Distribution of phenanthrene between soil and an aqueous phase in the presence of anionic micelle-like amphiphilic polyurethane particles

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Abstract

Sorption of micelle-like amphiphilic polyurethane (APU) particles to soil was studied and compared to that of a model anionic surfactant, sodium dodecyl sulfate (SDS). Three types of APU particles with different hydrophobicity were synthesized from urethane acrylate anionomers (UAA) and used in this study. Due to the chemically cross-linked structure, APU exhibited less sorption to the soil than SDS and a greater reduction in the sorption of phenanthrene, a model soil contaminant, to the soil was observed in the presence of APU than SDS even though the solubility of phenanthrene was higher in the presence of SDS than APU. A mathematical model was developed to describe the phenanthrene distribution between soil and an aqueous phase containing APU particles. The sorption of phenanthrene to the test soil could be well described by Linear isotherm. APU sorption to the soil was successfully described by Langmuir and Freundlich isotherms. The partition of phenanthrene between water and APU were successfully explained with a single partition coefficient. The model, which accounts for the limited solubilization of phenanthrene in sorbed APU particles, successfully described the experimental data for the distribution of phenanthrene between the soil and the aqueous phase in the presence of APU.
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1. Introduction

Polycyclic aromatic hydrocarbon (PAH) compounds are highly carcinogenic and known to contaminate groundwater when they are discharged to soil. PAH compounds are nonionic,

sparingly soluble in water, and predominantly exist in the sorbed state in soil through hydrophobic bonding. Sorbed PAHs may act as a long-term source of groundwater contamination. Since it was reported that the water solubility of organic pollutants was enhanced in the presence of dissolved organic matter [1] and surfactants [2], many researchers have been using surfactants to enhance desorption of sorbed PAHs from soil through solubilization of sorbed PAHs in surfactant micelles [3–10]. The distribution of PAHs between soil and water in the presence of surfactants was not only experimentally determined but also mathematically analyzed [7,8,11–13]. However, the loss of surfactants due to their sorption to soil has been recognized as a serious problem to be solved for field application [5–8,14–16]. As a result, recent research has been directed towards the design of surfactant-like molecules whose sorption to soil is minimized. Kim et al. succeeded in the synthesis of novel amphiphilic polyurethane (APU) nano-particles from amphiphilic nonionomers and used them for the extraction of soil-bound phenanthrene [17]. Sorption of these APU particles to soil was less than that of a conventional surfactant such as Triton X-100, especially at low concentrations. Due to such low sorption of APU to soil, sorption of phenanthrene to soil with the addition of APU was less than that with Triton X-100. Even though APU particles with different degrees of hydrophobicity were used, Kim et al. [17] could not find any significant differences in the sorption of APU particles to the soil. It is believed that this result might be due to the low organic carbon content of the soil used in that study (0.049%).

In this study, phenanthrene was used as a model PAH compound. A test soil was taken from an uncontaminated area near a coal mine in Samchok, Kangwon-Do, South Korea. Amphiphilic polyurethane nano-particles with different hydrophobicity were synthesized from amphiphilic anionomers and used as micelle-like molecules. Sodium dodecyl sulfate (SDS), one of the most popularly used anionic surfactants, was used as a model anionic surfactant for the comparison with APU. The distribution of phenanthrene between soil and an aqueous phase (sorption of phenanthrene to soil) in the presence of micelle molecules can be recognized as an index for the performance of these micelle molecules washing phenanthrene-contaminated soil.

The purpose of this study is to investigate how the sorption of phenanthrene to the soil is correlated with the affinity between micelle molecules (SDS and APU) and phenanthrene, and with sorption behaviors of micelle molecules to the soil. Enhanced solubility of phenanthrene with the addition of SDS or APU particles was measured using radio-labeled phenanthrene as an index for the affinity between micelle molecules and phenanthrene. Sorption of APU to the soil was determined from batch isotherm experiments. Then a mathematical model was developed to describe the experimental results of phenanthrene distribution between soil and an aqueous phase containing APU particles.

2. Experimental methods

2.1. Materials

Phenanthrene was used as a model PAH. The aqueous solubility of phenanthrene is reported to be 1.29 mg/l, and its octanol–water partition coefficient is 3700. Radio-labeled phenanthrene was purchased from Sigma Chemical Co. (9-^{14}C, 13.1 μCi/μmol) (St. Louis,

Table 1
Physical and chemical properties of soil used in this study

Properties	Values
Organic carbon	0.53%
pH in water	7.61
CEC (cation exchange capacity)	4.92 me/100 g
Sand	70.60%
Silt	18.32%
Clay	11.08%

MO, USA). The soil used in all experiments was taken from an uncontaminated area near a coal mine in Samchok, Kangwon-Do, South Korea. The soil sample was air-dried and was passed through a U.S. standard mesh size 10 sieve to remove the soil particles whose diameter was larger than 2 mm. Physical and chemical properties of the test soil, such as soil pH and organic carbon content, were measured by The Jeil Analysis Center (Bucheon, South Korea), and are summarized in Table 1. The organic content of the soil was 0.53%. Three types of APU particles were synthesized [18] and used in this study. Table 2 shows the molar ratios of the reagents used for the synthesis of APU particles. PTMG (polytetramethylene glycol, MW = 1000, Hyosung BASF, Seoul, South Korea) and DMPA (dimethylol propionic acid, Aldrich Chemical Co., Milwaukee, WI, USA) are the hydrophobic and the hydrophilic moieties of APU particles, respectively [18]. To denote the APU particles with different hydrophobicity, they are named as UAA 2:8, UAA 5:5, and UAA 6:4, where numbers represent the mole ratio of the hydrophobic (PTMG) and the hydrophilic (DMPA) moiety in their monomers. Hence UAA 2:8 is most hydrophilic and UAA 6:4 is most hydrophobic. The size of the synthesized APU particles was measured by dynamic light scattering and was in the range of 40–100 nm. All chemicals used in this study were of analytical grade.

2.2. Partition of phenanthrene between water and SDS or APU

Concentrations of phenanthrene in an aqueous phase containing SDS or APU were determined using a mixture of radio-labeled phenanthrene and non-labeled phenanthrene [3]. Concentrated phenanthrene solutions (35 g/l) were prepared in methylene chloride. Two milliliters of phenanthrene solution was added to a 25 ml glass scintillation vial equipped with open-top screw caps and Teflon-backed septa. After evaporation of methylene chloride,

Table 2
Molar ratios of the reagents used in the synthesis of APU particles

Symbols	Reagents[a]	Molar ratios
UAA 2:8	PTMG/DMPA/TDI/2-HEMA	0.2/0.8/1.5/1.5
UAA 5:5	PTMG/DMPA/TDI/2-HEMA	0.5/0.5/1.5/1.5
UAA 6:4	PTMG/DMPA/TDI/2-HEMA	0.6/0.4/1.5/1.5

[a] PTMG: polytetramethylene glycol (MW = 1000); DMPA: dimethylol propionic acid; TDI: 2,4-toluene diisocyanate; and 2-HEMA: 2-hydroxyethyl methacrylate.

