound may show different adsorption isotherm characteristics, as demonstrated in Figure 7, which shows isotherms of 3,4,5- and 2,4,6-trichlorophenol on  $\text{HDTMA}^+$ -smectite in water. Here, adsorption of the former compound yields a classic type I isotherm, whereas adsorption of the latter yields a type V isotherm. This comparison suggests that the 3,4,5-trichlorophenol interaction with the clay-organic complex is stronger than that of its 2,4,6-isomer. Different solvent-adsorbate interactions may also have produced these differences.

## DISCUSSION

The nature of the organic cation on the exchange complex of smectite and the nature of the solvent are of prime importance in determining the adsorption of

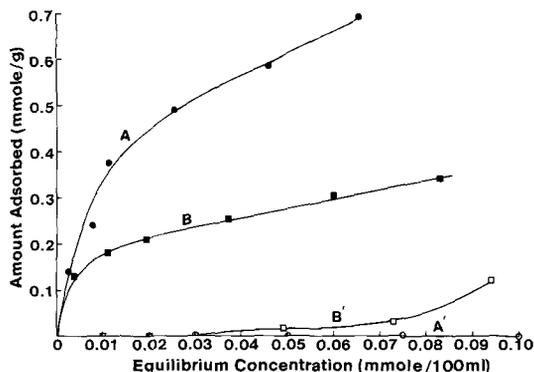


Figure 6. Adsorption isotherms for phenol from hexane (A) and water (A'), and 3,4,5-trichlorophenol from hexane (B) and water (B') onto TMA<sup>+</sup>-smectite.

phenol and its chloro-analogs. The different kinds of organic cations used in this study provided a variety of subtle properties which were expressed in a wide range of surface effects. These results agree with the earlier work of Garwood *et al.* (1983) and Boyd and Mortland (1985a, 1985b, 1986) where in the activities of adsorbed enzymes were shown to vary greatly depending on the micro-environments provided by different clay-organic complexes.

In the present work the adsorption observed for a particular molecule resulted from the product of two controlling factors: (1) adsorbent-adsorbate interactions, and (2) adsorbate-solvent interactions. Thus, in water solvent, phenol interacted strongly with water (hydrogen bonding) and was not attracted sufficiently to the hydrophobic surfaces of HDTMA<sup>+</sup>- and HDPY<sup>+</sup>-smectite to create a significant adsorption (Figures 1 and 2). With hexane as the solvent, phenol had a much less energetic interaction with this solvent, and the adsorbent-adsorbate interactions were strong enough to result in considerable adsorption (Figure 4). The observed adsorption was the resultant of the relative energies of the above two competing reactions. Similar arguments can be made for all the molecules used in this study. Significantly, the addition of each chlorine to the phenol structure reduced its energy of interaction with water (decreased water solubility, Table 2), thereby allowing a more significant hydrophobic interaction with such surfaces as HDTMA<sup>+</sup>- and HDPY<sup>+</sup>-smectite. The behavior of such clay-organic surfaces as TMPA<sup>+</sup>- and TMA<sup>+</sup>-smectite was less straightforward. For TMA<sup>+</sup> and probably TMPA<sup>+</sup>-clay, some surface oxygens of the silicate structure were exposed, inasmuch as these smaller organic cations could not cover all of the silicate surface. McBride and Mortland (1975) found that TMA<sup>+</sup>-smectite had a surface area of 210 m<sup>2</sup>/g (as measured by N<sub>2</sub> adsorption), which suggests considerable surface not covered by the TMA<sup>+</sup> cation. Consequently, such a surface may have had both hydrophobic properties bestowed on it by the organic

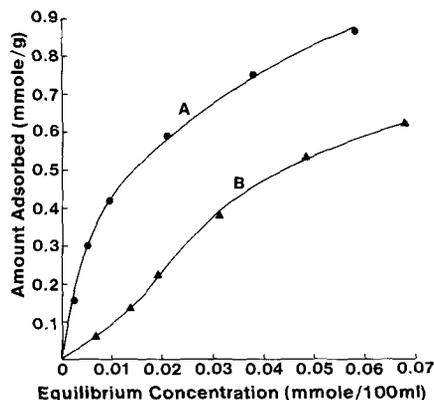


Figure 7. Adsorption isotherms for 3,4,5-trichlorophenol (A) and 2,4,6-trichlorophenol (B) onto HDTMA<sup>+</sup>-smectite from water.

species and more hydrophilic properties from the areas of exposed silicate oxygens.

A comparison of the adsorption behavior of TMA<sup>+</sup>- and HDTMA<sup>+</sup>-smectites illustrates the unique properties bestowed on the surface by the nature of the organic cation. The adsorption of 3,4,5-trichlorophenol by TMA<sup>+</sup>-smectite was greater from hexane than from water (Figure 6), directly opposite to results obtained for HDTMA<sup>+</sup>-smectite (Figure 4). For TMA<sup>+</sup>-smectite, the absence of water on the surface apparently increased the hydrophobicity and resulted in greater adsorbate-adsorbent interaction. Thus, more adsorption was noted from hexane. For HDTMA<sup>+</sup>-smectite, the hydrophobicity of this surface was not significantly altered by solvent effects, and the decrease in 3,4,5-trichlorophenol adsorption from hexane was due simply to increased adsorbate-solvent interaction. Another factor that could be important in these results is a sieving effect. Particularly where interlayer adsorption may be taking place, the size and shape of the organic cation may exclude adsorbate molecules.

The results obtained here suggest that clay minerals may be treated with specific organic cations that have specific adsorption properties for particular molecules, e.g., phenols. Such adsorption specificity is applicable in the removal of a particular target molecule from a solvent or in the chromatographic separation of closely related molecules. The sensitivity of these tailor-made clay-organic complexes for particular purposes is thus of interest for future development. These synthetic organo-clay complexes also appear to be useful in fundamental studies on the interactions of organic molecules with specific kinds of surfaces which can be varied with respect to hydrophobicity, aromaticity, and polarity.

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