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# Interactions of Organic Contaminants with Mineral-Adsorbed Surfactants

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Sorption of organic contaminants (phenol, *p*-nitrophenol, and naphthalene) to natural solids (soils and bentonite) with and without myristylpyridinium bromide (MPB) cationic surfactant was studied to provide novel insight to interactions of contaminants with the mineral-adsorbed surfactant. Contaminant sorption coefficients with mineral-adsorbed surfactants,  $K_{ss}$ , show a strong dependence on surfactant loading in the solid. At low surfactant levels, the  $K_{ss}$  values increased with increasing sorbed surfactant mass, reached a maximum, and then decreased with increasing surfactant loading. The  $K_{ss}$  values for contaminants were always higher than respective partition coefficients with surfactant micelles ( $K_{mc}$ ) and natural organic matter ( $K_{oc}$ ). At examined MPB concentrations in water the three organic contaminants showed little solubility enhancement by MPB. At low sorbed-surfactant levels, the resulting mineral-adsorbed surfactant via the cation-exchange process appears to form a thin organic film, which effectively "adsorbs" the contaminants, resulting in very high  $K_{ss}$  values. At high surfactant levels, the sorbed surfactant on minerals appears to form a bulklike medium that behaves essentially as a partition phase (rather than an adsorptive surface), with the resulting  $K_{ss}$  being significantly decreased and less dependent on the MPB loading. The results provide a reference to the use of surfactants for remediation of contaminated soils/sediments or groundwater in engineered surfactant-enhanced washing.

## Introduction

Sorption of an organic pollutant to soil has a major influence on its transport, bioavailability, and fate in natural environments. The sorption of nonionic organic compounds (NOCs) from water to most soils is due primarily to the partitioning into soil organic matter (SOM) (1–4). Adsorption of NOCs from water by relatively polar soil minerals is suppressed by the strong competitive adsorption of water. Extensive research (1–3, 5–7) has shown that the sorption of NOCs increases with increasing soil organic matter content and

decreasing water solubility of NOCs. Soils with high organic matter serve as large sinks of NOCs, limiting the NOC bioavailability; low organic-content soils and clays are ineffective in accepting organic contaminants. The potential for NOC leaching through the latter solids is high. As a result, many water-soluble organic chemicals are found as groundwater contaminants and pose a serious threat to human health.

Clays or soils with cation-exchange capacities (CECs) may be modified by ion exchange with large organic cations (e.g.,  $[(CH_3)_3N R]^+$ ) to increase their organic matter contents and thus to provide organophilic moiety favorable for sorption of organic contaminants (8–11). This simple modification has been performed in several previous studies to improve the retardation capacities of low organic matter soils and clays (12–17). According to Boyd and co-workers (12–13, 15, 16), the sorption of NOCs to the long-chain organic moiety of the exchanged cations occurs by partition, analogous to the process with soil organic matter (1, 2). The surfactant-derived organic matter is 10–30 times more effective on a unit weight basis than natural soil organic matter for sorbing nonpolar or weakly polar organic contaminants. Boyd et al. suggested that soils could be modified in situ with injections of cationic surfactant solution (14) to attenuate the mobility of organic contaminants and thus to prevent further down-gradient groundwater and aquifer contamination (16–20). Recently, it is also suggested that organic pollutants sorbed to surfactants may be directly available for degradation by attached cells (21–25). Therefore, surfactant-enhanced retention of organic pollutants and the subsequent degradation by microbes has become one of the promising schemes for contaminated soil and groundwater remediation.

Sorption of NOCs to sorbed surfactants (i.e., to hemimicelles, admicelles) has been investigated in a few studies (26–34). Holsen et al. (26) examined the sorption of several NOCs on SDS-coated ferrihydrite and found that the ones with lowest solubility have the highest sorption. They also found a linear relationship between NOC sorption and the amount of SDS on the ferrihydrite, suggesting that the adsorbed SDS was primarily responsible for the NOC uptake. Sun and Jaffe (28) found that the partitioning of phenanthrene with adsorbed dianionic surfactant phases (as monolayers and bilayers) is generally 5–7 times more effective than with the corresponding surfactant (as monomers and micelles) in water. Likewise, Nayyar et al. (29) reported partition coefficients of several organic contaminants with SDS sorbed on alumina that were higher in magnitude than the corresponding micellar partition coefficients. The reason for these differences has not been elucidated. Similar experiments were performed by Sun et al. (30) to obtain partition coefficients for three chlorinated NOCs to silt soils with a sorbed nonionic surfactant (Triton X-100). They observed that the sorbed surfactant enhanced NOC partitioning relative to the untreated soils. However, when the surfactant concentration in water was greater than the CMC (the critical micelle concentration), the aqueous micelles competed more effectively against the sorbed surfactant for NOC partitioning, leading to a net decrease in NOC distribution coefficients. Ko et al. (31, 32) investigated the partitioning of phenanthrene and naphthalene to aqueous surfactant micelles (SDS and Tween 80) and kaolinite-sorbed surfactants. They found that the carbon-normalized solute sorption coefficients with the sorbed surfactants ( $K_{ss}$ ) were the highest at low sorbed-surfactant levels and were reduced sharply with increasing sorbed-surfactant level. That is, the NOC distribution coefficients between the immobile and mobile phases varied