10 ml of SDS solutions or APU emulsions prepared at various concentrations were added to the vials. Since the amount of phenanthrene remaining in the vials was much larger than the solubility of phenanthrene in water, the loss of phenanthrene due to evaporation was inconsequential. The vials were sealed and gently agitated with a tube rotator for 7 days. Five milliliters of each sample was withdrawn and centrifuged at $4500 \times g$. One milliliter of the supernatants was transferred into a scintillation vial containing 10 ml of Ecolume cocktail, and the concentration of ^{14}C-phenanthrene in the aqueous phase was measured using a Liquid Scintillation Counter. At least three replicate experiments were performed for each condition.

2.3. Surface tension measurement for SDS and APU

The surface tension of SDS solutions and APU emulsions was determined with a Model 20 surface tensiometer (Fisher Scientific, Pittsburgh, PA, USA). This instrument operates on the du Nöuy principle using a platinum ring suspended from a torsion balance. Sample of SDS solutions or APU emulsions, prepared at various concentrations, were tested with the tensiometer at a controlled temperature ($25\,^{\circ}$C) until at least three consistent readings were obtained. Between each reading, the ring was cleaned with acetone and heated to redness in a gas flame.

2.4. Batch isotherm experiments for the sorption of SDS and APU particles to soil

Batch isotherm experiments were performed to determine the sorption of SDS and APU to the test soil. In the sorption experiments, 1 g of the soil was mixed with 10 ml of SDS solution or APU emulsions of various concentrations in glass vials with a screw cap. After the vials were rotated end-over-end for 3 days, they were allowed to stand until the test soil settled. 8 ml of supernatant was withdrawn from each vial and centrifuged at $4500 \times g$ to separate the soil from the SDS solutions or APU emulsions. To determine the amount of SDS or APU sorbed to the soil, the change in the concentrations of SDS or APU before and after mixing with the soil was measured. The concentrations of SDS or APU were determined using a MULTI N/C-300 Total Carbon Analyzer (Analytic Jeni. AG., Germany).

2.5. Batch experiments for the distribution of phenanthrene between an aqueous phase and the soil

Batch isotherm experiments were performed to determine the sorption of phenanthrene to the test soil in the absence of SDS and APU. A standard ^{14}C-phenanthrene aqueous solution (activity 0.056–0.068 µCi/ml) was prepared by a method described previously [19,20]. ^{14}C-phenanthrene solutions of various concentrations prepared by mixing the above standard solution with deionized water were added to glass vials (with screw caps) filled with 1 g of the soil. The vials were rotated end-over-end for 3 days to achieve the sorption equilibrium of phenanthrene. Then, the vials were allowed to stand until the test soil settled. 8 ml of supernatant was withdrawn from each vial, placed into PTFE centrifuge tubes, and centrifuged at $4500 \times g$ for 30 min to separate the soil from the aqueous solution. One milliliter of the supernatants was transferred into a scintillation vial containing 10 ml

of Ecolume cocktail, and the concentration of ^{14}C-phenanthrene in the aqueous phase was measured using a Liquid Scintillation Counter. To determine the amount of phenanthrene sorbed to the soil, the change in the concentrations of phenanthrene before and after mixing with the soil was measured. At least duplicate tests were performed for each experiment.

To determine the distribution of phenanthrene between an aqueous phase and the soil in the presence of SDS or APU, 9 ml of SDS solutions or APU emulsions of various concentrations, and 1 ml of the standard ^{14}C-phenanthrene solution were simultaneously added to glass vials (with screw caps) filled with 1 g of the soil. Concentrations of phenanthrene in the supernatants before and after 3-day mixing with the soil were measured.

3. Mathematical analysis

3.1. Partition of phenanthrene between water and APU

The distribution of phenanthrene between water and APU is mathematically described with a linear partition model [7,8]

$$K_m = \frac{C_{phe,m}}{C_{phe,w}} \tag{1}$$

where K_m is the partition coefficient of phenanthrene between water and APU (ml/mg); $C_{phe,w}$ is the concentration of phenanthrene in water excluding APU (mg/ml); $C_{phe,m}$ is the concentration of phenanthrene solubilized in the APU particles existing in the aqueous phase (mg/mg). Since the measured concentration of phenanthrene is the sum of the concentrations in water and in APU

$$\frac{(C_{phe} - C_{phe,w})}{C_{phe,w}} = K_m \cdot C_{APU} \tag{2}$$

where C_{phe} is the apparent concentration of phenanthrene in the aqueous phase containing APU particles (mg/ml); C_{APU} is the concentration of APU in the aqueous phase (mg/ml). Then K_m is a slope in the plot of C_{APU} versus $(C_{phe} - C_{phe,w})/C_{phe,w}$.

In the experiments solubilizing crystalline phenanthrene with APU, $C_{phe,w}$ and C_{phe} are the solubility of phenanthrene in pure water and that in the presence of APU particles, respectively. From the plot of phenanthrene solubility at various concentrations of APU particles, a partition coefficient of phenanthrene between water and APU (K_m) was determined from Eq. (2).

3.2. Sorption isotherms of phenanthrene and APU particles to soil

Sorption of phenanthrene and APU occurs when soil is exposed to them. A relationship between concentrations of a free species and sorbed one at equilibrium is sorption isotherm (defined at a given temperature)

$$S_j = f_j(C_j) \tag{3}$$

where function f_j denotes the sorption isotherm of a species j; C_j and S_j are the concentrations of free (mg/ml) and sorbed j (mg/g soil) at sorption equilibrium, respectively.

