



# Effect of amphiphilic polyurethane nanoparticles on sorption–desorption of phenanthrene in aquifer material

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## Abstract

Micelle-like amphiphilic nano-sized polyurethane (APU) nanoparticles were synthesized via chemical cross-linking reaction of nano-aggregates of urethane acrylate nonionomer (UAN) chain and were tested for extraction efficiency of sorbed phenanthrene from aquifer material. Even though the solubilizing performance and interfacial activity of APU nanoparticles were inferior to that of Triton X-100, in the low concentration region, APU nanoparticles could effectively reduce phenanthrene sorption on the aquifer material and extracted sorbed phenanthrene from the aquifer material, whereas Triton X-100 could not extract sorbed phenanthrene and rather increased phenanthrene sorption onto the aquifer materials. At higher concentrations, APU nanoparticles and Triton X-100 had almost the same soil washing effectiveness. This interesting result is mainly due to a lower degree of sorption of APU nanoparticles onto the aquifer material. The sorption of APU nanoparticles onto aquifer sand is largely hindered by their chemically cross-linked nature, resulting in better soil-washing performance of APU nanoparticles than Triton X-100.

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## 1. Introduction

Contamination of soil and groundwater by hydrophobic organic carbons (HOCs) is caused by leakage from storage tanks, spillage, or improper disposal of wastes. Once in the soil matrix, HOCs are a source of dissolved contaminants [1–5]. Among HOCs, polyaromatic

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hydrocarbon (PAH) are of special interest because they are strongly sorbed to soil or sediment, as a consequence, sorbed PAHs may act as a long-term source of groundwater contamination. Consequently many researchers have been using surfactants to enhance desorption of sorbed PAHs from soil through solubilization of sorbed PAHs in surfactant micelles [6–13]. Surfactant-enhanced remediation techniques have shown significant potential in their application to the removal of PAHs in the soil remediation process. Some of the disadvantages of these techniques are micelle breakage and loss of surfactant through sorption to soil. In addition, Surfactant-enhanced desorption and washing process is only effective when surfactant dose is greater than its critical micelle concentration (CMC), because most of surfactant molecules below CMC are sorbed onto soil below its CMC [8–11,14–16]. As a result, recent research has been directed towards the design of a surfactant that minimizes their losses and the development of surfactant recovery and recycling technique. The purpose of this work is to evaluate the potential for and advantages of novel amphiphilic polyurethane (APU) nanoparticles for the in situ extraction of sorbed PAHs.

Amphiphilic polyurethane nanoparticles, formed by amphiphilic urethane acrylate, represent a microphase-separated structure similar to that of surfactant micelles and can form very stable dispersions at aqueous phase. In our previous paper, we reported on the extraction of sorbed phenanthrene from aquifer materials using anionic cross-linked polyurethane nanoparticles dispersed at aqueous phase [17]. These nanoparticles were shown to adsorb weakly to a sandy aquifer in batch experiments, which is attributed to the chemically cross-linked nature of their microstructure. In most of the tests with the anionic cross-linked polyurethane nano-network emulsions, a very high level (95%) of the hydrophobic tested pollutant (phenanthrene) was extracted from the aquifer sand with extremely low loss of the applied nanoparticles. Relatively few pore volume washings were needed to achieve a high level of remediation. However, these anionic polyurethane nanoparticles were easily and rapidly aggregated in the presence of ionic compounds such as  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , etc. This finding led us to develop stable polyurethane nanoparticles at aqueous solution containing large amount of ionic compounds. We synthesized a new kind of amphiphilic urethane acrylate nonionomer (UAN) chain that has hydrophilic polyethylene oxide (PEO) pendant chain and polypropylene oxide (PPO)-based hydrophobic backbone. This chain can form very stable amphiphilic polyurethane (APU) nanoparticles at aqueous phase whose structure is similar to that of nonionic surfactant micelle.

This research focused on the application of APU nanoparticles to remove sorbed PAHs, so we present here distribution data for phenanthrene between the aqueous phase and aquifer materials as well as information on the desorption of sorbed phenanthrene from aquifer materials in the presence of APU nanoparticles. These results are compared with batch systems containing nonionic surfactant, Triton X-100, aquifer materials and phenanthrene aqueous solution.

