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Organic Cosolvent Effects on Sorption Kinetics of Hydrophobic Organic Chemicals by Organoclays

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Data obtained from batch kinetics sorption experiments for naphthalene and diuron using two organoclays [trimethylphenylammonium (TPMA)-clay and benzyldimethyltetradecylammonium (BDTDA)-clay] in aqueous and methanol–water systems were analyzed with a first-order one-site mass transfer model (OSMTM) to obtain kinetic parameters. The mass transfer coefficient (ϵ) exponentially decreased as the sorption coefficient (K_p) increased, and a log-linear increase in ϵ was observed with an increase in the volume fraction of cosolvent (f^c) in the system. Regression equations relating ϵ to f^c , measured in mixed solvents, could be extrapolated to $f^c = 0$ to obtain the coefficients in aqueous systems. The organic cosolvent effects on the sorption kinetics behavior of naphthalene and diuron depended on the sorbate structure, the cosolvent fraction, and the arrangement of the exchanged quaternary alkylammonium ions in montmorillonite-clay interlayers.

Introduction

Organoclays can be produced by replacing exchangeable inorganic cations with quaternary alkylammonium cations. This treatment reduces the hydration of the clay, increases the interlamellar spacing, and simultaneously decreases the exposed aluminosilicate mineral surface area (1–6). As the inorganic cations are progressively replaced by the organic cations, the surface properties of a clay may change considerably from highly hydrophilic to increasingly hydrophobic. This new hydrophobic phase formed on the clay is derived mainly from the alkyl hydrocarbon moieties of the alkylammonium cations.

Due to their high sorption capacity, organoclays have been proposed as (a) components of bentonite slurry walls and landfill clay liners because they may act both as sealants and as effective sorbents of dissolved organic contaminants and (b) sorbents in wastewater treatment processes (5–7). For organoclays to be used effectively in these operations, an understanding of the sorption kinetics of hydrophobic organic chemicals (HOCs) on organoclays is essential.

Most of the previous research on sorption of organic solutes by organoclays has focused on sorption equilibrium in aqueous systems (3, 5–8). The presence of water-miscible

organic solvents at many waste disposal and industrial sites warrants investigating the sorptive behavior of organoclays in both cosolvent and aqueous systems, given their potential use in containment barriers. The investigation of organic cosolvents effects on sorption of HOCs to date has focused mainly on natural soils and sediments (9–12). These studies showed that sorption of HOCs was inversely related to their solubility in solvent mixtures. This relationship is described by the log-linear cosolvency model, for the sorption and transport of HOCs in soils in several binary solvent mixtures (9–15). Similar results were reported by Nzengung (16) and Nzengung et al. (17) for the equilibrium sorption of HOCs by several organoclays in binary solvents. The influence of organic cosolvents on sorption kinetics has also been investigated for many HOCs during transport in soil columns. It was shown that the desorption rate coefficient (k_d) estimated from the two-site kinetics model (TSKM) increased with increasing volume fraction of cosolvent (13, 18, 19). An inverse linear relationship between the logarithms of the value of (k_d) and the equilibrium sorption coefficient (K_p) was established (18–21). Currently no research is reported in the literature on sorption kinetics of HOCs on organoclays in both aqueous and mixed-solvent systems.

The purpose of this paper is therefore to investigate the impact of organic cosolvents on the rate of sorption of two probe HOCs (naphthalene and diuron) by organoclays and to test the applicability of the log-linear cosolvency model in predicting sorption kinetics parameters. Comparisons are made with soil systems for which similar data are available.

Experimental Section

Materials. Naphthalene and diuron used as probe HOCs were obtained as reagent-grade chemicals from Fisher Scientific (Pittsburgh, PA). Naphthalene was selected because it is an ideal hydrophobic sorbate without polar functional groups. Diuron is a HOC with polar functional groups, but its hydrophobic surface area (HSA) is similar to that of naphthalene (9, 22). Naphthalene and diuron also represent two classes of chemicals present in industrial and agricultural wastewater, respectively. In addition, a large volume of sorption data in aqueous and mixed-solvent systems is available for these compounds (9, 11, 12, 15, 17). Some of the important properties of these chemicals and their structures that were reported by Nzengung et al. (17) are presented in Table 1. The source and purity of radiolabeled naphthalene and diuron, the scintillation liquid, and methanol used in this study were also reported by Nzengung et al. (17). The Na-montmorillonite was separated from a reference clay, SWy-1, obtained from the Source Clay Repository of the Clay Minerals Society (Columbia, MO). Reagent-grade trimethylphenylammonium chloride (TPMA) was obtained from Fisher Scientific, and benzyldimethyltetradecylammonium chloride dihydrate (BDTDA) was purchased from Aldrich Chemical Co. (Milwaukee, WI). TPMA- and BDTDA-clays were chosen as sorbents to represent organoclays having simple organic ions and complex (long-chained) organic ions, respectively.