Several models have been used to describe sorption isotherms. Among them, Linear, Langmuir, and Freundlich isotherm are the most well-known sorption isotherms. Linear isotherm can be simply described as

$$S_j = K_1(j)C_j \tag{4}$$

where $K_1(j)$ is the sorption equilibrium constant of j (ml/g soil) in Linear isotherm. In Langmuir isotherm, the relationship between C_j and S_j is as follows

$$\frac{S_j}{S_{j,\max}} = \frac{K_L(j)C_j}{1 + K_L(j)C_j} \tag{5}$$

where $K_L(j)$ is the sorption equilibrium constant of j in Langmuir isotherm (ml/mg); $S_{j,\max}$ is the maximum of S_j (mg/g soil). Freundlich isotherm is described as

$$S_j = K_F(j)C_j^{n(j)} \tag{6}$$

As shown in Eqs. (4)–(6), two parameters are used for Langmuir isotherm ($K_L(j)$ and $S_{j,\max}$) and Freundlich isotherm ($K_F(j)$ and $n(j)$), whereas only one parameter is used for Linear isotherm ($K_1(j)$). Therefore, Linear isotherm is simple, but least accurate in explaining the sorption data. Parameters of each isotherm model were determined by minimizing the sum of the relative squared errors (SRSE) between experimental data and model predictions

$$\text{SRSE} = \sum_{i=1}^{NP} \left(\frac{S_{j,m}^i - S_{j,d}^i}{S_{j,m}^i} \right)^2 \tag{7}$$

where NP is the total number of data points; $S_{j,m}^i$ is the concentration of sorbed APU of the ith data point predicted by the isotherm model; $S_{j,d}^i$ is the corresponding observed value. This method to determine the goodness of fit based on SRSE is usually called chi-square test [23].

In this study, Linear isotherm was first used to describe the experimental data for the sorption of phenanthrene and APU particles. If Linear isotherm failed in describing the data, Langmuir and Freundlich isotherms were used.

3.3. Distribution of phenanthrene between an aqueous phase and soil

The distribution of phenanthrene between the soil and the aqueous phase in the presence of APU can be described by concentration ratios of phenanthrene in the soil to that in the aqueous phase, as follows [7,8,21,22]

$$K_d = \frac{S_{phe}}{C_{phe}} \tag{8}$$

where K_d is a distribution coefficient of phenanthrene between an aqueous phase and the soil in the presence of APU; S_{phe} denotes the concentration of phenanthrene in the soil (g/g soil).

The mathematical expression of S_{phe} in Eq. (8) varies depending on the participation of sorbed APU particles on the solubilization of phenanthrene. Therefore, K_d can be mathematically calculated using a partition coefficient of phenanthrene between water and APU, and sorption isotherms of phenanthrene and APU. For example, if sorbed APU does not solubilize phenanthrene, S_{phe} in Eq. (8) should account for phenanthrene in soil only

$$S_{phe} = f_{phe}(C_{phe,w}) \tag{9}$$

where f_{phe} denotes the sorption isotherm of phenanthrene. If the sorbed APU solubilizes phenanthrene as well as APU in water, S_{phe} in Eq. (8) should account for phenanthrene not only in soil but also in the sorbed APU particles

$$S_{phe} = S_{phe,S} + C_{phe,m} S_{APU} = f_{phe}(C_{phe,w}) + K_m C_{phe,w} \cdot f_{APU}(C_{APU}) \tag{10}$$

where $S_{phe,S}$ is the concentration of phenanthrene in soil only (mg/g soil); S_{APU} is the concentration of APU in soil (mg/g soil); f_{APU} is the sorption isotherm of APU. If phenanthrene solubilization in the sorbed APU is not as efficient as that in APU particles in water, S_{phe} in Eq. (8) is then

$$S_{phe} = f_{phe}(C_{phe,w}) + \eta K_m C_{phe,w} \cdot f_{APU}(C_{APU}) \tag{11}$$

where η is an effectiveness factor, which is primarily a fitting factor used to describe the limited solubilization of phenanthrene in the sorbed APU particles. Then, Eq. (8) can be rearranged to give

$$K_d = \frac{f_{phe}(C_{phe,w}) + \eta K_m C_{phe,w} \cdot f_{APU}(C_{APU})}{C_{phe,w}(1 + K_m \cdot C_i)} \tag{12}$$

Using Eqs. (2) and (11), $C_{phe,w}$ in Eq. (12) can be calculated from the following mass balance for phenanthrene

$$C_{phe,0} V = C_{phe} V + S_{phe} M_S = C_{HOC,w} V(1 + K_m \cdot C_{APU})$$
$$+ [f_{phe}(C_{phe,w}) + \eta K_m C_{phe,w} \cdot f_{APU}(C_{APU})] \cdot M_S \tag{13}$$

where $C_{phe,0}$ is the initial concentration of phenanthrene in the aqueous phase prior to mixing with APU and the soil (mg/ml); V is the volume of the aqueous phase (ml); M_S is the mass of the soil used in the experiment (g).

Concentrations of APU in the aqueous phase (C_{APU}) can be calculated from the following mass balance

$$C_{APU,0} V = C_{APU} V + f_{APU}(C_{APU}) M_S \tag{14}$$

where $C_{APU,0}$ is the initial concentration of APU in the aqueous phase prior to sorption to the soil (mg/ml).

In this study, K_m and sorption isotherms for phenanthrene (f_{phe}) and APU particles (f_{APU}) were determined from experimental data. Combining Eqs. (12)–(14), K_d was calculated. The value of η was determined by minimizing SRSE between model-predicted and experimentally determined distribution coefficients of phenanthrene (K_d) between the soil and the aqueous phase in the presence of APU.

4. Results and discussions

4.1. Enhanced solubility of phenanthrene in the presence of SDS and APU

In order to investigate the capability of APU particles in solubilizing phenanthrene, the apparent solubility of phenanthrene was measured with the addition of APU particles, and compared with that measured with SDS.

Fig. 1 shows the enhanced solubility of phenanthrene in the presence of SDS or APU particles. The enhanced solubility, defined as $(C - C_0)/C_0$, represents the partition of phenanthrene between SDS or APU and water. C denotes the apparent concentration of phenanthrene in an aqueous solution containing SDS or APU, and C_0 the concentration of phenanthrene in pure water. The solubility of phenanthrene increased with the increase of the APU particle dose, indicating that micelle-like APU particles could solubilize phenanthrene within their hydrophobic interiors, just like surfactant micelles. The enhancement in the solubility of phenanthrene in the presence of any type of APU particles was less than that in the presence of SDS. Among APU particles, UAA 6:4, the most hydrophobic one, showed the highest capability of solubilizing phenanthrene. These results imply that SDS would show a better performance for washing phenanthrene-contaminated soil than APU
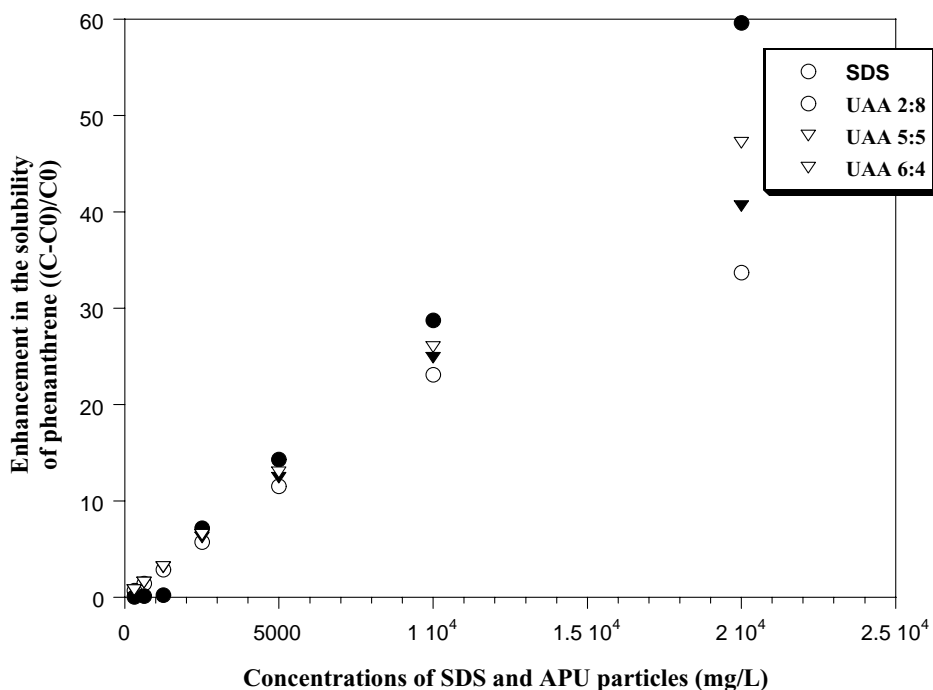