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TABLE 1. Properties of Four Studied Solids<sup>a</sup>

solids	bentonite 1	bentonite 2	soil 1	soil 2
CEC (mequiv/100 g)	60.0	105	3.51	19.8
SA (m <sup>2</sup> /g)	22.5	60.9	3.82	5.51
f <sub>oc</sub> (%)	0.057	0.040	0.51	1.28

<sup>a</sup> CEC = cation exchange capacity, SA = BET-(N<sub>2</sub>) surface area, and f<sub>oc</sub> = fraction of organic carbon content.

generally with surfactant concentration because of the competition between sorbed and aqueous surfactants for NOC partition.

The ability of surfactants to enhance the water solubility and mobilization of NOCs provides a potential means of remediating contaminated soils by use of surfactant solutions (35, 36). There has been a great interest in surfactant-enhanced remediation (SER) technologies in recent years (32, 37). The fundamental interactions between soil, surfactant, and contaminant govern both the processes of SER and surfactant-enhanced retardation, so the studies would contribute to the design of the SER technology for organic contaminated soils.

The main objective of the current study is to account for the variation of  $K_{ss}$  of a solute with the sorbed surfactant level on a solid. Toward this end, we studied the distribution of both polar and nonpolar organic solutes (phenol, *p*-nitrophenol, and naphthalene) in several solid–water systems in the presence of a cationic surfactant, myristylpyridinium bromide (MPB). Two soils and two bentonites were chosen as reference solids, which sorbed varied amounts of MPB. The use of a relatively homogeneous cationic surfactant (MPB) in this study enables one to describe more precisely the change in the sorbed surfactant structure (and thus the effect on  $K_{ss}$ ) with respect to the surfactant concentration in water, especially the well-defined CMC. Since the magnitude of  $K_{ss}$  for a solute at a given surfactant level influences the overall solid–water distribution of the solute, the information gained also contributes to a better understanding of the impact of a surfactant on the contaminant soil/sediment–water distribution.

## Materials and Methods

**Materials.** Naphthalene, *p*-nitrophenol, phenol, and myristylpyridinium bromide (MPB) were of analytical grade and were used without further treatment. Octanol–water partition coefficients of naphthalene, *p*-nitrophenol, and phenol are 1950, 93, and 30, respectively, and their aqueous solubilities are 32.05, 80 190, and 16 000 µg/mL at 25 °C, respectively (38). The molar molecular weight of MPB is 374.4 g/mol. Two soils and two original bentonites were selected for sorption experiments. The two soils were collected from Zhejiang province, China. The bentonite 1 and bentonite 2 used were primarily Na<sup>+</sup>-montmorillonite, collected from Zhejiang Province and Mongolia Autonomy, respectively, in China. The air-dried soil and bentonite samples were sieved to obtain particles less than 100 mesh in all experiments. The properties of studied soils and bentonites, such as BET-N<sub>2</sub> surface area (SA), organic carbon contents (f<sub>oc</sub>), and cation-exchanged capacity (CEC), are presented in Table 1. The organic carbon contents were determined using LECO CS-344 type carbon-sulfate analyzer at the condition of 50% relative humidity and 25 °C. The BET-N<sub>2</sub> surface areas were determined using Coulter-100CX surface area analyzer. The cation-exchange capacities were determined with ion exchange methods (39).

**Analytical Methods.** Aqueous naphthalene, phenol, *p*-nitrophenol and MPB were quantified by ultraviolet spectrophotometry at absorbance wavelength 223 nm, 287, 317, and 259 nm, respectively. The pH values of analyte solutions

were controlled at 11 and 3, respectively, for phenol and *p*-nitrophenol in order to ensure phenol in the ionic state and *p*-nitrophenol in the molecular state because analytical wavelength and sensitivity of them were affected by pH values. The MPB concentration in solution was controlled at less than 212 µg/mL in order to eliminate the effects of MPB on the analytical wavelength and sensitivity of naphthalene, phenol, and *p*-nitrophenol. The molar absorptivities (ε, L·mol<sup>-1</sup>·cm<sup>-1</sup>) are ε<sub>223 nm</sub> = 92 849 for naphthalene, ε<sub>287 nm</sub> = 2525 for phenol, ε<sub>317 nm</sub> = 9758 for *p*-nitrophenol, and ε<sub>223 nm</sub> = 3856, ε<sub>259 nm</sub> = 4337, ε<sub>287 nm</sub> = 32, and ε<sub>317 nm</sub> = 23 for MPB. All analysis utilized standard external calibration curves over their linear response regions and was made well above the instrumental and method detection limits.

