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Effect of Ten Quaternary Ammonium Cations on Tetrachloromethane Sorption to Clay from Water

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■ The mineral surface of Wyoming bentonite (clay) was modified by replacing inorganic ions by each of 10 quaternary ammonium compounds, and tetrachloromethane sorption to the modified sorbents from water was studied. Tetrachloromethane sorption from solution to clay modified with tetramethyl-, tetraethyl-, benzyltrimethyl-, or benzyltriethylammonium cations generally is characterized by relatively high solute uptake, isotherm nonlinearity, and competitive sorption (with trichloroethene as the competing sorbate). For these sorbents, the ethyl functional groups yield reduced sorptive capacity relative to methyl groups, whereas the benzyl group appears to have a similar effect on sorbent capacity as the methyl group. Sorption of tetrachloromethane to clay modified with dodecyltrimethyl(2-phenoxyethyl)-, dodecyltrimethyl-, tetradecyltrimethyl-, hexadecyltrimethyl-, or benzyldimethylhexadecylammonium bromide is characterized by relatively low solute uptake, isotherm linearity, and noncompetitive sorption. For these sorbents, an increase in the size of the nonpolar functional group(s) causes an increase in the organic carbon normalized sorption coefficient (K_{oc}). No measurable uptake of tetrachloromethane sorption by the unmodified clay or clay modified by ammonium bromide was observed.

Introduction

Wyoming bentonite, which is predominantly a montmorillonitic clay, is commonly used as a liner for waste-disposal ponds and as a principal component of slurry walls. Montmorillonite is characterized by alternating layers of tetrahedral silica and octahedral aluminum coordinated with oxygen atoms. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay (1). This charge imbalance is offset by exchangeable cations (typically Na^+ or Ca^{2+}) at the clay surface. The layered structure of the clay allows expansion (swelling) after wetting, which in turn exposes additional mineral surface capable of cation adsorption. These factors, in combination with its small particle size, cause montmorillonite to exhibit a high cation-exchange capacity relative to other natural soils. However, the mineral surfaces of montmorillonite and most other natural soils are relatively ineffective sorbents for nonionic organic compounds in aqueous systems, primarily because of the strong dipole interaction of water with the negatively charged mineral surface (2-9).

In aqueous systems, quaternary ammonium cations can be retained by both the outer and interlayer surfaces of an expandable clay particle by an ion-exchange process and are not easily displaced by smaller cations such as H^+ , Na^+ , or Ca^{2+} . The sorptive properties of the modified clay surface may be significantly altered by this substitution

reaction. For example, Smith and Bayer (10) described semiquantitatively the effect of five quaternary ammonium cations on the sorption of diuron to natural soil from water. They showed that the presence of these cations in the soil-water mixture increased the percent removal of diuron from the aqueous phase relative to soil-water mixtures with no quaternary ammonium cations present. More recently, Boyd et al. (11) suggested that the substitution of Na^+ and Ca^{2+} ions by quaternary ammonium ions with large alkyl groups in expandable clays creates an organic medium at the mineral surface through a conglomeration of alkyl chains. This medium may be capable of sorbing nonionic organic contaminants from water by a partition process. These investigators (11) found a linear uptake of benzene and trichloroethene from water by bentonite saturated with hexadecyltrimethylammonium cations (HTMA). The resulting sorption coefficients normalized to the organic content of the HTMA-modified clay are of comparable magnitude to the heptane-water partition coefficients of the respective solutes. On the other hand, clays substituted with small tetramethylammonium (TMA) cations show a strong, nonlinear uptake of benzene and small aromatic molecules from water, which is attributed to adsorption onto the TMA-treated surface (12, 13). Adsorption of these solutes by TMA-clay from water also exhibits a size- and shape-selective effect, disfavoring sorption of large solute molecules. These results may have great practical utility, as the use of clay treated with quaternary ammonium ions as a liner for waste-disposal facilities and as a component of slurry walls at ground-water-contamination sites is likely to increase the attenuation of dissolved nonionic organic contaminants.