Fig. 1. Enhanced solubility of phenanthrene in the aqueous phase containing SDS or APU particles (*C*: solubility of phenanthrene in the presence of SDS or APU particles; C_0: solubility of phenanthrene in the absence of SDS or APU particles).

Table 3
Partition coefficients of phenanthrene between water and APU particles (K_m)

APU particles	K_m (ml/mg surfactant)
UAA 2:8	1.84 ± 0.11
UAA 5:5	2.14 ± 0.08
UAA 6:4	2.42 ± 0.04

particles used in this study, and that the more hydrophobic APU would be better than the less hydrophobic APU.

As shown in Fig. 1, Eq. (2) gave a satisfactory fit of the experimental data of phenanthrene solubilization in the presence of APU particles. Slopes of the fitting lines are partition coefficients of phenanthrene between water and the tested APU particles, K_m (Table 3). As shown in Table 3, K_m increases as the hydrophobicity of APU particles increases.

Fig. 2 shows surface tension of SDS and APU as a function of concentrations in an aqueous phase. At the same concentration, SDS solutions exhibited a greater decrease in surface tension compared to APU solutions, indicating that SDS molecules have greater interfacial activity. The APU particles are synthesized by polymerization of urethane acrylate anionomers (UAA) in an aqueous phase. They exhibit a micelle-like structure as the hydrophilic moieties (carboxylate anions) of UAA orient toward the aqueous phase to form the ionic exterior, and the cross-linked hydrophobic moieties of UAA make up the hydrophobic interior inside of APU particles [18]. Hence there should not be a dramatic change in the surface tension as shown in Fig. 2, and APU particles do not exhibit Critical Micelle Concentration (CMC).
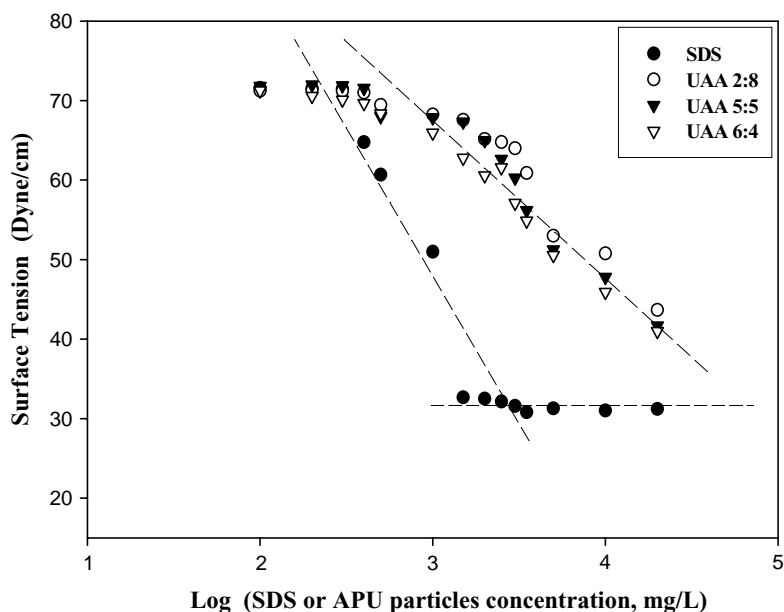

Fig. 2. Surface tension for SDS or APU solutions.

UAA 6:4, which was more hydrophobic than UAA 5:5 and UAA 2:8, had higher surface tension than either UAA 5:5 or UAA 2:8. The surface tension of UAA 5:5 was higher than that of UAA 2:8 at the same concentration. The order of interfacial activities of APU particles used in this study was identical with the order of phenanthrene solubility in the presence of APU.

4.2. Sorption isotherms of phenanthrene, SDS and APU particles to the soil

Fig. 3 shows the sorption isotherm of phenanthrene to the test soil. Linear isotherm model (Eq. (4)) successfully described the experimental data, and the sorption equilibrium constant of phenanthrene (K_1(phe)), the slope of the line in Fig. 3, was 288 ± 1 ml/g soil. If Linear isotherm is used to describe the sorption of a certain hydrophobic organic compound (HOC) to soil, the sorption equilibrium constant on a soil basis, i.e. $K_1(j)$, can be converted to that on a soil organic carbon basis ($K_{OC}(j)$)