### Solubility Enhancement of Organic Compounds by MPB.

Batch experiments were conducted to determine the extent of the solubility enhancement of naphthalene, phenol, and *p*-nitrophenol by MPB. Solutions with a series of MPB concentrations were placed in 50 mL Erlenmeyer flasks with glass caps, and the test solute (naphthalene, phenol, and *p*-nitrophenol) was subsequently added to each Erlenmeyer flask in amount slightly more than required to saturate the solution. The initial MPB concentrations were set at a large range of values below and above the nominal CMC of MPB in 0.005 mol/L CaCl<sub>2</sub> solution. Duplicate samples were prepared for each surfactant concentration; these samples were then equilibrated on a gyratory shaker for 48 h at 25 ± 0.5 °C and 150 rpm. The samples were subsequently centrifuged at 4000 rpm for 20 min to completely separate the undissolved solute. An appropriate aliquot of the supernatant was then carefully withdrawn with a volumetric pipet and diluted to appropriate volume with deionized water. Naphthalene, phenol, and *p*-nitrophenol in solution were analyzed by UV. The apparent solubilities of organic compounds in MPB solutions were computed from the final UV readings. To eliminate the effect of MPB on the analysis of naphthalene, phenol, and *p*-nitrophenol, the blanks with the same MPB concentrations and without organic solutes were also analyzed.

**Sorption of MPB onto Solids.** Batch experiments were conducted to determine MPB equilibrium sorption isotherms. Appropriate amounts of solids (i.e., 1.0 g for soil 1, 0.5 g for soil 2, 0.1 g for bentonite 1, and 0.05 g for bentonite 2) were placed in 50 mL Erlenmeyer flasks with glass caps, to which 20 mL of 0.005 mol/L CaCl<sub>2</sub> solution with different amounts of MPB was added. The initial MPB concentrations spanned over a large range of values below and above the nominal CMC of MPB in the 0.005 mol/L CaCl<sub>2</sub> solution. The flasks were shaken for 12 h at 25 ± 0.5 °C on a gyratory shaker at 150 rpm. The solution and solid phases were separated by centrifugation at 4000 rpm for 10 min. An appropriate aliquot of the supernatant was removed and analyzed for MPB by UV. The MPB equilibrium concentration was computed from the final UV readings, while the amount of MPB sorbed was computed simply from the difference of the initial and final MPB concentrations.

**Sorption of Organic Contaminants to Solids.** Sorption of organic pollutants onto solids from water in the presence or absence of MPB were determined. Varied quantities of an organic pollutant were added to the 50 mL Erlenmeyer flasks with glass caps, which contained appropriate amounts of a solid (i.e., 1.0 g for soil 1, 0.5 g for soil 2, 0.1 g for bentonite 1, and 0.05 g for bentonite 2) in 20 mL of 0.005 mol/L CaCl<sub>2</sub> solution with a given concentration of MPB (0–3504.4 µg/mL). The flasks were shaken for 12 h at 25 ± 0.5 °C on a gyratory shaker at 150 rpm to reach the equilibration state. The solution and solid phase were separated by centrifugation at 4000 rpm for 10 min. An amount of supernatant was removed and analyzed for organic pollutant and MPB by UV. No major changes in UV spectral pattern of the organic

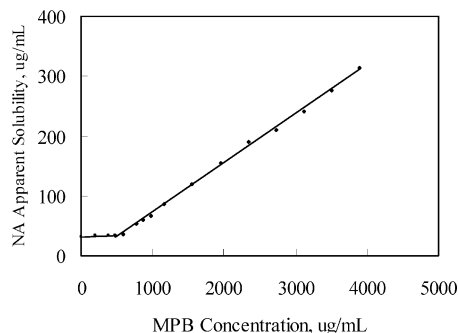


FIGURE 1. Water solubility enhancement of naphthalene as a function of MPB solution at 25 °C.

pollutant were observed when the MPB concentration in solution was less than 0.4 CMC. The equilibrium concentrations of organic solutes were computed from the final UV readings, while the sorbed amounts were computed simply from the difference of the initial and final solute concentrations. The losses of the compounds by photochemical decomposition and sorption to the flask were found to be negligible. The volatilization losses of organic compounds were calculated from their Henry's law constants and the headspace.