The present study further analyzes the effect of the molecular structure of quaternary ammonium cations associated with a montmorillonitic clay on the sorption of a nonionic organic contaminant, tetrachloromethane. Ten quaternary ammonium cations composed of various alkyl and aromatic groups were selected for study to provide a wide range of molecular sizes and configurations. In addition to the practical value of optimizing the effect of these cations on the uptake of contaminants by clay, the purpose of this research is to provide a better understanding of the mechanistic interaction of nonionic organic compounds and organic matter at the mineral-water interface.

Experimental Section

The sorbent used in this study, Wyoming bentonite, was obtained from the American Colloid Co. It contains 3.6% sand, 7.3% silt, and 89.1% clay. The organic carbon content is 0.1%, and the cation-exchange capacity is 78.5 mequiv/100 g. This sorbent will be referred to as "clay" throughout this paper. A total of 250 μCi of [^{14}C]tetra-

Table I. Organic Carbon Contents, Langmuir-Type Isotherm Parameters, and Regression Correlation Coefficients for Tetrachloromethane Sorption to Four Organoclay Sorbents

| | sorbent | | | |
|----------------------|----------|----------|-----------|-----------|
| | TMA-clay | TEA-clay | BTMA-clay | BTEA-clay |
| organic C content, % | 1.80 | 3.49 | 4.21 | 5.75 |
| a, mmol/g | 0.14 | 0.08 | 0.15 | 0.11 |
| b, L/mmol | 1.46 | 2.11 | 2.23 | 3.69 |
| corr coeff | 0.992 | 0.997 | 0.996 | 0.998 |

chloromethane (specific activity equal to 4.3 mCi/mmol) and 50 μ Ci of [14 C]tetraethylammonium (TEA) bromide (specific activity equal to 3.0 mCi/mmol) was obtained from Du Pont NEN. A total of 100 μ Ci of [14 C]trichloroethene (specific activity equal to 4.1 mCi/mmol) was obtained from Sigma Chemical Co. [14 C]tetrachloromethane and [14 C]trichloroethene were mixed with non-radioactive tetrachloromethane and trichloroethene, respectively, to yield net volumes of 4.0 mL of each pure liquid. Similarly, [14 C]tetraethylammonium bromide was mixed with nonradioactive tetraethylammonium bromide to yield a net mass of 5.0 g. The resultant chemical and radiochemical purity of each radioisotope was greater than 99%. All quaternary ammonium compounds were obtained from Aldrich Chemical Co. and were used as received. Their chemical purities, molecular structures, and abbreviations are given in Figure 1.

The addition of a quaternary ammonium cation to an aqueous clay suspension resulted in strong uptake of the cation by the clay. The resultant cation-clay complexes were considered to be unique sorbents and are specified by the cation abbreviation in Table I followed by "clay." For example, combining dodecyltrimethylammonium bromide (DTMA) with clay and water produced a modified clay identifiable as DTMA-clay. With the exception of ammonium-clay, these sorbents will be generally referred to as "organoclay complexes" or simply "organoclays."

The sorption of tetrachloromethane, trichloroethene, and TEA to unsubstituted clay, ammonium-clay, and organoclay complexes from water was quantified by using a conventional batch equilibration method. For tetrachloromethane sorption to DTMA-, TTMA-, HTMA-, DDPA-, and BDHA-clay, 6.0 g of clay, 55 mL of deionized water, the appropriate organic cation, and tetrachloromethane were combined in 50-mL (nominal volume) disposable glass centrifuge tubes with Teflon-lined septum caps. For TEA sorption to clay, 2 g of clay, 55 mL of deionized water, and TEA were combined in the 50-mL glass centrifuge tubes described above. For tetrachloromethane and trichloroethene sorption to ammonium-, TMA-, TEA-, BTMA-, and BTEA-clay complexes, 0.5 g of clay, 15 mL of deionized water, the appropriate cation, and tetrachloromethane were combined in 15-mL (nominal volume) disposal glass centrifuge tubes. The amount of quaternary ammonium cation added was based on the desired organic carbon content or percentage of cation-exchange capacity of the resultant ammonium- or organoclay complex.

The effect of a competing solute, trichloroethene, on the sorption of tetrachloromethane to each of the organoclay complexes also was studied. For these cases, equal volumes of trichloroethene and [14 C]tetrachloromethane were added to each centrifuge tube.