$$K_{OC}(j) = \frac{K_1(j)}{f_{OC}} \tag{15}$$

where f_{OC} is the organic carbon content of the soil. Since the organic carbon content of the test soil is 0.53%, K_{OC}(phe) in this study is $54,300 \pm 200$ ml/g organic carbon. The value of K_{OC}(HOC) has been shown to vary widely depending on the composition of soil organic matter (SOM) [24,25]. Hence the value of K_{OC}(phe) in this study (54,300 ml/g organic
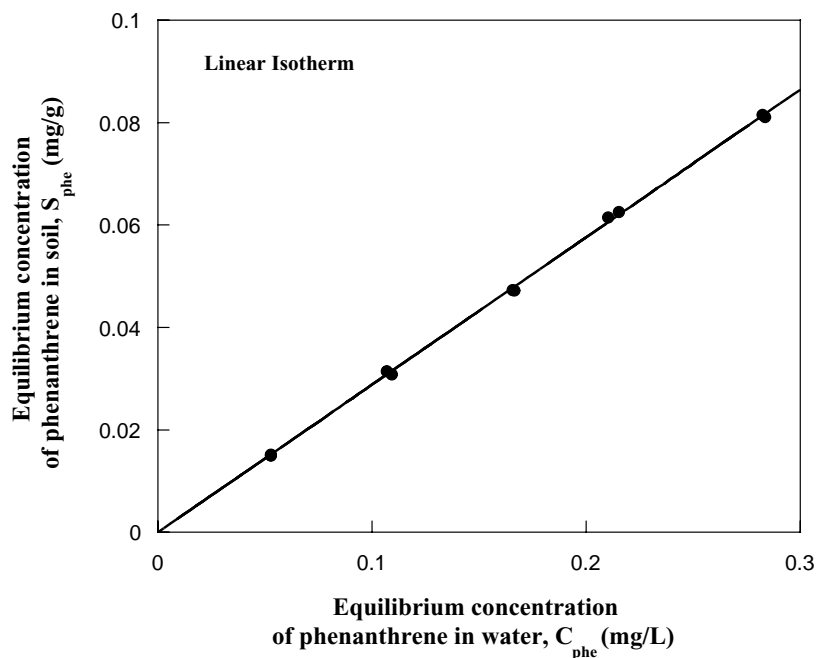

Fig. 3. Sorption isotherm of phenanthrene simulated by Linear isotherm. The slope of the fitting line is the sorption equilibrium constant of phenanthrene, and its value is 288 ± 1 ml/g.
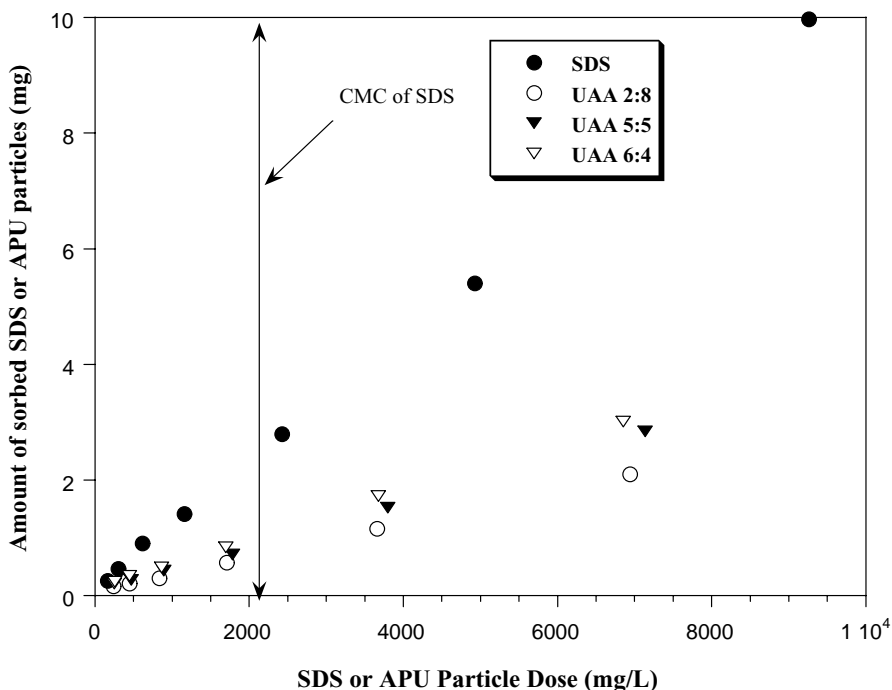
Fig. 4. Sorption of SDS and APU particles to the soil as a function of SDS or APU dose.

carbon) is believed to be in close agreement ($\pm 10\times$) with the reported K_{OC}(phe) values for phenanthrene sorption to a river sediment (22,900 ml/g organic carbon) [26], aquifer sand (42,000 ml/g organic carbon) [27], and humic acid (9800 ml/g organic carbon) [28].

Fig. 4 shows the sorption of SDS and APU particles onto the test soil at various concentrations. In all concentration regions, the sorption of SDS onto the soil is much larger than the sorption of APU particles. This result is mainly due to the structural difference between SDS and APU. Below CMC, SDS molecules exist in water not as micelles but as monomeric molecules and can be easily sorbed onto the soil. Above CMC, SDS molecules exist in water as micelles that are quite stable structures as the hydrophobic moieties of SDS molecules are associated in the core of a micelle by hydrophobic interaction. As shown in Fig. 3, the fraction of sorbed SDS at concentrations above CMC is a little lower than that at concentrations below CMC. It is believed that the interaction of SDS with the test soil was stronger than the hydrophobic interaction of the hydrophobic moieties of SDS molecules, and that the amount of sorbed SDS increased even after the dose of SDS was higher than its CMC. APU is a chemically cross-linked polymer molecule whereas an SDS micelle is a physically self-assembled form of monomeric molecules. Hence the sorption of APU to soil should be lower than that of SDS. Interestingly, the sorption of more hydrophobic APU was higher than that of less hydrophobic APU, and it is believed to be the effect of the soil organic carbon. Organic carbon content of the soil used in this study was 0.53%.
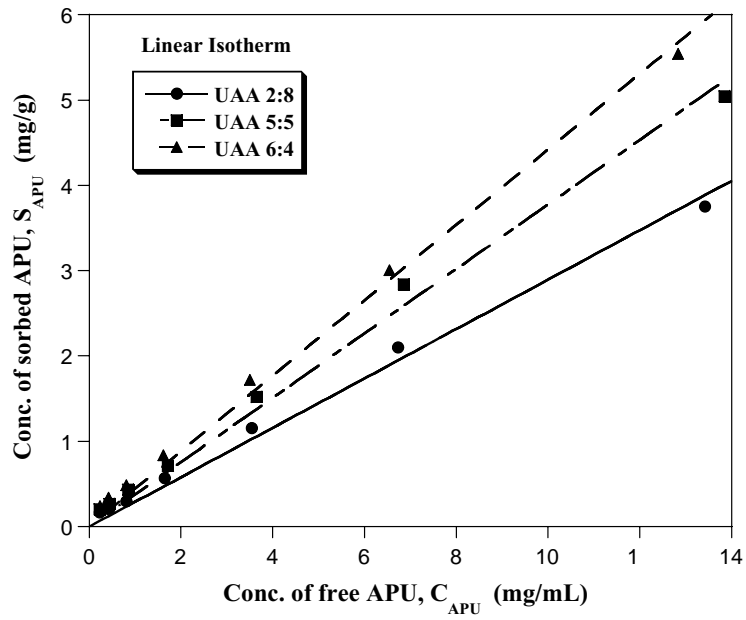
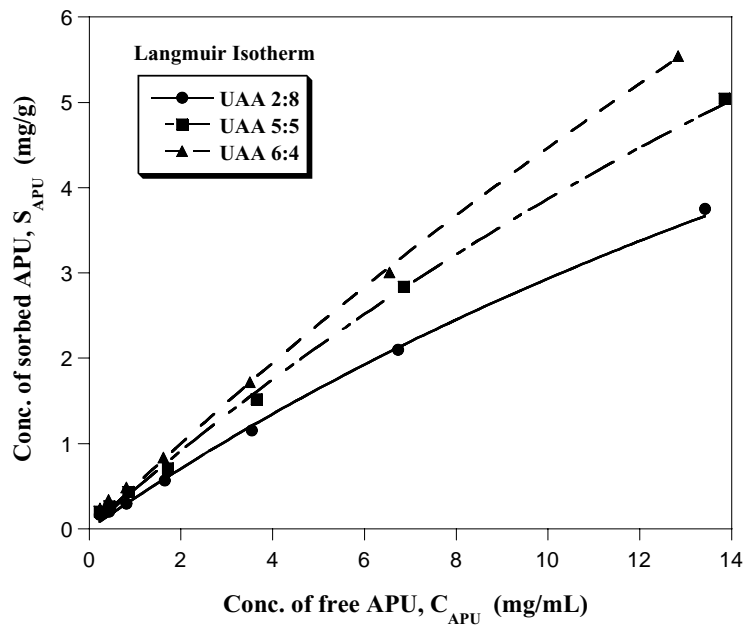Fig. 5. Sorption isotherm of APU particles simulated by Linear isotherm.