## Results and Discussion

**Solubility Enhancement of Organic Contaminants by MPB in Aqueous Solution.** To account for the overall solute distribution, we consider first the extent of solute water solubility enhancement. The apparent water solubility of a solute in a surfactant solution has been developed (35), as

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc} \quad (1)$$

where  $S_w^*$  is the apparent solute solubility at a total stoichiometric surfactant concentration of  $X$ ;  $S_w$  is the intrinsic solute solubility in "pure water";  $X_{mn}$  is the concentration of the surfactant as monomer in water (mass/mass, dimensionless) ( $X_{mn} = X$ , if  $X \leq \text{CMC}$ ;  $X_{mn} = \text{CMC}$ , if  $X > \text{CMC}$ );  $X_{mc}$  is the concentration of the surfactant as micelle in water ( $X_{mc} = X - \text{CMC}$ );  $K_{mn}$  is the partition coefficient of the solute between surfactant monomer and water; and  $K_{mc}$  is the solute partition coefficient between the aqueous micellar phase and water.

Water solubility enhancement of naphthalene, phenol, and *p*-nitrophenol by MPB at concentrations ranging from below to above the normal CMC was assessed. Results indicated that solubilities of phenol and *p*-nitrophenol were hardly enhanced by MPB, i.e.,  $X_{mn}K_{mn} + X_{mc}K_{mc} \approx 0$ , because of their high aqueous solubility and thus small  $K_{mn}$  and  $K_{mc}$ . Figure 1 shows a linear fit to the raw data. The water solubility of naphthalene was significantly enhanced by MPB above the CMC; the apparent aqueous solubility increases with increasing MPB concentration. The observed difference in solubility enhancement by MBP above and below the CMC is a result of the different abilities of micelles and monomers to concentrate a solute (naphthalene) by partition interaction. The data of  $K_{mn}$ ,  $K_{mc}$ , and  $S_w$  for naphthalene and CMC for surfactant are calculated from the solubility-enhancement data and presented in Table 2.

**Sorption Behavior of MPB onto Solids.** Sorption isotherms of MPB onto two bentonites and two soils are shown in Figure 2. The sorption of MPB to the bentonite is very strong, due partly to the cation exchange (12). The uptake by the two soils is much lower in magnitude because of their lower CECs. All MPB isotherms are type-I. On all solids, the MPB uptake reaches a plateau when the MPB equilibrium concentration in water is approximately equal to the CMC

TABLE 2. Solubility Enhancement Data of Naphthalene with MPB and Associated  $K_{mn}$ ,  $K_{mc}$ , CMC, and  $S_w$  Values

MPB concn	equation of solubility enhancement	corr coeff, $r$	$K_{mn}$ (mL/g)	$K_{mc}$ (mL/g)	CMC ( $\mu\text{g/mL}$ )	$S_w$ ( $\mu\text{g/mL}$ )
$\leq \text{CMC}$	$Y = 0.00418X + 31.27$	0.958	134	2640	531	31.3
$> \text{CMC}$	$Y = 0.0825X - 10.27$	0.999				

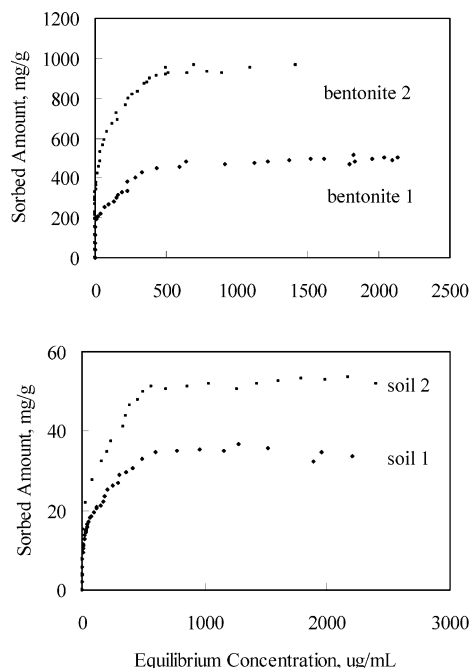


FIGURE 2. Sorption of MPB onto two bentonites and two soils.

(531  $\mu\text{g/mL}$ ). Since the CMC for a surfactant is analogous to the water solubility of an ordinary solute, the surfactant is expected to exhibit a limiting uptake capacity on solids at the point of CMC in water. On progressing toward this limiting value, the sorbed surfactant (MPB) undergoes presumably a structural change from submonolayer to bilayer or multilayer on the solid (40), the state of which, as described later, having an important consequence on the ability of the sorbed surfactant to take up an organic contaminant. At low MPB concentrations, MPB is sorbed preferentially by cation exchange onto the solid surface to form an "adsorbed film", and then further sorption at high MPB concentrations creates a partitionlike medium, which may be viewed as a surface-micelle phase.