The centrifuge tubes were equilibrated in the dark at 20 $^{\circ}$ C. During equilibration, the tubes were rotated con-

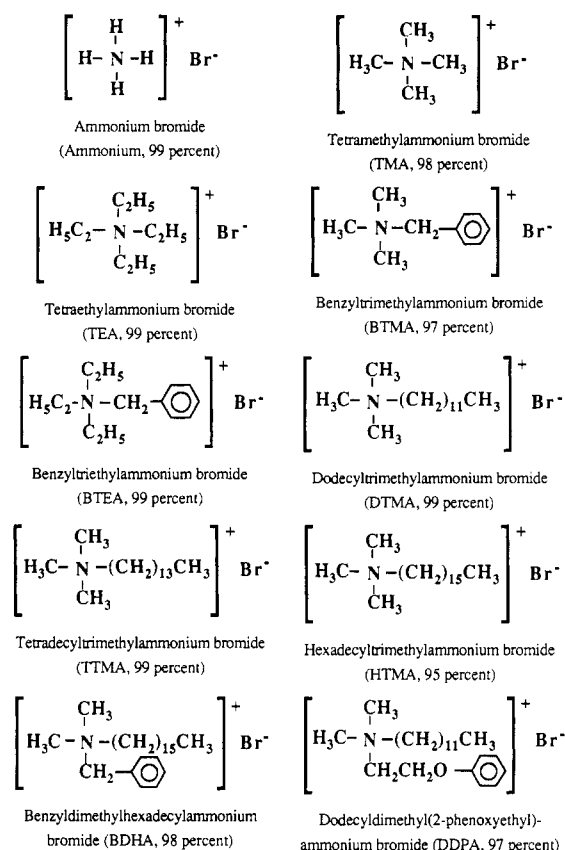


Figure 1. Molecular structures, abbreviations, and percent chemical purities of 10 quaternary ammonium compounds.

tinuously to facilitate mixing. Kinetic experiments conducted over a 30-day period indicated that solute equilibrium between the aqueous and solid phases was reached after approximately 12 h of incubation. Nevertheless, in all experiments a 48-h incubation time was used to ensure equilibrium. After incubation, the tubes were centrifuged for 60 min at 2000g ($g = 9.81 \text{ m/s}^2$). A 1.0-mL aliquot of the supernatant was removed from each centrifuge tube and combined with 10 mL of scintillation cocktail in a 20-mL glass scintillation vial. The radioactivity in the sample was quantified subsequently by use of a Packard Tri-Carb 1900CA liquid scintillation analyzer. All radioactivity measurements were corrected for quench by using an external standard. The equilibrium solute concentration (C_e) in the supernatant from the centrifuge tube was then determined from a standard curve relating disintegrations per minute to aqueous concentration. The equilibrium concentration of the solute on the clay or organoclay complex (C_s) was determined by difference.

To ensure the quality of the data, one "background" and two "blank" samples were prepared and handled in parallel with the previously described centrifuge tubes for each isotherm. A background sample consisted of clay, water, and quaternary ammonium cation combined in a centrifuge tube without a radioisotope. These samples were used to quantify the ambient, or background, radiation, and to ensure that the glassware, clay, water, and cation were not contaminated with radioactivity. A blank sample consisted of water, quaternary ammonium cation, and radioisotope combined in a centrifuge tube without the clay. These samples were used to determine losses of the solute caused by sorption to glassware, biodegradation, volatilization, etc. In general, solute recovery was from 95 to 105%. If solute recovery was less than 90%, the accompanying experimental isotherm was repeated. Because solute recovery generally was high, the isotherm data were not adjusted

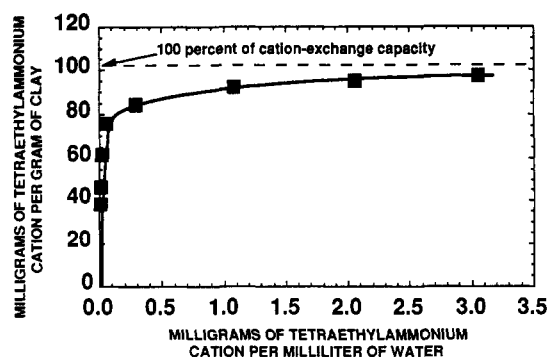


Figure 2. Tetraethylammonium (TEA) uptake by clay from water.