Preparation of Organoclays and X-ray Diffraction Analysis. The organoclays were prepared as described in detail by Nzengung (16). These procedures were also summarized by Nzengung et al. (17). Na-montmorillonite was converted to Ca-montmorillonite by ion exchange. The product was washed thoroughly with distilled–deionized water, quick frozen, and freeze-dried. The Ca-clay was converted to organoclay by ion exchange with aqueous solutions of the two quaternary ammonium salts. The organic carbon content of the organoclays was determined by measuring the carbon

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TABLE 1. Important Solute and Sorbent Properties^a and Some Experimental Results

property	TMPA-clay	BDTDA-clay
total OC (%)	7.4	17.7
CEC % occupied	76	87
basal spacing (Å)	14.5	17.7
net separation of clay layers (Å)	5.1	8.3
max swelling (Å)	0.7	none
layers of surfactant	1	2
diuron [$\Phi = \alpha\beta\sigma$]	10.1 (8.4–12)	5.60 (5.0–6.2)
α^c	1.2 (1.0–1.4)	0.66 (0.59–0.73)
σ^c	8.44	8.44
naphthalene [$\Phi = \alpha\beta\sigma$]	8.0 (7.2–8.8)	8.0 (7.2–8.8)
α^c	0.90 (0.8–1.0)	0.90 (0.8–1.0)
σ^c	8.95	8.95

^a From Nzengung et al. (17); numbers in paratheses are 95% confidence intervals.

dioxide produced from combustion in an oxygen atmosphere with a microcoulometer. The organic carbon content is presented in Table 1.

Oriented aggregates of the natural clay and the organoclays were prepared by allowing aqueous or 95% ethanol suspensions of the clay-sized material (<2 μm) to dry on glass slides at room temperature and humidity. Non-oriented aggregates, treated for 24 h in methanol–water mixtures, were analyzed while wet to determine the degree of swelling in cosolvents. The basal spacing (d_{001}) determined by X-ray diffraction and degree of swelling are presented in Table 1.

Batch Sorption Kinetics Experiments. Sorption kinetics experiments were conducted using a batch sorption method (20). The volume fractions of methanol used ranged from 0 to 0.5. For each sorbent–sorbate combination, the experiments were conducted in varying volume of solution to mass of clay ratio to optimize the accuracy of determination of HOC in solution (9, 12, 17). For each set of batch experiments, the appropriate amount of organoclay was weighed into 50-mL Pyrex glass centrifuge tubes. Then the tubes were filled with the appropriate solution and capped with a Teflon–silicone septum. An initial concentration of 0.6 mg/L was used for naphthalene, and 10 mg/L was used for diuron experiments. All solutions were spiked with the corresponding ¹⁴C-labeled compound to give final radiation activity in each tube of 0.2 nCi/mL. The centrifuge tubes were continuously rotated on a shaker at ambient temperature (25 °C). At selected time intervals, pairs of tubes were centrifuged (at 1700g for 30 min). The ¹⁴C activity of the supernatant solution was assayed by liquid scintillation counting. For quality control, several “background” and “blank” samples were prepared and handled in parallel with the experimental centrifuge tubes.

Model Development and Data Analysis. Many models have been developed to describe sorption kinetics of HOCs in aquifer materials, soils, and sediments (20, 21, 23–27). In this paper, we present solutions for the one-site mass transfer model (OSMTM) for sorption kinetics of HOCs on organoclays (in batch systems) for both aqueous and mixed-solvent systems. The model described here is similar to the one-site kinetic approach proposed independently by Selim et al. (25) and Cameron and Klute (26). The OSMTM is a model in which the adsorption rate is a first-order function of the concentration difference between the solution and sorbed phases. All sorption sites are assumed to be kinetically controlled. Adsorption and desorption in the batch reactor (according to the OSMTM) are conceptualized as follows:

$$K_p C \stackrel{\epsilon}{\rightleftharpoons} S \quad (1)$$

where ϵ is the mass transfer coefficient (h^{-1}) and K_p is the

partition equilibrium coefficient (mL/g). The mass transfer coefficient governs the movement of solute into and out of the sorption region of the sorbent. The coefficient ϵ is related to the diffusional and characteristic length properties of the sorbent, the diffusivity of the sorbate, and the effect of sorption on diffusivity (13).