The saturated capacities of MPB ( $Q_{\text{MPB}}^0$ ) are 35.0 mg/g (soil 1), 52.0 mg/g (soil 2), 500.0 mg/g (bentonite 1), and 940.0 mg/g (bentonite 2). The values of  $Q_{\text{MPB}}^0$  are positively correlated with the CECs of solids by a linear relationship:

$$Q_{\text{MPB}}^0 = 8.669 \text{ CEC} \quad (2)$$

If the MPB sorption to solids occurs exclusively by cation exchange, the estimated saturation capacities should be

$$Q_{\text{MPB}}^0 = \frac{\text{CEC} \times m_{\text{solid}} \times M}{100 \times m_{\text{solid}}} = 3.744 \text{ CEC} \quad (3)$$

where  $Q_{\text{MPB}}^0$  is the saturated capacities of MPB, mg/g;  $m_{\text{solid}}$  is the solid mass in sorption experiments, g;  $M$  is the molar molecular weight of MPB ( $M = 374.4 \text{ g/mol}$ ); CEC is the cationic exchange capacities of solid, mequiv/100 g. The difference between eq 2 with eq 3 suggested that an additional sorption mechanism be involved in the MPB uptake by solids. It appears that a collective effect occurs in the MPB uptake,



TABLE 3. Equilibrium MPB Concentrations and Calculated Surfactant-Derived Organic Carbon Contents ( $f_{\text{soc}}$ ) in Solids

MPB initial concn, $\mu\text{g/mL}$	bentonite 1		bentonite 2		soil 1		soil 2	
	MPB equiv concn, $\mu\text{g/mL}$	$f_{\text{soc}}$ , %	MPB equiv concn, $\mu\text{g/mL}$	$f_{\text{soc}}$ , %	MPB equiv concn, $\mu\text{g/mL}$	$f_{\text{soc}}$ , %	MPB equiv concn, $\mu\text{g/mL}$	$f_{\text{soc}}$ , %
0	0	0	0	0	0	0	0	0
195	$\approx 0$	3.09	0.73	5.91	1.16	0.32	$\approx 0$	0.64
389	$\approx 0$	5.95	1.07	11.4	2.36	0.64	9.87	1.24
779	2.02	11.2	2.62	20.2	30.1	1.22	85.5	2.24
973	12.5	13.7	3.01	24.1	62.3	1.48	159	2.62
1168	47.7	15.5	31.4	27.0	115	1.71	235	2.99
1560	110	19.2	90.6	32.5	249	2.12	390	3.72
1750	146	21.0	140	34.4	322	2.80	502	3.97
1950	161	22.7	256	35.5	427	2.61	683	4.01
2340	294	25.2	294	39.7	684	3.06	1040	4.10
2530	311	26.7	350	41.8	854	2.96	1260	4.02
2730	363	28.0	436	43.0	1140	3.00	1430	4.12
2920	526	28.1	496	44.0	1170	2.86	1610	4.16
3120	655	28.7	694	44.4	1380	3.12	1780	4.21
3500	1010	29.2	1090	44.0	1740	3.40	2170	4.23

in which the MPB sorbed initially through ion exchange on minerals induces a subsequent uptake through London forces (41, 42). According to the sorbed amount of MPB, the surfactant-derived organic carbon contents on the solid ( $f_{\text{soc}}$ ) could then be calculated, as given in Table 3.

#### Solid–Water Distribution of Contaminants with MPB.

In the presence of a surfactant, the distribution coefficient of contaminant (solute) in solid–water mixtures is influenced by the surfactant distribution between solid and solution phases. As shown by Lee et al. (43), the apparent solute distribution coefficient in solid–water mixtures with a coexisting surfactant ( $K_d^*$ ) may be expressed in the form of

$$K_d^* = \frac{K_{\text{oc}} f_{\text{oc}} + f_{\text{soc}} K_{\text{ss}}}{1 + K_{\text{mn}} X_{\text{mn}} + K_{\text{mc}} X_{\text{mc}}} \quad (4)$$

where  $K_d^*$  is the ratio of bound NOC to mobile NOC.  $f_{\text{oc}}$  (Table 1) and  $f_{\text{soc}}$  (Table 3) are the natural organic-carbon fraction and the surfactant organic-carbon fraction in the solid, respectively, and  $K_{\text{oc}}$  and  $K_{\text{ss}}$  are the carbon-normalized solute distribution coefficients with the natural organic matter and the sorbed surfactant in solid, respectively. In eq 4,  $f_{\text{oc}} K_{\text{oc}} = K_d$  is the solute sorption coefficient with the soil without the addition of surfactant, in which case  $X_{\text{mn}} K_{\text{mn}} + X_{\text{mc}} K_{\text{mc}} = 0$ .