## 2. Experimental methods

### 2.1. Materials

Phenanthrene was used as a model polyaromatic hydrocarbon (PAH). Its aqueous solubility of phenanthrene is reported to be 1.29 mg/l, and its octanol–water partition coefficient is

3700 [18]. Radio-labeled phenanthrene was purchased from Sigma ( $9\text{-}^{14}\text{C}$ ,  $13.1\ \mu\text{Ci}/\mu\text{mol}$ ). The aquifer sand used in all experiments was obtained from a quarry in Newfield, NY, USA. The organic content of the sand was reported to be  $0.049 \pm 0.012\%$  [18]. A size analysis of the sand has been previously reported and revealed that 47.2 and 47.6% of the sand were in the fine (0.1–0.25 mm) and medium (0.25–0.5 mm) size ranges, respectively [18]. The remaining constituents include very fine sand (0.05–0.1 mm) at 3.7%, coarse sand (>0.5 mm) at 0.2%, and silt and clay at 1.2%.

In the synthesis of amphiphilic urethane acrylate nonionomer (UAN) precursor chains, poly(propylene oxide triol) (PPO triol, MW = 700 and 1000, Korea Polyol), 2,4-toluene diisocyanate (TDI, Aldrich), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich), and polyethylene glycol (PEG, Mw = 600 and 1500, Aldrich) were used as received. Potassium persulfate (KPS, Wako Pure Chemicals Co.) was recrystallized from distilled deionized (DDI) water.

## 2.2. Synthesis of amphiphilic urethane acrylate nonionomer (UAN) and amphiphilic polyurethane (APU) nanoparticles

The synthesis of a UAN chain, schematically illustrated in Fig. 1, was carried out through three-step process. Each reaction was performed in a 500 ml four-neck vessel with stirrer, thermometer, and an inlet system for nitrogen gas. The detailed synthetic procedure was illustrated in our previous papers [19,20]. The molar ratio of TDI/PPO triol/2-HEMA/PEG was 3/1/2/1. The polystyrene equivalent molecular weight of synthesized UAN chains is a 3750–6700 weight average molecular weight with a polydispersity of 1.93–2.01. Components used to synthesize UAN nanoparticles is summarized in Table 1. The characterization of synthesized UAN chains based on  $^1\text{H-NMR}$  spectra was reported in our preceding papers [19,20].

To prepare amphiphilic polyurethane (APU) nanoparticles dispersed in water, UAN chains were first mixed with distilled deionized water with vigorous stirring. Obtained UAN emulsions were then cross-linked via polymerization in the presence of potassium persulfate (KPS) to form APU nanoparticles dispersed in water. Initiator radicals first formed in the aqueous phase penetrate into the oil phase to initiate the cross-linking reaction between the vinyl end-groups of the precursor UAN chains. The nanoparticle synthesized using UAN 700-1, 700-2, and 1000 chain is named as APU 700-1, 700-2, and 1000 nanoparticles, respectively. The chemical components used for the synthesis of APU nanoparticles are summarized at Table 2.

The size of the prepared APU nanoparticles was measured by dynamic light scattering measurement. Particle sizes were in the range of 23.4–32.10 nm. As the chain length of

Table 1  
Components for the synthesis of UAN chains and their molecular weight

Molar ratio of TDI/PPO triol/HEMA/PEG	Mw of PPO triol	Mw of PEG	Symbol	Mw of UAN
3/1/2/1	700	600	UAN 700-1	3750
3/1/2/1	700	1500	UAN 700-2	4120
3/1/2/1	1000	1500	UAN 1000	6700