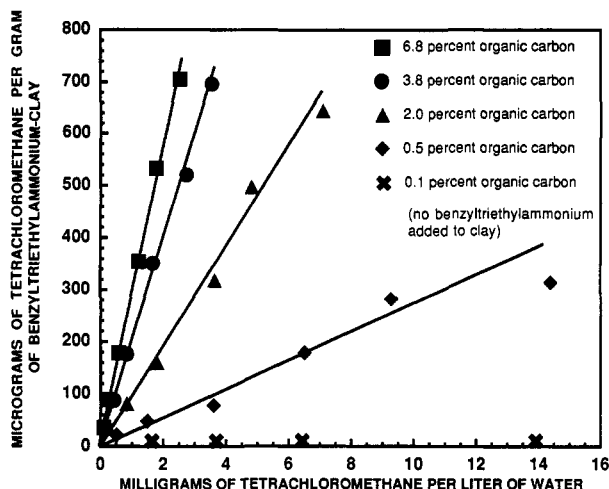


Figure 3. Tetrachloromethane sorption from water to clay (0.1% organic carbon) and benzyltriethylammonium-clay (0.5–6.8% organic carbon).

to account for the percent recovery.

The organic carbon content of the clay and organoclay complexes and the cation-exchange capacity of the clay were quantified by Huffman Laboratories, Golden, CO.

Results

Figure 2 shows the strong retention of the TEA cation by the clay. The independent variable in the graph is the equilibrium aqueous TEA concentration, C_e , and the dependent variable is the equilibrium sorbed TEA concentration, C_s .

The isotherms in Figure 3 shows the effect of one of the organic cations, benzyltriethylammonium bromide (BTEA), on the sorption of tetrachloromethane to clay from water at relatively low aqueous solute concentrations. The lower isotherm in Figure 3 (0.1% organic carbon) quantifies the sorption of tetrachloromethane to clay in the absence of BTEA. The remaining isotherms (0.5–6.8% organic carbon) quantify tetrachloromethane sorption to clays exchanged with increasing amounts of BTEA.

The graphs shown in Figure 4 quantify tetrachloromethane sorption to BTMA-clay (graph A) and HTMA-clay (graph B) in both the presence and absence of a binary solute (trichloroethene). The organic carbon contents of the BTMA-clay and the HTMA-clay are 3.8 and 6.2%, respectively. In contrast to Figure 3, the isotherm data extend to C_e values greater than 50% of the aqueous solubility of tetrachloromethane. Tetrachloromethane sorption from water to BTMA-clay (graph A) is characterized by isotherm nonlinearity, competitive sorption, and relatively strong solute uptake. Tetrachloromethane sorption from water to HTMA-clay (graph B) is charac-

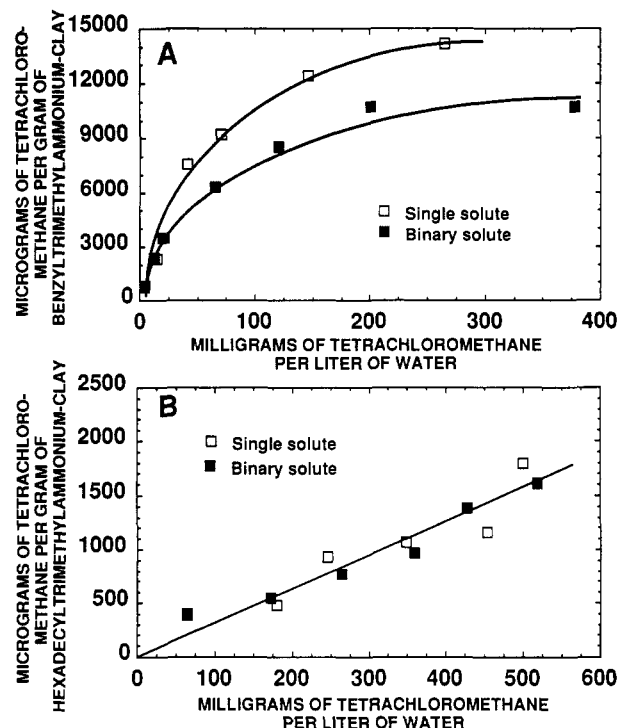


Figure 4. Tetrachloromethane sorption to benzyltriethylammonium-clay with 3.8% organic carbon (A) and hexadecyltrimethylammonium-clay with 6.16% organic carbon (B). The binary solute is trichloroethene.

terized by isotherm linearity, noncompetitive sorption, and relatively weak solute uptake.