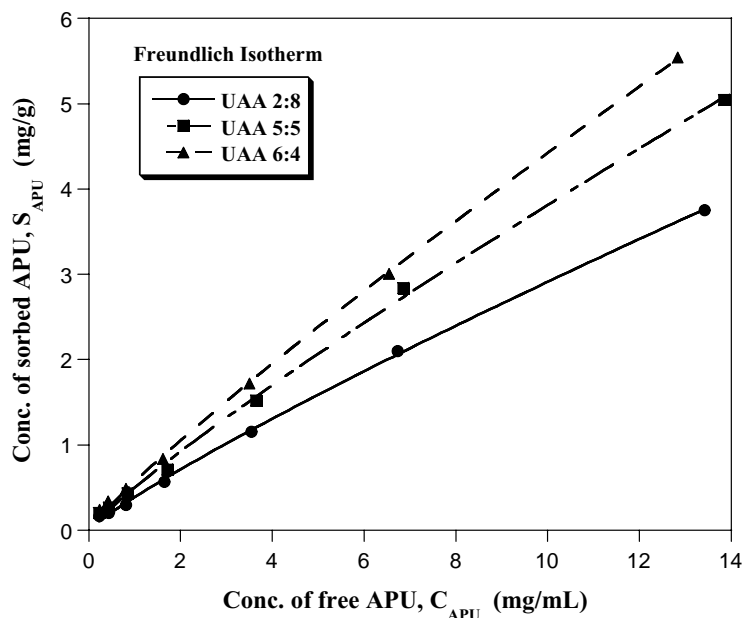Fig. 6. Sorption isotherm of APU particles simulated by Langmuir isotherm.

Fig. 7. Sorption isotherm of APU particles simulated by Freundlich isotherm.

In the previous study [17] where soil with an organic carbon content of 0.049% was used, APU particles did not show a difference in the soil sorption. Solubilization of phenanthrene was largest with the most hydrophobic APU, but the sorption to the soil that should be minimized was smallest for the least hydrophobic APU. Hence, there is a need to scrutinize the distribution of phenanthrene between the soil and the aqueous phase in the presence of APU particles.

The experimental data of APU sorption to the test soil shown in Fig. 4 were curve-fitted with Linear (Eq. (4)), Langmuir (Eq. (5)), and Freundlich isotherms (Eq. (6)), and they are plotted in Figs. 5–7. Model parameters are summarized in Tables 4–6 with the values of SRSE. Correlation coefficients were higher than 0.99 for all isotherm models (data not shown). Langmuir and Freundlich isotherms described the experimental data better than Linear isotherm, so these two isotherms were used in the calculation of the distribution of phenanthrene between the soil and the aqueous phase in the presence of APU particles.

Table 4
Parameters of Linear isotherm model (Eq. (4)) for APU sorption to soil

APU particles (j)	$K_1(j)$ (ml/g soil)	SRSE[a]
UAA 2:8	0.289 ± 0.008	0.0884
UAA 5:5	0.378 ± 0.010	0.1579
UAA 6:4	0.442 ± 0.010	0.1368

[a] SRSE: sum of the relative squared errors.

Table 5
Parameters of Langmuir isotherm model (Eq. (5)) for APU sorption to soil

APU particles (j)	$S_{j,max}$ (mg/g soil)	$K_L(j)$ (ml/mg)	SRSE
UAA 2:8	13.6 ± 2.2	0.0275 ± 0.0058	0.0319
UAA 5:5	19.9 ± 3.3	0.0241 ± 0.0050	0.0201
UAA 6:4	32.6 ± 9.0	0.0159 ± 0.0051	0.0414

Table 6
Parameters of Freundlich isotherm model (Eq. (6)) for APU sorption to soil

APU particles (j)	$K_F(j)$ (mg/g soil)	$n(j)$	SRSE
UAA 2:8	0.391 ± 0.015	0.872 ± 0.017	0.0079
UAA 5:5	0.502 ± 0.028	0.881 ± 0.024	0.0288
UAA 6:4	0.588 ± 0.022	0.891 ± 0.017	0.0169

4.3. Distribution of phenanthrene between the soil and the aqueous phase in the presence of APU particles

Distribution of phenanthrene between the test soil and water was studied with and without the addition of SDS and APU. K_d values are shown in Fig. 8 as a function of initial
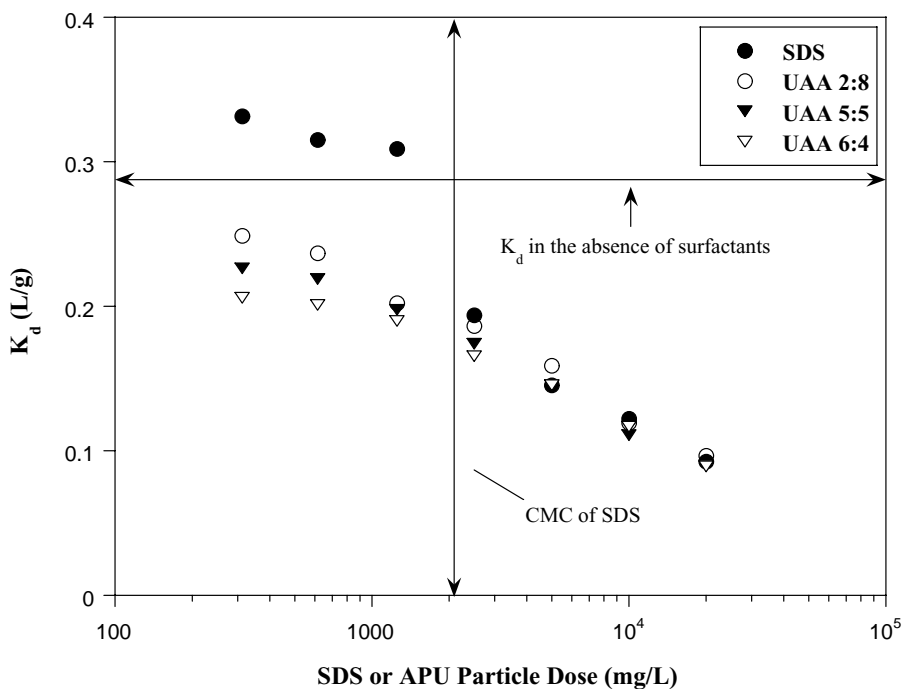