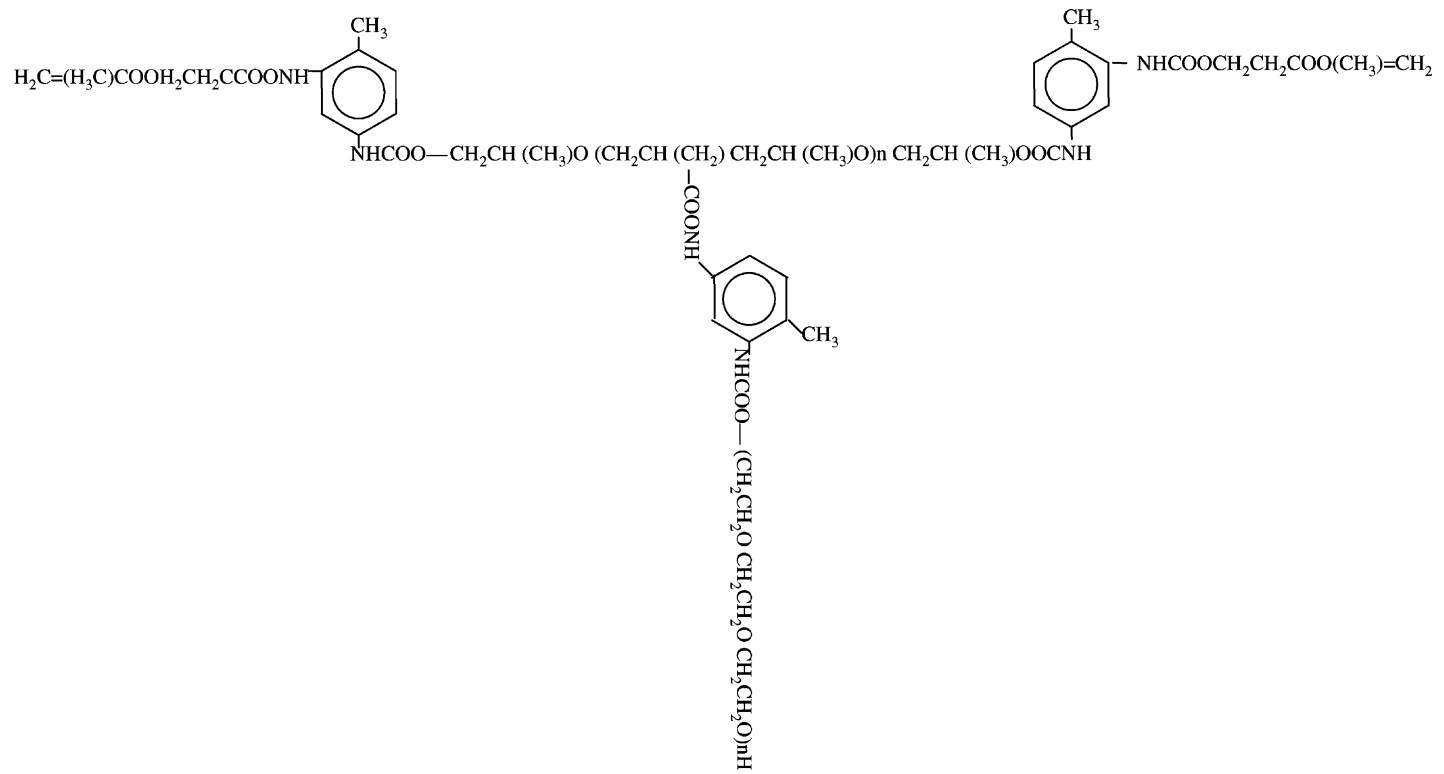


Fig. 1. Schematic presentation of the molecular structure of UAN chains.

Table 2  
Components for the synthesis of APU particles and size of APU particles

	Ingredient			Particle Size (nm)
	UAN (18 g)	Water (g)	KPS (g)	
APU 700-1	UAN 700-1	62	0.05	Aggregated
APU 700-2	UAN 700-3	62	0.05	32.10
APU 1000	UAN1000	62	0.05	23.40

APU: amphiphilic polyurethane nanoparticles; UAN: urethane acrylate nonionomer; KPS: potassium persulfate.

polyethylene glycol increased, size of APU nanoparticle decreased (Table 2). Among UAN chains, UAN 700-1 did not form a stable dispersion (APU 700-1 nanoparticles) in water. Therefore, each experiments in this study was carried out using APU 700-2 and APU 1000 nanoparticles.