With the exception of ammonium-clay, the characteristics of tetrachloromethane sorption to different organoclay complexes are similar to the characteristics of the isotherms of either graph A or graph B in Figure 4. Tetrachloromethane sorption to TMA-, TEA-, BTMA-, and BTEA-clay generally was characterized by isotherm nonlinearity, competitive sorption, and relatively high solute uptake. Tetrachloromethane sorption to DTMA-, TTMA-, HTMA-, BDHA-, and DDPA-clay was characterized by isotherm linearity, noncompetitive sorption, and relatively low solute uptake. Therefore, these two groups of sorption data were separated for analysis. No measurable uptake of tetrachloromethane by ammonium-clay was observed.

The data for all nonlinear single- and binary-solute isotherms have been fit to the linear, Langmuir-type equation given by

$$\frac{C_e}{C_s} = \frac{1}{ba} + \frac{C_e}{a} \quad (1)$$

where C_e and C_s are in millimoles per liter and millimoles per gram, respectively. The values of the parameters a and b are determined by a linear regression of C_e/C_s versus C_e/C_s . The slope and intercept of the plot are $1/a$ and $1/ba$, respectively. The parameters a and b for the single-solute isotherms are given in Table I, along with the organic carbon contents of the sorbents and the regression correlation coefficients. The single- and binary-solute isotherm data were compared statistically by use of a multiple-regression analysis with a dummy variable (14). Results of this analysis indicate that the presence of the binary solute reduces tetrachloromethane sorption to TEA-, BTMA-, and BTEA-clay relative to the single-solute case at a p value of 0.05. No competitive effect was observed for tetrachloromethane sorption to TMA-clay in the presence of trichloroethene.

Table II. Linear Isotherm Parameters, Organic Carbon Contents, and Regression Correlation Coefficients for Tetrachloromethane Sorption to Five Organoclay Sorbents

| | sorbent | | | | |
|------------------------------|-----------|-----------|-----------|-----------|-----------|
| | DTMA-clay | TTMA-clay | HTMA-clay | BDHA-clay | DDPA-clay |
| sorption coeff, K_d , kg/L | 1.36 | 1.51 | 3.12 | 6.56 | 7.64 |
| organic C content, % | 7.56 | 6.97 | 6.16 | 7.13 | 6.57 |
| log K_{oc} | 1.26 | 1.34 | 1.70 | 1.96 | 2.07 |
| corr coeff | 0.94 | 0.81 | 0.95 | 0.94 | 0.94 |

For the remaining linear isotherms, a regression model that presupposes a zero contaminant concentration on the clay in response to a zero aqueous contaminant concentration was used and is given by

$$C_s = K_d C_e \quad (2)$$

where K_d is the sorption (distribution) coefficient. For a set of n data points of the form (C_e^i, C_s^i) , $i = 1, n$, differentiation of the sum of the squares of the residuals (SSR) with respect to K_d is given by

$$\frac{\partial(\text{SSR})}{\partial K_d} = -2 \sum_{i=1}^n C_e^i (C_s^i - K_d C_e^i) \quad (3)$$

The SSR is minimized by setting eq 3 equal to zero. The value of K_d can then be calculated as follows:

$$K_d = \frac{\sum_{i=1}^n C_e^i C_s^i}{\sum_{i=1}^n (C_e^i)^2} \quad (4)$$

The sorption coefficient can be normalized by the organic carbon content of the sorbent with

$$K_{oc} = K_d / f_{oc} \quad (5)$$

where K_{oc} is the organic carbon normalized sorption coefficient and f_{oc} is the organic carbon fraction of the sorbent, which is equal to the percent organic carbon divided by 100. The values of K_d , percent organic carbon, log K_{oc} , and the sample correlation coefficient for the linear tetrachloromethane sorption isotherms are presented in Table II. Analysis of single- and binary-solute isotherm data shows that the isotherm pairs are coincident for each sorbate-sorbent system in Table II at a p value of 0.05.