Fig. 8. Distribution of phenanthrene between soil and aqueous phase as a function of SDS or APU dose.

concentrations of SDS or APU. In the absence of SDS and APU particles, the concentration ratio of phenanthrene in the soil to that in pure water was 0.288 l/g. Then sorption behaviors of phenanthrene to the test soil in the presence of SDS and APU can be divided into two regions: one region with K_d higher than 0.288 l/g, and the other region with K_d lower than 0.288 l/g.

With low doses of SDS (312.5–1250 mg/l), K_d values were higher than that in pure water (0.288 l/g), whereas K_d values with the same doses of APU (312.5–1250 mg/l) were lower than 0.288 l/g. With high doses of either SDS or APU particles (2500–20,000 mg/l), K_d values were lower than 0.288 l/g. Even though the enhancement in the solubility of phenanthrene in the presence of SDS was larger than that in the presence of APU in any concentration (see Fig. 1), the sorption of phenanthrene to the soil was reduced not by the addition of SDS but by the addition of APU particles at low doses (312.5–1250 mg/l). Even at the high doses (2500–20,000 mg/l), degrees of phenanthrene sorption to the soil in the presence of SDS were similar to those in the presence of APU. This result is believed to be caused by the larger sorption of SDS to the soil (see Fig. 4). It has been reported that surfactants or organic material sorbed to the soil may result in an enhanced sorption of HOC to the soil [6,8,12,13,19,29].

Comparing three types of APU particles used in this study, a greater reduction of phenanthrene sorption was observed in the presence of the more hydrophobic APU at the low doses (312.5–1250 mg/l). At the high doses (2500–20,000 mg/l), the degrees of phenanthrene sorption were quite similar regardless of the hydrophobicity of APU. To predict K_d values for APU particles, the model (Eq. (12)) was used assuming that sorbed APU does
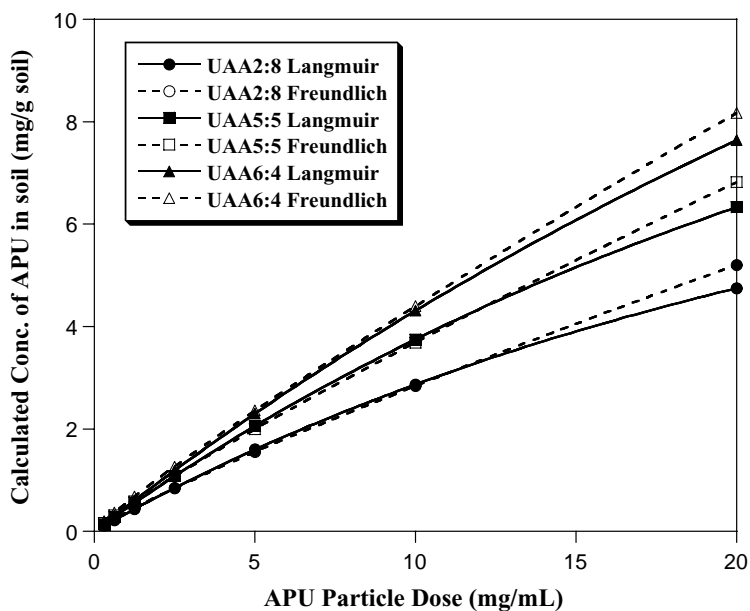

Fig. 9. Concentrations of APU particles in the soil (S_{APU}) calculated from Eq. (14) using Langmuir isotherm or Freundlich isotherm.
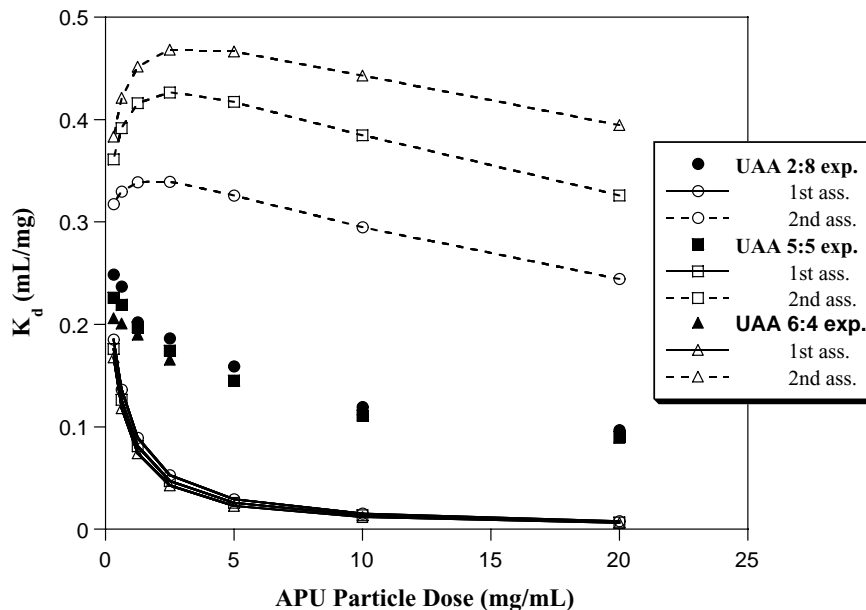
Fig. 10. Distribution coefficients of phenanthrene between the soil and the aqueous phase in the presence of APU particles. Model predictions were performed with assuming either that sorbed APU particles do not solubilize phenanthrene (first assumption), or that sorbed APU particles solubilize phenanthrene as well as free APU particles (second assumption). Experimentally determined K_d values are denoted by filled symbols, while K_d values calculated based on the first assumption are depicted by dashed lines (- - -), and K_d values calculated based on the second assumption are shown by solid lines (—).