### 2.3. Solubilization of crystalline phenanthrene with Triton X-100 or APU solutions

The solubility of phenanthrene in surfactant or APU solutions was determined using a mixture of radio-labeled phenanthrene and nonlabeled phenanthrene [6]. Concentrated phenanthrene solutions (35 g/l) were prepared in methylene chloride. Phenanthrene solution 2 ml was placed in a 25 ml glass scintillation vial equipped with open-top screw caps and Teflon-backed septa. After evaporation of the methylene chloride, Triton X-100 or APU aqueous solutions (10 ml) of various concentrations was added to the vials. The concentration of Triton X-100 and APU nanoparticles in the aqueous solution was 93–2000 mg/l and 138–140,000 mg/l, respectively. Since a amount of phenanthrene remaining in the vials was much greater than the solubility of phenanthrene in water, the loss of phenanthrene due to evaporation was inconsequential [6]. The vials were sealed and gently agitated with a rotary tumbler for 7 days. After completion of mixing, 5 ml of supernatant was withdrawn and centrifuged at an acceleration  $15,000 \times g$ . One milliliter sample was transferred into a scintillation vial containing 10 ml of Ecolume cocktail, and the concentrations of  $^{14}\text{C}$ -phenanthrene in the aqueous phase was measured using a liquid scintillation counter (LSC). At least four replicate experiments were performed for each condition.

### 2.4. Sorption of APU nanoparticles and Triton X-100 onto the aquifer material

In the sorption of APU nanoparticles or Triton X-100 onto aquifer sand, 1 g of sand was mixed with 10 ml of APU emulsions (138–140,000 mg/l) or Triton X-100 (93–95,000 mg/l) solutions of various concentrations in glass vials with a screw cap. After the vials were rotated end-over-end for 2 days, 5 ml of supernatant was withdrawn from each and centrifuged at  $15,000 \times g$  to separate the sand from the APU emulsion. At least four replicate experiments were performed for each condition. To determine the sorbed amount of APU nanoparticles to the aquifer sand, the change in the concentration of APU nanoparticles was measured before and after mixing with the aquifer sand. The concentration of APU nanoparticles

(219 nm) and Triton X-100 (275.5 nm) in aqueous phase was determined using UV-Vis spectrophotometer (Shimadzu 3210).

### 2.5. Surface tension tests

The surface tension of the Triton X-100 solution and APU solutions was determined with a Model 20 surface tensiometer (Fisher Scientific.). This instrument operates on the du Nöuy principle using a platinum ring suspended from a torsion balance. Each aqueous sample was tested with the tensiometer at controlled temperature (25 °C) until at least three consistent surface tension reading were obtained. Between each reading, the ring was cleaned with acetone and heated to redness in a gas flame.

### 2.6. Phenanthrene distribution between aqueous phase and aquifer material

Many researchers have represented the sorption of hydrophobic organic compounds (HOC) on the soil or sediment in terms of the distribution of compounds between the soil and aqueous solutions. The distribution of HOC between the aqueous phase and the soil is significantly changed with the addition of surfactant, because surfactant molecules enhance the apparent solubility of HOC in aqueous phase through micellar solubilization of HOC [6–13,21,22]. The partitioning of HOC in soil can be reduced by the surfactant molecules existing in aqueous phase. Consequently, this distribution of compounds can be used as an index for evaluating the soil-washing performance of a surfactant and estimated as [9–11].

$$K_d = \frac{[\text{HOC}]_s}{[\text{HOC}]_w + [\text{HOC}]_{\text{mic}}} = \frac{\text{mol. of HOC sorbed/g of solid}}{\text{mol. of HOC in aqueous and micellar solution/l}}$$

where  $K_d$  is the partition coefficient of HOC between solid and aqueous-pseudophase,  $[\text{HOC}]_s$  is a ratio of the moles of HOC sorbed per gram of solid (mol/g),  $[\text{HOC}]_w$  is a ratio of the moles of HOC in water per liter of solution (mol/l), and  $[\text{HOC}]_{\text{mic}}$  is the moles of HOC in micelles per liter of solution (mol/l).

To determine  $K_d$  of phenanthrene between aquifer material and aquifer phase in the absence and presence of interfacial agents, three kinds of batch tests were conducted as follows.