For the sorbents given in Table I, the mass of added organic cation equals 41% of cation-exchange capacity. For the sorbents in Table II, the mass of added organic cation was chosen to give an organic carbon content of about 7%, which corresponds to cation-exchange capacities of about 30 (DDPA) to 50% (DTMA).

Discussion

The cationic quaternary ammonium compounds shown in Figure 1 are solids at room temperature. With the exception of ammonium bromide, they are classified as surface-active agents (surfactants) because each molecule has a nonpolar hydrocarbon group and an ionic, polar component. The molecular structures of the selected compounds are diverse, with alkyl-chain lengths ranging from 0 to 16 carbon atoms. Four of the selected quaternary ammonium compounds have an aromatic functional group.

Unlike nonionic organic compounds, large organic cations can effectively displace inorganic ions such as Ca^{2+} and Na^+ from the negatively charged mineral surfaces of clay and natural soil by ion exchange (7, 15–22). As a result, organic cations are strongly retained by the clay surface until the concentration of the cation on the clay approaches the cation-exchange capacity. This observation is supported by the isotherm data for TEA in Figure 2. The data in Figure 2 indicate that essentially 100% of the

TEA is retained by the clay when the number of moles of added TEA is less than 90% of the cation-exchange capacity.

Similarly, the organic carbon content data in Tables I and II and Figure 3 agree well with the clay organic carbon content predicted by assuming that 100% of the added quaternary ammonium cation is retained by the clay. The predicted organic carbon contents for TMA-, TEA-, BTMA-, and BTEA-clay (Table I) are 1.6, 3.1, 3.9, and 5.1%, respectively. The predicted organic carbon contents for DTMA-, TTMA-, HTMA-, BDHA-, and DDPA-clay (Table II) are all 7%. Similarly, the predicted organic carbon contents for the BTEA-clay isotherms in Figure 3 are 0.5, 1.8, 3.4, and 6.8%. The agreement between predicted and measured organic carbon contents is indicative of the strong uptake of the quaternary ammonium cations by the clay from water.

The isotherms in Figure 3 were generated at equilibrium aqueous tetrachloromethane concentrations less than 2% of its solubility [800 mg/L at 25 °C (23)]. These trace concentrations are representative of concentrations typically observed in the field. As such, these isotherms illustrate several important characteristics. First, the lowest isotherm (0.1% organic carbon) describes the sorption of tetrachloromethane to clay that has not been amended with quaternary ammonium cations. As evidenced by the data, sorption to the clay is negligible. The hydrated mineral surface of the clay prevents tetrachloromethane adsorption and the low organic carbon content of the clay (0.1%) results in negligible solute uptake by partition. By contrast, the addition of a relatively small amount of BTEA (0.5–6.8% organic carbon) causes a dramatic increase in the uptake of tetrachloromethane relative to the untreated clay. These results encourage continued investigation into the feasibility of the treatment of clay with quaternary ammonium cations for use in slurry walls and as liners at waste disposal sites.

Second, consider the magnitude of uptake and linearity of the isotherms in Figure 3. If tetrachloromethane uptake by BTEA-clay was the result of a partition interaction between water and an organophilic medium created by the organic cation at the clay surface, the resulting organic carbon normalized partition coefficient (K_{oc}) for each isotherm in Figure 3 would be expected to be of a magnitude comparable to the octanol-water partition coefficient (K_{ow}) of tetrachloromethane. However, the values of K_{oc} for the isotherms of Figure 3 range from 5000 to 6000, whereas the K_{ow} for tetrachloromethane is 440 (23). This discrepancy suggests that tetrachloromethane sorption to the BTEA-clay is caused primarily by adsorption rather than by partition alone. For partition equilibria, the isotherm should be linear over a wide range of C_e values relative to the aqueous solubility of the solute. Although the isotherms in Figure 3 are highly linear, the C_e values are less than 2% of the aqueous solubility of tetrachloromethane. This linearity may be attributed to a Henry's law type effect at dilute concentration. Therefore, experimental extension of the isotherm for BTEA-clay to C_e values greater than 50% of the aqueous solubility of