A material balance expressions for the rate of sorbate sorption in a batch reactor is given for the OSMTM as

$$\frac{V}{M} \frac{dC}{dt} = \epsilon(S - K_p C) \quad (2)$$

where M is the mass of solid phase in the batch reactor (g), V is the volume of the solution phase (mL), and t is time (h). At equilibrium

$$S_e = K_p C_e \quad (3)$$

The total mass of sorbate in the batch reactor (M_t) is given by

$$M_t = MS + VC = VC_0 \quad (4)$$

where C_0 is the initial solution concentration (mg/L). Then, eq 2 can be written in terms of solution concentration as

$$\frac{dC}{dt} = \epsilon \left[C_0 - \left(1 + \frac{K_p M}{V} \right) C \right] \quad (5)$$

which integrates to

$$C_{(t)} = C_e + [C_0 - C_e] \exp \left[- \left(\frac{\epsilon}{\psi} \right) t \right] \quad (6a)$$

where

$$C_e = \frac{C_0}{\left(1 + \frac{K_p M}{V} \right)} = \frac{M_t}{(V + MK_p)} \quad (6b)$$

$$C_0 = \frac{M_t}{V} \quad (6c)$$

$$\psi = \frac{C_e}{C_0} = \frac{1}{\left(1 + \frac{K_p M}{V} \right)} \quad (6d)$$

where C_e is the solution-phase concentration at equilibrium (mg/mL) and S_e is the sorbed-phase concentration at equilibrium (mg/g). If $C_{(t)}$ is determined with time (t) and K_p is known, the unknown parameter for OSMTM is the mass transfer coefficient ϵ (eq 6a).

For each solute, the parameter measured in these experiments was the concentration in solution [$C_{(t)}$] at a given time [t] relative to the initial amount present (C_0) at time $t = 0$. The relative solution concentrations $C_{(t)}/C_0$ were plotted against appropriate sorption times. Estimation of kinetic parameters using the OSMTM was accomplished by coupling eq 6a with a nonlinear least-squares optimization program (28). One parameter (ϵ) was optimized while the values of the linear sorption equilibrium coefficients (K_p) were fixed. The K_p values (Table 2) were independently determined from the isotherm data of Nzengung (16) within the range of the equilibrium solution concentration of each kinetic experiment.

The ϵ – K_p Relationship. The log–log relationship between the desorption rate coefficient k_2 calculated using the two-site kinetics model (TSKM) and the sorption coefficient K_p has been reported by Brusseau et al. (18, 19). They also showed that [$k_2 = \epsilon/(1 - F)$], where F is the fraction of sorbent experiencing instantaneous equilibrium. Note that for the

TABLE 2. Sorption Kinetics and Equilibria Parameters

sorbate-sorbent	f^c	K_p^a (mL/g)	ϵ (1/h)	time to attain sorption equilibrium (h)
Naph-TMPA	0	7505	0.11 ± 0.01	4
	0.1	2926	0.15 ± 0.01	2
	0.3	447	0.47 ± 0.03	2
	0.5	99	0.91 ± 0.04	1
diur-TMPA	0	393	0.70 ± 0.07	4
	0.1	75	1.01 ± 0.23	2
	0.3	18	1.21 ± 0.36	0.5
	0.5	37	1.02 ± 0.11	4
Naph-BDTDA	0	3165	0.24 ± 0.01	12
	0.1	2147	0.40 ± 0.02	10
	0.3	203	0.55 ± 0.03	6
	0.5	41	0.95 ± 0.20	4
Diur-BDTDA	0	1415	0.27 ± 0.04	22
	0.1	609	0.38 ± 0.05	14
	0.3	227	0.61 ± 0.07	4
	0.5	41	0.95 ± 0.20	4

^a Calculated from Nzengung (16) for sorption equilibria data corresponding to solution equilibrium concentration for kinetics experiments; \pm SD, standard deviation.

OSMTM, $F = 0$. Assuming that a log-log relationship also exists between the mass transfer coefficient (ϵ) calculated from the OSMTM and K_p , an empirical relationship between ϵ and K_p can be used (18):

$$\ln(\epsilon) = B - A \ln(K_p) \quad (7)$$

where A and B are regression coefficients. Equation 7 has been shown to be valid for sorption kinetics of HOCs on various sorbents during leaching experiments carried out in aqueous and mixed-solvent systems (18, 19).