not solubilize phenanthrene ($\eta = 0$ in Eq. (12)) or that sorbed APU solubilizes phenanthrene as well as APU in the aqueous phase ($\eta = 1$ in Eq. (12)). Concentrations of APU in the aqueous phase (C_{APU}) and in the soil (S_{APU}) were calculated from Eq. (14), using Langmuir isotherm (Eq. (5) and Table 5) or Freundlich isotherm (Eq. (6) and Table 5). The values of C_{APU} were almost the same, regardless of the type of APU particles and of sorption isotherms (data not shown). The values of S_{APU} calculated using these two isotherms are shown in Fig. 9. The values of K_d were calculated from Eq. (12) with $\eta = 0$ or 1 are shown in Fig. 10 with the experimentally determined K_d. For all three types of APU particles, the model prediction with $\eta = 0$ underestimated K_d while the model prediction with $\eta = 1$ overestimated. A possible explanation for the failure in the model prediction is that solubilization of phenanthrene in sorbed APU particles would be limited compared to that in free APU particles. Sorption of APU particles was not affected by the addition of phenanthrene (data not shown), and it cannot explain the failure in the model prediction. To incorporate the limited solubilization of phenanthrene in sorbed APU particles in the model, various values of η as a fitting factor were considered on a trial and error basis. The values of K_d calculated with $\eta = 0.425$ for UAA 2:8, $\eta = 0.30$ for UAA 5:5, and $\eta = 0.25$ for UAA 6:4 were in good agreement with the experimentally determined coefficients as shown in Fig. 11.
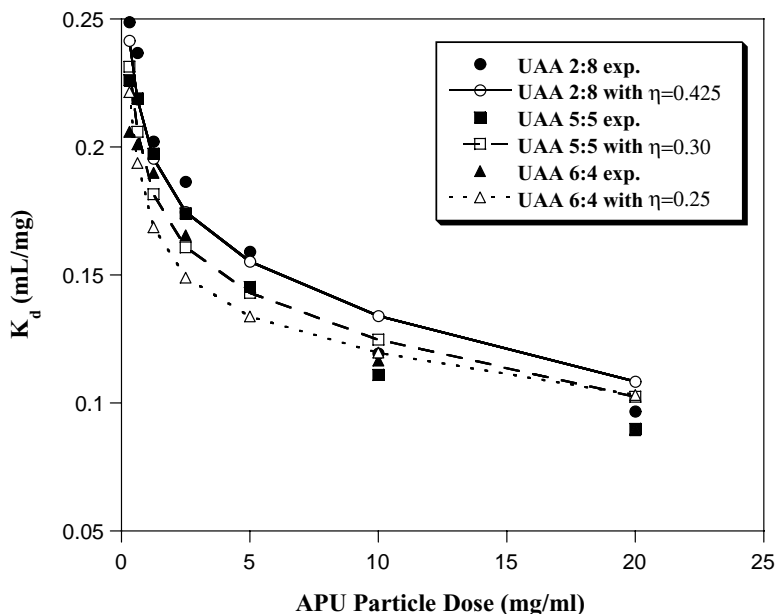
Fig. 11. Distribution coefficients of phenanthrene between the soil and the aqueous phase in the presence of APU particles. Model predictions were performed assuming $\eta = 0.425$ for UAA 2:8, $\eta = 0.3$ for UAA 5:5, and $\eta = 0.25$ for UAA 6:4. Experimentally determined K_d values are denoted by filled symbols, while mathematically calculated K_d values for UAA 2:8, UAA 5:5, and UAA 6:4 are shown by a solid line (—), a dashed line (- - -), and a dotted line ($\cdots$), respectively.

Chiou [12] and Lee et al. [13] suggested that: (i) sorption of conventional surfactants to soil took place not only by adsorption to soil mineral matter but also by partition into soil organic matter; (ii) the surfactants partitioned into SOM were not be subject to aggregation and HOC solubilization in the micelle could not be expected; (iii) only the adsorbed surfactants could form a molecular aggregation and solubilize HOCs inside. However, APU particles sorbed to SOM as well as to soil mineral matter are believed to solubilize phenanthrene inside. This is because APU particles used in this study are polymeric molecules in which surfactant-like urethane acrylate anionomers are aggregated by a chemical cross-linking. But phenanthrene solubilization inside APU particles sorbed to SOM should be less efficient than that inside APU particles sorbed to soil mineral matter due to the hydrophobic nature of SOM. As shown in the experimental results of APU sorption, the sorption of more hydrophobic APU was larger than that of less hydrophobic APU. Also the fraction of APU sorbed to SOM in total APU sorbed to the soil would be higher for more hydrophobic APU due to the hydrophobic nature of SOM. Therefore, the effectiveness of phenanthrene solubilization inside sorbed APU particles (η) should be lower for more hydrophobic APU than that for less hydrophobic APU.

Consequently, it can be tentatively concluded that the relatively low degree of sorption to the soil causes APU particles to effectively reduce phenanthrene sorption to the soil, regardless of their relatively low solubilization capacity of phenanthrene. Also the similar

conclusion can be made to APU particles with different hydrophobicity. Even though an APU particle with the lower hydrophobicity has a lower capability of solubilizing phenanthrene than an APU particle with the higher hydrophobicity, it can exhibit the similar or even higher reduction of phenanthrene sorption to the soil because of its relatively lower degree of sorption to the soil, especially to SOM.

5. Conclusions

Micelle-like amphiphilic APU particles exhibited a greater reduction of phenanthrene sorption to the soil than SDS below CMC of SDS, and a similar reduction above CMC of SDS, even though enhancement of phenanthrene solubility by APU was less than that by SDS at any concentration. This is believed to be due to the lower sorption of APU to the soil than that of SDS. APU particles with different hydrophobicity showed similar reduction of phenanthrene sorption to the soil regardless of their hydrophobicity, even though enhancement of phenanthrene solubility was greatest with the addition of the most hydrophobic APU particles. This result is also believed to be caused by the difference in APU sorption to the soil. Sorption of APU particles to the test soil with an organic carbon content of 0.53% increased as the hydrophobicity of added APU particles increased. A mathematical model was developed to describe the phenanthrene distribution between soil and an aqueous phase containing APU particles. The sorption of phenanthrene and APU to the test soil could be well described by Linear isotherm and Langmuir or Freundlich isotherm, respectively. The partition of phenanthrene between water and APU was successfully explained with a single partition coefficient. The model, which accounts for the limited solubilization of phenanthrene in sorbed APU particles, successfully described the experimentally determined distribution coefficients of phenanthrene between the soil and the aqueous phase in the presence of APU particles. From this study, it can be concluded that the soil washing performance of interfacial agents such as SDS and APU strongly depends not only on their capability of solubilizing hydrophobic contaminants, but also on their sorption to a target soil.

Acknowledgements

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