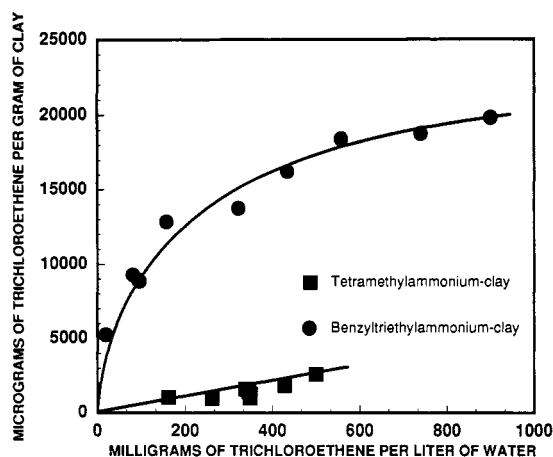


Figure 5. Trichloroethene sorption to benzytriethylammonium-clay and tetramethylammonium-clay.

tetrachloromethane was conducted, and a distinctly non-linear isotherm was observed (data not shown).

Considering the data in Figure 4 and Tables I and II, it is apparent that the molecular structure of the quaternary ammonium cation affects both the magnitude and the mechanism of tetrachloromethane sorption to the organoclay complex. Tetrachloromethane sorption to TEA-, BTMA-, and BTEA-clay (Table I) is characterized by distinctly nonlinear isotherms, relatively strong solute uptake, and a competitive effect. This behavior is typical of an adsorption process wherein the nonionic solute is attracted by London (van der Waals) forces to an organic surface formed by the quaternary ammonium cations. The cations are retained on the mineral surface by electrostatic forces.

Sorption of tetrachloromethane to TMA-clay also was characterized by isotherm nonlinearity and relatively strong solute uptake. No competitive sorption effect was observed, however. In an attempt to explain this result, sorption of the competitive solute, trichloroethene, to TMA-, TEA-, BTMA-, and BTEA-clay was quantified. Some of these data are shown in Figure 5, which compares the sorption of trichloroethene to TMA- and BTEA-clay. For both cases, the mass of retained organic cation is 41% of cation-exchange capacity. These results indicate that trichloroethene uptake by TMA-clay is very weak relative to uptake by BTEA-clay. Trichloroethene uptake by TEA- and BTMA-clay is similar to the uptake by BTEA-clay. Therefore, tetrachloromethane sorption to TMA-clay does not exhibit a strong competitive effect. The reason for the weak uptake of trichloroethene by TMA-clay is not exactly known. As the uptake of aromatic organic solutes by TMA-clay has been shown to be size and shape selective (12), it is possible that the larger molecular dimension of trichloroethene relative to tetrachloromethane reduces solute association with the small methyl groups in the $N(CH_3)_4^+$ tetrahedron.

In contrast to the data discussed above, tetrachloromethane sorption to DTMA-, TTMA-, HTMA-, BDHA-, and DDPA-clay (Table II) is characterized by linear isotherms, relatively weak solute uptake, and noncompetitive sorption. In addition, it has been shown previously that the sorption of seven nonionic solutes to natural soil treated with HTMA cations decreases with increasing solute solubility (24). This behavior is typical of a partition process, wherein the nonionic solute distributes itself between an aqueous and organic phase in proportion to its solubility in the two phases. In addition, the $\log K_{oc}$ values given in Table II (1.26–2.07) are less than the $\log K_{ow}$ value of 2.64 for tetrachloromethane.

The difference in sorption mechanism between the two groups of organoclay complexes appears to be related to the alkyl-chain length rather than to the presence of an aryl functional group. All the organic cations that led to contaminant adsorption effects (Table I) have short alkyl functional groups (two carbon atoms or less), whereas the organic cations that caused a partition-like contaminant uptake (Table II) have at least one large alkyl functional group (12 carbon atoms or more). Therefore, the presence of one or more large alkyl groups appears to prevent the organic cations from forming a modified clay surface capable of strong adsorption. Presumably, such large chains cannot be effectively "anchored" to the clay surface (13) because their lack of polarity and charge prevents a strong interaction with the polar, interlamellar mineral surface. Conglomeration of these long and flexible alkyl chains produces an organic medium for solute partition (11). This explanation is supported by the data of Table II, which show that as the length of the cations' hydrocarbon chain increases from 12 to 16 carbon atoms (DTMA to HTMA), the sorption coefficient increases from 1.36 to 3.12 kg/L. Smaller and more rigid functional groups (e.g., methyl, ethyl, benzyl) may be expected to be tightly anchored to the clay surface. The size and rigidity of these groups prevent them from forming an effective partition medium. The modified clay surface reduces the hydrophilicity of the mineral and thereby allows the nonionic solute to compete effectively with water for adsorption.