The Log-Linear Cosolvency Model and ϵ - f^c Relationship. The sorption coefficient (K_p) for the sorption of HOCs on soil materials in binary solvents has been related to the volume fraction of cosolvent using the following log-linear cosolvency model (9, 10):

$$\ln(K_p^m) = \ln(K_p^w) - \Phi f^c \quad (8a)$$

$$\Phi = \beta^c \alpha^c \sigma^c \quad (8b)$$

$$\sigma^c = \frac{\Delta\gamma^c \text{HSA}}{kT} \quad (8c)$$

where β^c is the constant for solvent-water interaction (we assumed $\beta^c = 1$ for water-methanol interaction), σ^c is the empirical constant for solvent-sorbate interaction (cosolvency power), α^c is the empirical constant for solvent-sorbent interaction, HSA is the hydrocarbonaceous surface area of solute (\AA^2), $\Delta\gamma^c$ is the difference in interfacial free energy density ($\text{erg}/\text{\AA}^2$) between HSA and solvents, k is the Boltzmann constant (erg/K), T is the temperature (K), and subscripts m and w refer to mixed-solvent and aqueous systems, respectively.

Equations 7 and 8a can be used to derive the relationship between ϵ and f^c :

$$\ln(\epsilon^m) = \ln(\epsilon^w) + A\Phi f^c \quad (9)$$

where A is the slope of $\log[\epsilon - K_p]$ functionality. From eq 9, ϵ^m should increase with an increase in f^c . The slope of eq 9 can be used to estimate the value of Φ and thus other parameters included in Φ . The validity of the relationships in eqs 7 and 9 will be tested and discussed using sorption kinetic data obtained from this study.

Results

OSMTM Simulations. In Figure 1, the relative concentration

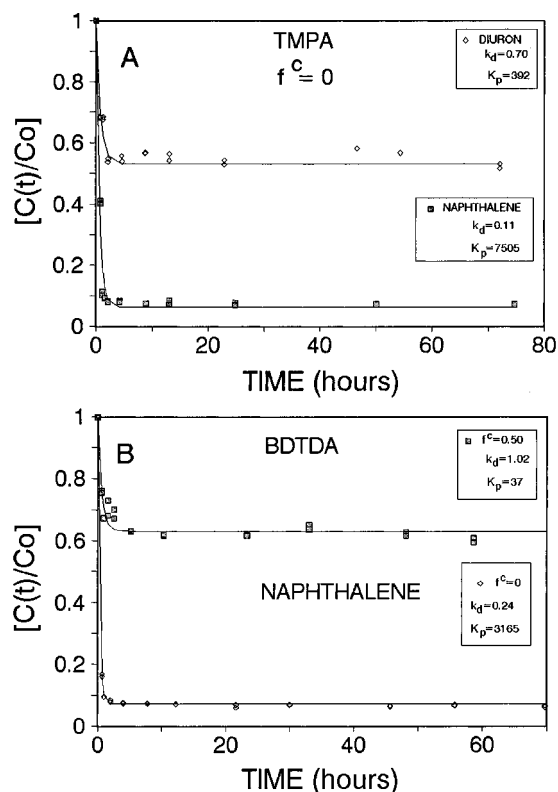


FIGURE 1. Experimental data points (symbols) and one-site mass transfer model (OSMTM) simulations (solid lines) for sorption of naphthalene and diuron by TMPA- and BDTDA-montmorillonite. (A) Sorption approach to equilibrium in aqueous solution using TMPA-clay. (B) Sorption approach to equilibrium in 0 and 50% volume fraction of methanol in water using BDTDA-clay. Model parameters (K_p , K_m , and ϵ) are included.

in solution $[C_0/C_0]$ of naphthalene and diuron during sorption on TMPA-clay and BDTDA-clay are plotted as a function of time. Only representative plots are presented in Figure 1, but the rest of the data are presented in Table 2. The approach to sorption equilibrium for naphthalene and diuron in both organoclays was generally rapid. The OSMTM simulations provided a good description of all the experimental data obtained from aqueous and mixed solvent systems.