### 2.7. Protocol I: Distribution of phenanthrene between aquifer material and pure water

A  $^{14}\text{C}$ -phenanthrene solution (activity 0.056–0.068  $\mu\text{Ci/ml}$ ) was prepared by a method described previously [23,24]. For the sorption of phenanthrene onto the aquifer, 1 ml of the  $^{14}\text{C}$ -phenanthrene from the prepared solution was placed in a glass vial with a screw cap. The different vials were filled with varying amounts of sand. The samples were agitated using a rotary tumbler for 1 day. Supernatant (5 ml) was withdrawn and centrifuged at an acceleration  $15,000 \times g$  to separate the soil from the aqueous solution. One milliliter sample was transferred into scintillation vials (Poly-Q vial P/N 566740, Beckman Coulter, USA) containing 10 ml of Ecolume cocktail (Ready Safe P/N 141349, Beckman Coulter, USA) and

the concentrations of  $^{14}\text{C}$ -phenanthrene in the aqueous phase was measured using a liquid scintillation counter (LSC). At least four replicate experiments were performed for each test.

### 2.8. Protocol II: Distribution of phenanthrene between aquifer material and aqueous pseudophase

A 9 ml Triton X-100 solution (93–95,000 mg/l) or APU emulsion (138–140,000 mg/l) of various concentrations and 1 ml of  $^{14}\text{C}$ -phenanthrene aqueous solution was simultaneously added into scintillation vials containing 1 g of aquifer, and then the vials were agitated using a rotary tumbler for 2 days. After completion of mixing, the vials were then centrifuged ( $15,000 \times g$ ) to separate the soil from the aqueous solution. Supernatant (1 ml) was withdrawn was transferred into scintillation vials containing 10 ml of Ecolume cocktail, and the concentrations of  $^{14}\text{C}$ -phenanthrene in the aqueous phase was measured using a liquid scintillation counter (LSC). At least four replicate experiments were performed for each variable.

### 2.9. Protocol III: Desorption of sorbed phenanthrene by Triton X-100 or APU nanoparticles

A  $^{14}\text{C}$ -phenanthrene aqueous solution (1 ml) was placed in a scintillation glass vial containing 1 g of aquifer sand and agitated using a rotary tumbler for 2 days. After completion of mixing, 9 ml of Triton X-100 solution (93–95,000 mg/l) or APU emulsion (138–140,000 mg/l) of various concentrations was placed in the vials, and re-agitated using a rotary tumbler for 2 days, at which point they were then centrifuged ( $15,000 \times g$ ) to separate the soil from the aqueous solution. A 1 ml samples of supernatant was withdrawn was transferred into scintillation vials containing 10 ml of Ecolume cocktail, and the concentrations of  $^{14}\text{C}$ -phenanthrene in the aqueous phase was measured using a liquid scintillation counter (LSC).

## 3. Results and discussions

### 3.1. Enhanced solubility of phenanthrene

Amphiphilic molecules, surfactant can increase solubility of HOC molecules in water phase because the hydrophobic core of surfactant micelles can accommodate a certain amount of lipophilic organic compound as a solubilize. This solubilization capability of surfactant makes itself useful materials for soil-washing process. So, the enhanced solubility of a certain HOC by a surfactant can be used as an index for evaluating a surfactant for soil-washing process and wastewater treatment process for sorbed and solubilized HOC. To investigate the effectiveness of APU nanoparticles in solubilizing a given HOC, the apparent solubility of phenanthrene in water in the presence of APU nanoparticles was examined and compared with Triton X-100 solution.

Fig. 2 shows enhanced solubility of phenanthrene in the presence of APU nanoparticles or Triton X-100. The enhanced solubility ( $C/C_0$ ) represents an increase of phenanthrene