To the right of eq 4, the  $f_{\text{oc}} K_{\text{oc}}$ ,  $f_{\text{soc}}$ , and  $(1 + X_{\text{mn}} K_{\text{mn}} + X_{\text{mc}} K_{\text{mc}})$  terms can all be well determined experimentally, so that the only remaining term that impacts  $K_d^*$  and cannot be determined directly is  $K_{\text{ss}}$ . As mentioned earlier,  $K_{\text{ss}}$  is expected to vary with  $f_{\text{soc}}$ , due presumably to a structure change of the sorbed surfactant with the loaded mass. The present experiments with well measured sorption data using several contaminants and a relatively homogeneous cationic surfactant (MPB) on two soils and two bentonite samples are intended to rationalize the observed surfactant concentration dependence of the solute  $K_{\text{ss}}$  value.

The sorption capacities of naphthalene, phenol, and *p*-nitrophenol on MPB-sorbed solids are much higher than on MPB-free solids. The  $K_d^*$  values for naphthalene, phenol, and *p*-nitrophenol on solids with MPB are calculated.

In the absence of MPB,  $K_d^*$  is equal to  $K_d$ . The  $K_d$  values for all three solutes are proportional to  $f_{\text{oc}}$  values. Sorption coefficients of naphthalene with bentonites in water without MPB are nearly zero because the  $f_{\text{oc}}$  values are very small. The sorption coefficients normalized to  $f_{\text{oc}}$  (i.e.,  $K_{\text{oc}} = K_d/f_{\text{oc}}$ ) are 934, 38.8, and 16.9 mL/g, respectively, for naphthalene, *p*-nitrophenol, and phenol, which are positively related to the octanol–water partition coefficients ( $K_{\text{ow}}$ 's) of the solutes.

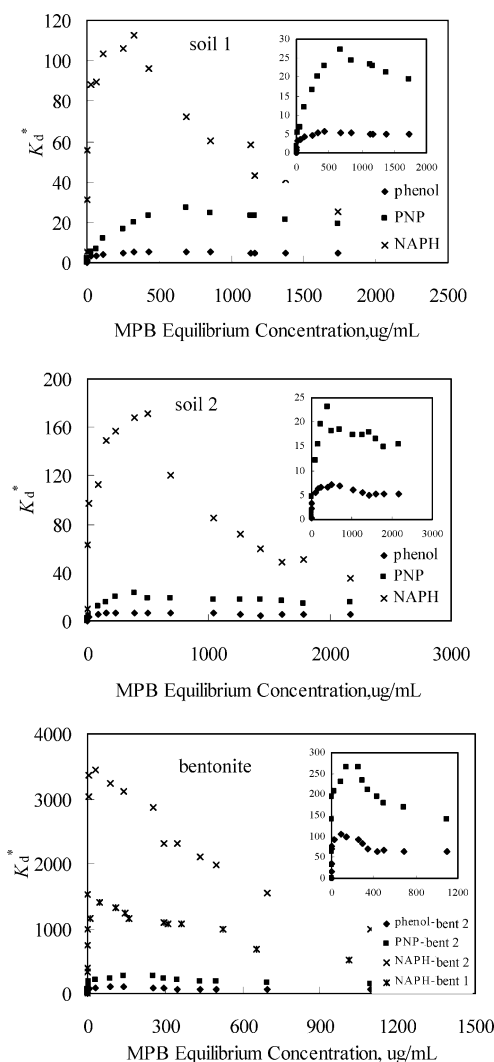


FIGURE 3. The apparent partition coefficients of phenol, *p*-nitrophenol, and naphthalene in relation to the MPB concentration.

The relationships between  $K_d^*$  values of naphthalene, phenol, and *p*-nitrophenol on the four solids and respective MPB equilibrium concentrations are presented in Figure 3 (insets for phenol and *p*-nitrophenol). As shown, the  $K_d^*$  values are higher than the  $K_d$  values, which indicates that the levels of MPB applied decreases the contaminant mobility, a trend noted for other contaminants at low-to-moderate

surfactant levels when the solid has a low  $f_{oc}$  value (43). For phenol and *p*-nitrophenol on solids, the  $K_d^*$  values increase with increasing MPB concentration until they reach a maximum and then decrease slowly afterward. For naphthalene on solids, the  $K_d^*$  values increase with increasing MPB concentration until a maximum is reached and then decrease quite sharply with MPB concentration when the water solubility of naphthalene is significantly enhanced.