The time to attain sorption equilibrium decreased with increasing f^c in all sorbate-organoclay systems. The equilibrium time refers to the first time when there was no additional change in solution concentration. For example, the sorption of naphthalene on BDTDA-clay equilibrium was attained in 12 h at $f^c = 0$ and in 4 h at $f^c = 0.5$ (Table 2). For diuron sorption by BDTDA-clay, equilibrium was reached in about 22 h at $f^c = 0$ and in 4 h at $f^c = 0.5$ (Table 2). Meanwhile, equilibrium was reached in about 4 h in all experiments with TMPA-clay at $f^c = 0$. Sorption of diuron by TMPA-clay at $f^c = 0.5$ was so rapid that a fitted ϵ value could not be obtained from the model.

Relationship between ϵ and K_p . The relationship between the mass transfer coefficient (ϵ) and the equilibrium sorption coefficient (K_p) for the data presented in Table 2 is plotted in Figure 2 according to eq 7. For the two probe compounds and two organoclays studied, ϵ decreased exponentially with increasing K_p . The log-log relationship between ϵ and K_p for aqueous data and cosolvent data separately revealed no significant difference between the slope of the lines or their intercepts. This implies that the $[\epsilon - K_p]$ relationship developed for mixed-solvent systems can be used for kinetic data obtained in aqueous systems. All data are therefore fitted to one line in Figure 2, with a slope of -0.38 .

The ϵ - f^c Relationship. The impact of cosolvent on sorption kinetics was evaluated by regressing the logarithm

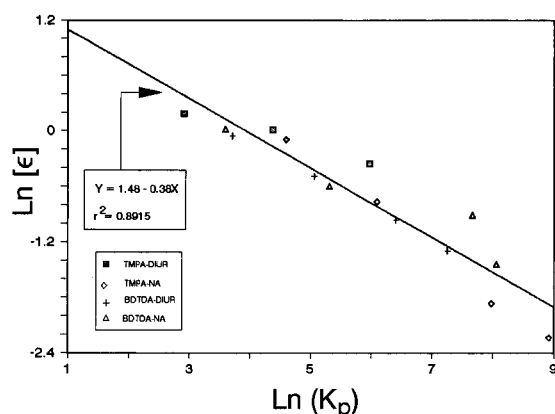


FIGURE 2. Log-log relationship between mass transfer coefficient and equilibrium sorption constant (K_p) of naphthalene and diuron by two organoclays in aqueous and mixed solvents.

of the mass transfer coefficient ϵ with respect to f^c (Figure 3). The log-linear relationships obtained from the regression analysis indicate that eq 9 provides a good description of experimental data, except for the sorption of diuron by TMPA-clay ($r^2 = 0.86$) mainly due to the fact that only three pairs of data were regressed (Figure 3C). For each sorbate-sorbent combination, ϵ values increased exponentially as f^c was increased in the system.

The slope of each line in Figure 3 consists of the product $[A\Phi]$. Since the value of A is known from the $\epsilon-K_p$ relationship for each HOC-organoclay combination, the slopes were used to calculate the values of Φ (Table 3). The calculated $[\Phi]$ values using our kinetics data are within or close to the 95% confidence interval of the $[\Phi]$ values reported for sorption equilibrium data [(17) and Table 3]. The major difference is between Φ values of naphthalene and diuron during sorption on BDTDA-clay.

The $\ln(\epsilon) - f^c$ regression lines obtained from cosolvent kinetic data only were extrapolated to $f^c = 0$ to calculate values in aqueous systems. The calculated and measured parameters compare reasonably well (Table 3).

Discussion

The time to attain sorption equilibrium (Table 2) for naphthalene and diuron was shorter in TMPA-clay (with a short alkyl chain) than in BDTDA-clay (with a long alkyl chain). Also the value of the mass transfer coefficient for both compounds obtained in TMPA-clay was larger than that from BDTDA-clay at each f^c . This implies that differences in the mode of interaction of diuron and naphthalene with the two organoclays exist.