TMA- and BTMA-clay have distinctly higher capacities for tetrachloromethane than TEA- and BTEA-clay, indicating that, in the absence of a large alkyl group, the substitution of ethyl for methyl functional groups reduces the effectiveness of the organic cation to act as an adsorbent surface at the clay-water interface. The benzyl group appears to have a similar effect as the methyl group in this regard, as evidenced by the similar sorptive capacities of the TMA-clay and BTMA-clay. The result suggests that an increase in chain length reduces the rigidity of the organic surface and consequently weakens adsorption of tetrachloromethane. While the partition effect should increase with alkyl-chain length, the ethyl group appears to be too small to form an effective partition medium.

It is also important to note the difference in the sorption of tetrachloromethane to ammonium-clay versus TMA-clay. No measurable uptake of tetrachloromethane by the ammonium-clay was observed, but tetrachloromethane was strongly adsorbed by the TMA-clay. Much like Ca^{2+} or Na^+ ions, a dipole is induced in the ammonium ion from the electric field created by the negative charge at the clay surface. As a result, the ammonium ion is strongly hydrated and significant sorption of the nonionic solute is prohibited because of the hydration effect and the absence of an organic moiety in the cation.

The data in Table II also indicate that substitution of an aromatic functional group (BDHA) or an ethylene oxide aromatic functional group (DDPA) for a methyl group in organoclays containing a large alkyl group results in a further increase in the sorption coefficient to values of 6.56 and 7.64 ($\log K_{oc}$ equal to 1.96 and 2.07), respectively, indicating that these functional groups also increase the solvency of the organic medium for tetrachloromethane. The $\log K_{oc}$ value for the sorption of tetrachloromethane to soil organic matter is estimated to be 1.9 (2), indicating that DTMA, TTMA, and HTMA are slightly less effective sorbent media than soil organic matter when applied to the clay in an amount equal to 7% organic carbon. However, application of BDHA and DDPA to the clay (also at 7% organic carbon) produced sorbents with an organic

phase that shows a similar partition effect as natural soil organic matter with regard to the sorption of tetrachloromethane.

The log K_{oc} value for the sorption of tetrachloromethane to the HTMA-clay used in this study compares well with the value of 1.7 for the sorption of trichloroethene to HTMA-clay (about 7% organic carbon) reported by Boyd et al. (11). This is not surprising given the similar water solubilities of these two solutes. The work of Boyd et al. (11) also indicates that the K_{oc} values of benzene and trichloroethene are a function of the amount of HTMA on the clay. At organic carbon contents greater than 13%, the K_{oc} values are comparable to heptane-water partition coefficients, which are 5–10 times greater than the K_{oc} values for soil organic matter. These differences may be attributed to the density of alkyl chains in the organic medium formed by the different amounts of HTMA incorporated into the interlamellar spaces of the clay. Thus, the closer correspondence of the K_{oc} values from Table II with K_{oc} data for natural soil organic matter can be better explained by the size and alkyl-chain density of the organic medium formed in organoclays rather than by the composition and polarity of the organic medium in comparison with soil organic matter.

Finally, these results can be related to natural soil-water systems. The organic matter fraction of natural soil has been correlated repeatedly to the sorption of nonionic organic contaminants from water (25–30), and the sorption process has been attributed to solute partition between water and the soil organic matter (2–9, 31). The data for many organoclay systems comply with these observations. Natural soil organic matter is known to be a complex mixture of macromolecular organic substances of different sizes that generally are classified as humic and fulvic acids and humin (32). The relatively diverse macromolecules present in natural organic matter lead to the formation of a highly amorphous organic substance, which acts as a partition medium for the sorption of nonionic organic solutes.

Acknowledgments

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Registry No. Tetrachloromethane, 56-23-5; trichloroethane, 79-01-6.

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