The  $K_d^*/K_d$  values are 4.89–150.0 (soil 1) and 3.13–42.9 (soil 2) for *p*-nitrophenol, 5.45–50.27 (soil 1) and 14.28–44.91 (soil 2) for phenol, and 4.65–20.49 (soil 1) and 3.48–16.86 (soil 2) for naphthalene. The  $K_d^*/K_d$  ratios are negatively correlated with solid  $f_{oc}$  and contaminant  $K_{ow}$ , which extends the useful observations by others (43). Thus, the  $K_d^*/K_d$  values of contaminants are considerably higher with bentonite that have extremely low  $f_{oc}$  values and high CECs than on the soils with relatively high  $f_{oc}$  values and low CECs. Figure 3 also shows that the MPB concentrations corresponding to the maximum  $K_d^*$  were negatively related to the solid's CEC and the solute's  $K_{ow}$ .

**Interactions of Contaminants with Mineral-Sorbed Surfactant.** According to eq 4, the sorption of organic pollutants to a MPB-sorbed solid is promoted by the sorption to both solid organic matter and surfactant-derived organic matter and is weakened by the dissolved surfactant if it enhances the solute solubility. From the determined  $K_d^*$  and  $K_d$  values, the solute solubility enhancement factor with MPB, i.e.,  $(1 + X_{mn}K_{mn} + X_{mc}K_{mc})$ , and solid  $f_{oc}$  values, the associated  $K_{ss}$  values can then be calculated for subsequent analyses.

The calculated  $K_{ss}$  values for phenol, *p*-nitrophenol, and naphthalene by eq 4 are always larger than the corresponding micellar  $K_{mc}$  and solid  $K_{oc}$  values. Previous studies have also found the  $K_{ss}$  value to be generally larger than the  $K_{mc}$  (28, 29, 31, 32). Ko et al. (31, 32) postulated that this difference results from geometric differences between sorbed and dissolved surfactant aggregates.

Figure 4 shows the dependence of the  $K_{ss}$  values for phenol, *p*-nitrophenol, and naphthalene on MPB equilibrium concentration. For these compounds, as the amount of sorbed MPB on the solid increases, the respective  $K_{ss}$  values increase sharply to a maximum at low surfactant concentration and then decrease with increasing surfactant concentration. Although the  $K_{ss}$  values for all contaminants are larger than their  $K_{mc}$  values, the  $K_{ss}$  approach the  $K_{mc}$  at high MPB levels. Ko et al. (31, 32) reported that  $K_{ss}$  values decrease with increasing SDS sorption for nonpolar NOCs such as naphthalene and phenanthrene; Nayyar et al. (29) reported a similar observation for a polar NOC, naphthol, in SDS-alumina systems. To our knowledge, there have been no previous reported  $K_{ss}$  values that increase sharply to a maximum before they decline at higher surfactant loading, similar to the present observation.

The very high  $K_{ss}$  values at low surfactant levels and the subsequent transition of  $K_{ss}$  to lower values that are comparable with  $K_{mc}$  cannot be explained on the basis of a simple structure change of the sorbed surfactant aggregate. The very large  $K_{ss}$  values at low surfactant levels suggests that the sorbed surfactant at low levels does not act as a partition phase but instead as an adsorptive surface (or a surface film) on which the contaminant adsorbs. This adsorptive force arises from the attractive forces of mineral surfaces, which attract the organic contaminant from water after the surface is covered by a thin layer of the sorbed surfactant; without this surfactant film, water will be more strongly adsorbed instead, thus minimizing the adsorption of organic contaminants. It appears that as a large amount of surfactant is being sorbed, the initial film then grows into a bulklike phase to which the solute partitions. This transition leads to a reduction in  $K_{ss}$  with the surfactant loading, which eventually becomes comparable with the  $K_{mc}$  values. Thus, when the