The difference in sorption kinetics behavior of naphthalene and diuron in the two organoclays may be attributed in part to the different arrangement of the quaternary ammonium ions in the clay interlayer and to the observed organoclay-organic carbon swelling of TMPA-clay in methanol. The measured basal spacing (d_{001}) values of 14.5 and 17.7 Å were obtained for TMPA- and BDTDA-montmorillonites, respectively (Table 1). These d_{001} values include the thickness of the 2:1 aluminosilicate sheet (9.4 Å), which was subtracted to obtain the net separation of clay flakes. A net interlayer separation of 5.1 and 8.3 Å was obtained for TMPA- and BDTDA-clay, respectively. The width of an alkyl chain is about 4 Å. These dimensions are consistent with an arrangement in which the shorter chained TMPA ions served as pillars that hold the clay layers apart. However, the complex BDTDA ions appear to be sorbed in two parallel layers with their long chains between the clay sheets. Jaynes and Boyd (7) and Boyd et al. (5, 6) have suggested that the triangular bases of TMPA ions could be aligned parallel to the clay sheets, and presumably the bases adhere alternately to the upper and

lower clay layers. The larger d_{001} values of BDTDA-montmorillonite correspond to the formation of bilayers and paraffin complexes in which the long-chained alkyl groups are in direct contact with each other.

The interlayer diffusion or permeation of naphthalene molecules (width = 5.6 Å) that are flat-shaped and smaller than the interlayer spacing of TMPA-clay is expected to be faster than in BDTDA-clay, because the TMPA ions expanded the clay layers. This explains the short time to reach sorption equilibrium for naphthalene in TMPA-clay. However, for diuron sorption on TMPA-clay, the very short time to attain equilibrium is attributed to the exclusion of the bulky diuron (width = 6.6 Å) molecules from the interlayers of TMPA-clay. Due to the large size of diuron molecules relative to the net organoclay interlayer separation, diuron molecules were excluded from the interlayers causing it to sorb much faster than naphthalene molecules in TMPA-clay. This is also evident from comparing the mass transfer coefficients for both chemicals in TMPA-clay, where higher mass transfer coefficients are obtained for the excluded diuron (Table 2). We believe that diuron was mostly adsorbed on TMPA's phenyl moieties exchanged at the clay edges. About 20% of the CEC of Na-montmorillonite in distilled water is located at the edges, and 80% is located in the clay interlayers (29, 30). For the TMPA-clay, the smaller K_p value for diuron (about 19 times less at $f^c = 0$) as compared to that of naphthalene (Table 2) further supports this argument.

Although we have argued that diuron was excluded from TMPA-clay as compared to naphthalene, this exclusion simply reduced the interlayer surface area and organic carbon available for sorption of diuron and did not affect the exponential decrease in K_p values with an increase in f^c as predicted by the log-linear cosolvency model (eq 8a). Actually this is analogous to using sorbents containing different organic carbon contents as was reported for the sorption of diuron on various soils in methanol-water systems (9). In that study, all data collected from the different soils were used to calculate a single Φ value for diuron.

The arrangement of the alkyl chains of BDTDA ions in two parallel chains between the clay layers impeded sorption of naphthalene and diuron in the organoclay interlayers. This also implies that sorption of both naphthalene and diuron by BDTDA-clay was mainly due to the approximately 20% of the organic cation exchanged at the edges of the clay. This exclusion effect is again demonstrated by the smaller K_p value (3165) for naphthalene sorption on BDTDA-clay as compared to sorption on TMPA-clay ($K_p = 7505$). Note that TMPA-clay contains less organic carbon than BDTDA-clay (Table 1). Similarly, the K_p values for diuron that are excluded from the interlayers of both organoclays are proportional to the amount of organic carbon estimated to be residing on the clay edges (Tables 1 and 2). Using aqueous K_p values reported in Table 2, the decreasing order of sorption was TMPA-Naph > BDTDA-Naph > BDTDA-DIUR > TMPA-DIUR.

The sorption coefficients determined for naphthalene and diuron sorption by organoclays (17) are much higher than those reported in the literature for both HOCs in soils (9, 12). However, the time to achieve sorption equilibrium is much longer in soils (weeks to months) than in organoclays. As such, sorption kinetics of HOCs in soils is described by the two-site kinetic model (18, 20), while the OSMTM describes HOC sorption by organoclays. The differences in sorption kinetics for these two probe compounds in soils and organoclays is attributed to (1) the relatively heterogeneous surfaces of soils, (2) the aggregate nature of soils, (3) the complex (amorphous and condensed) soil organic matter that can induce various interactions with HOCs (33), and (4) the arrangement of the alkyl ammonium cations in interlayers of montmorillonite that can produce a relatively more amorphous organic carbon.

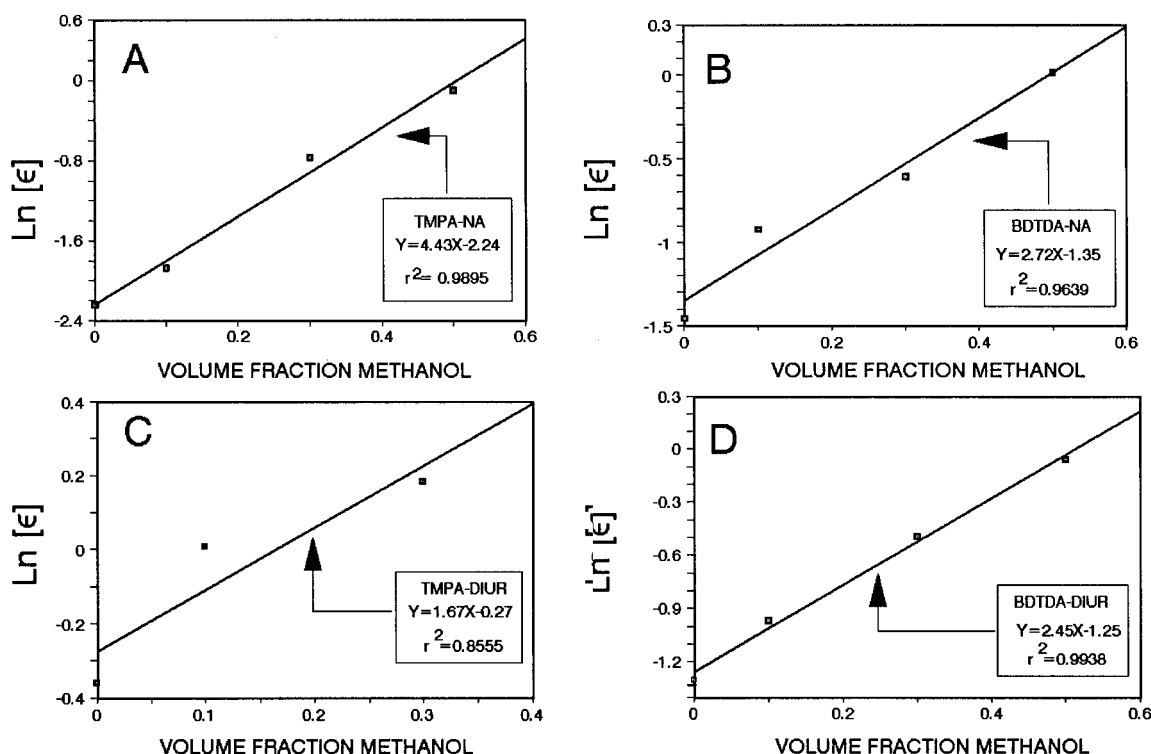


FIGURE 3. Log-linear relationship between mass transfer coefficient and volume fraction of cosolvent (f^c): Naphthalene-TMPA-clay (A), naphthalene-BDTDA-clay (B), diuron-TMPA-clay (C), and diuron-BDTDA-clay (D).

TABLE 3. Calculated ($\Phi = \alpha\sigma$) from Kinetics and Equilibrium Sorption Data and Calculated ϵ^w from Aqueous Cosolvent Data^a

clay-chemical	$[\Phi = \alpha\sigma]$ equilibria	$[\Phi = \alpha\sigma]$ kinetics	$[\epsilon - K_p]$ (A)	r^2	cosolvent extrapolated $[\epsilon^w$ (1/h)]	aq measured $[\epsilon^w$ (1/h)]
Naph-TMPA	8.0 (7.2–8.8)	8.67	0.51	0.99	0.11	0.11
Naph-BDTDA	8.0 (7.2–8.8)	9.74	0.28	0.91	0.30	0.24
Diuron-TMPA	10.1 (8.4–12)	9.67	0.17	0.93	0.91	0.70
Diuron-BDTDA	5.6 (5.0–6.2)	6.92	0.35	0.98	0.31	0.27

^a Numbers in parentheses are 95% confidence intervals.

The exponential decrease in the values of ϵ with an increase in K_p values observed in this study (Figure 1) is similar in form to that observed between k_2 and K_p for the sorption of several HOCs on soils and aquifer materials in aqueous and methanol-water systems (18, 20). Note that k_2 was obtained from the two-site kinetic model.

Effect of Solvent, Sorbate, and Organoclay Interactions on Sorption Kinetics. The mass transfer coefficient increased exponentially with increase in methanol in the system (Table 2). The increase in ϵ values with increase in cosolvent is similar to that observed for sorption kinetics of HOCs in soils and was attributed to an increase in the diffusive mass transfer in soil organic matter (13, 18). For organoclays, an increase in cosolvent fraction in the system changed the conformation of the alkyl hydrocarbon moieties of the organic cations sorbed on the clay (17).