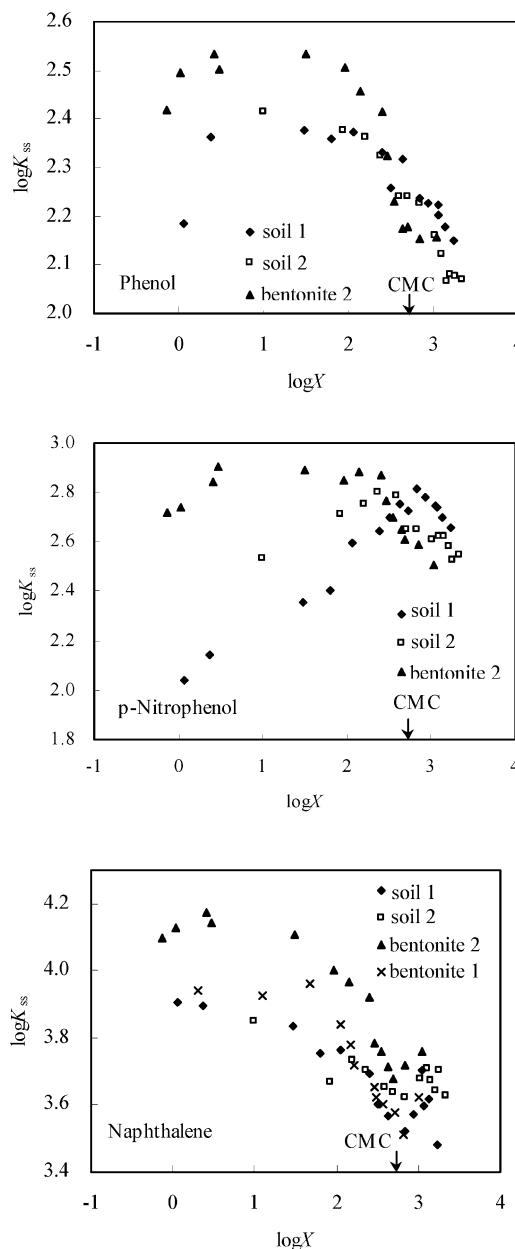


FIGURE 4. The  $K_{ss}$  values of phenol, *p*-nitrophenol, and naphthalene in relation to the MPB concentration.

MPB sorption reaches saturation, the  $K_{ss}$  values of a contaminant with different solids become comparable (Figure 5). In addition, without this transition, it will not be possible for  $K_d^*$  to reach a maximum at a surfactant concentration below the CMC, because the sorbed MPB reaches saturation near the CMC (Figure 2) and there is practically no solute solubility enhancement by MPB below the CMC (Figure 1). The transition of  $K_{ss}$  with surfactant concentration depends presumably on solid properties (e.g., the CEC) and the contaminant properties (e.g., the water solubility or  $K_{ow}$ ) as well as the surfactant type.

From the present study, the observed ratios of  $K_{ss}$  to  $K_{oc}$  (i.e.,  $K_{ss}/K_{oc}$ ) range from 6.95 to 20.2 for phenol, from 2.82 to 20.7 for *p*-nitrophenol, and from 3.26 to 13.4 for naphthalene. The maximum  $K_{ss}/K_{oc}$  values for the three pollutants range from 13.4 to 20.7, which indicates that surfactant-derived organic matter is a more powerful medium to sorb organic contaminants than natural soil organic matter. Sorbed cationic surfactants are known to enhance the organic pollutant transfer from water into surfactant-derived organic

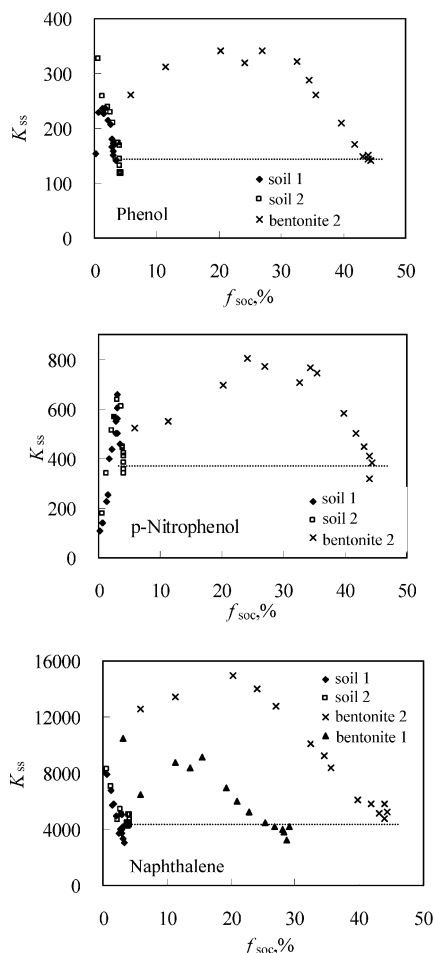


FIGURE 5. The  $K_{ss}$  values of phenol, *p*-nitrophenol, and naphthalene in relation to the surfactant-derived organic carbon ( $f_{soc}$ ).

matter by decreasing the interfacial tension between water and solids and by concentrating the pollutant into the surfactant-derived organic matter (34, 37).

In summary, the sorbed cationic surfactant at low levels behaves as a more powerful medium for sorbing organic pollutants than does the dissolved surfactant in micellar form. It is found that the sorbed cationic surfactant at low levels on solids, especially bentonite clays, functions effectively as an adsorptive surface rather than a partition phase. The reverse becomes true for the sorbed surfactant at high loading in solids. This unique transition is supported by the very large  $K_{ss}$  values of contaminants at low MPB levels on solids and the subsequent large reduction to values comparable with the solution micellar  $K_{mc}$  values. This view should improve the interpretation of the observed contaminant distribution coefficients in solid–water systems where the system is also contaminated by cationic surfactants at different levels.

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