The $\ln(\epsilon)$ vs f^c regression lines obtained for cosolvent kinetics data were used to calculate ϵ values in aqueous systems. The measured and calculated data compare reasonably (Table 3). The rate of increase in ϵ values with an increase in the volume fraction of methanol in sorption of naphthalene and diuron on BDTDA-clay was 2.7 and 2.5, respectively. However this rate was significantly different (4.4 for naphthalene and 1.7 for diuron) for TMPA-clay (Figure 3). The high rate of change of ϵ with increasing methanol content (Figure 3a) is attributed to the enhanced permeation of naphthalene molecules into the clay interlayer due to the swelling of TMPA-clay. Recall that the clay interlayer did not

play a significant role in the sorption of naphthalene and diuron by BDTDA-clay and diuron by TMPA-clay. Thus, the steric effects observed in the sorption of these two probe HOCs by the two organoclays can be ascribed to size and shape exclusion effects of the solute molecules and to the arrangement of the organic cations in the interlayers of montmorillonite (sorbate-sorbent effects).

We have used the $\epsilon - f^c$ functionality independently determined from kinetics and equilibrium studies to verify if sorbate-sorbent interactions are important for organoclays. Kinetic parameters have been used to show that estimated Φ values of TMPA-clay for both naphthalene and diuron are not different (Table 3). Similar results were obtained using the equilibrium sorption data of Nzengung et al. (17; Table 1). Meanwhile, for BDTDA-clay, the estimated Φ values for diuron are significantly different from those of naphthalene (Table 3). We have attributed the difference between Φ values for naphthalene and diuron obtained with BDTDA-clay to sorbate-organoclay (sorbate-sorbent) interactions. This interaction, which was not accounted for in the log-linear cosolvency model (eq 8a), is important in sorption by organoclay (17) and may account for the relatively large K_p for diuron using BDTDA-clay. Based on the composition of TMPA and BDTDA ions, stronger hydrophobic interactions should exist between diuron and BDTDA-clay than for diuron and TMPA-clay. The Φ values of naphthalene and diuron for the same organoclay in the same binary solvent should not be different because their effective HSA are similar [HSA for

diuron is estimated as 147 \AA^2 (9), which is not very different from $HSA = 156 \text{ \AA}^2$ for naphthalene (32)].

To account for the difference in Φ estimated independently from our kinetic and equilibrium data, we propose that eq 8b should be modified to include an additional term for HOC-organoclay (i.e., sorbate-sorbent) interaction (eq 10):

$$\Phi = \beta^c \alpha^c \sigma^c \omega \quad (10)$$

where ω is the additional HOC-organoclay interaction and other terms have been defined earlier. To make a quantitative estimation of such interactions, we assumed that naphthalene sorption by TMPA- and BDTDA-clays was not affected by any interactions other than those considered in the log-linear cosolvency model (eqs 8a–c). Dividing Φ values of diuron with those of naphthalene obtained independently from our kinetics and equilibrium studies (Table 3) yields ω of 0.7 for BDTDA-clay and ω of 1.1 for TMPA-clay. A value of $\omega < 1$ indicates additional HOC-organoclay interactions not included in eq 8b, and $\omega = 1$ indicates the absence of additional interactions. Thus, the BDTDA-clay was more effective in sorbing diuron than the TMPA-clay at all fractions of methanol in water. The macroscopic approach used to identify the effect of additional specific HOC-organoclay interactions is not direct, and these data are limited. However, the effect has been independently demonstrated for both sorption kinetics and equilibria data using two types of organoclays and two probe compounds of similar HSA.

The use of cosolvent sorption kinetics data to extrapolate mass transfer coefficients in aqueous systems has far reaching practical implications. First, sorption kinetics of HOCs should not be a limiting factor when organoclays are used in sedimentation basins and treatment ponds often designed with residence times less than 2–4 h. Second, for HOCs that are strongly sorbed, the use of mixed solvents will reduce the potential for HOCs to sorb to container walls, will reduce the time to attain sorption equilibrium, and will minimize microbial breakdown of HOCs. Third, that a log–log relationship between ϵ and K_p exists for sorption of HOCs by organoclay. This relationships can be used to predict the mass transfer coefficient of HOC based on its equilibrium sorption coefficient [K_p]. However, data for more HOCs are needed to support the validity of this relationship.

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