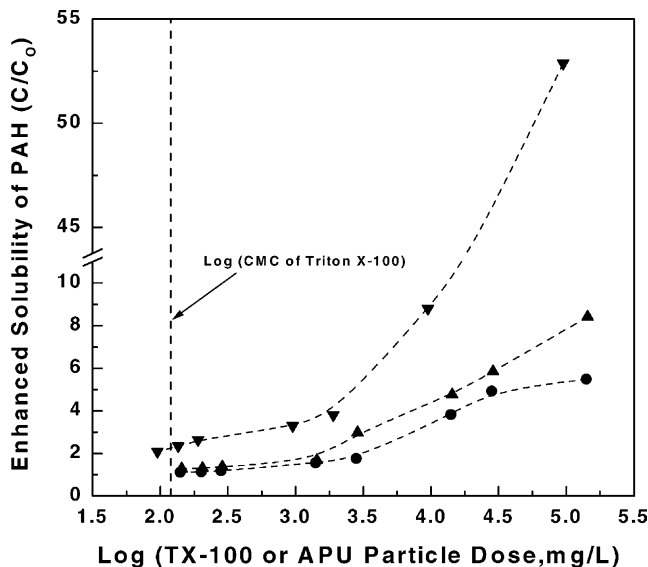


Fig. 2. Enhanced solubility of phenanthrene at aqueous phase in the presence of Triton X-100 or APU nanoparticles: (●) APU 700-2; (▲) APU 1000; and (▼) Triton X-100.

solubility in water:  $C$  is the concentration of phenanthrene in aqueous solution containing APU nanoparticles or Triton X-100 and  $C_0$  is the concentration of phenanthrene in pure water phase. The solubility of phenanthrene in the aqueous phase increases with the increase of APU nanoparticle dose in aqueous solution, indicating micelle-like APU nanoparticles can solubilize phenanthrene within their hydrophobic interiors just like the solubilization of HOC in surfactant micelles. At the same concentration (2000 mg/l), Triton X-100 micelles and APU nanoparticles can solubilize approximately 50 times and 3.7–4.8 times, respectively the phenanthrene that an equal amount of pure water will solubilize. Our results indicates that APU nanoparticles can solubilize phenanthrene within their hydrophobic interior but the solubilizing efficiency of APU nanoparticles for phenanthrene is much worse than that of Triton X-100 solutions.

An alternative method in quantifying surfactant solubilizing performance for HOC is measuring the distribution of HOC between micelles and water phase. This result can be represented as partition coefficient,  $K_m$ , and be calculated by using the following formula [9–13,16]:

$$K_m = \frac{X_m}{X_a}$$

where  $X_m$  and  $X_a$  denotes the mole fraction of HOC in the micelles and the mole fraction of HOC in aqueous phase, respectively.

In our preceding paper, the  $\log K_m$  values in APU nanoparticle solutions were examined and compared to those of Triton X-100 solutions [20].  $\log K_m$  values in APU nanoparticle solution were in the range of 2.25–2.55 which is much smaller than that of phenanthrene in



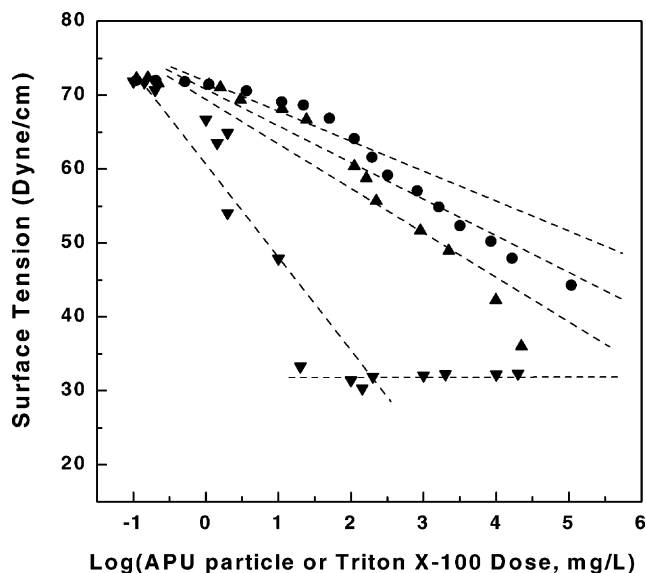


Fig. 3. Surface tension for Triton X-100 and APU nanoparticle solutions: (●) APU 700-2; (▲) APU 1000; and (▼) Triton X-100.

Triton X-100 solution ( $\log K_m = 5.70$ ) as reported at previous papers [6,16]. The foregoing results show that APU nanoparticles have a lower solubilizing efficiency and affinity with phenanthrene than Triton X-100.

Fig. 3 shows surface tension as a function of concentration of APU nanoparticles and Triton X-100 in an aqueous phase. At the same concentration, Triton X-100 solutions exhibited a greater decrease in surface tension compared to APU nanoparticles solutions, indicating that Triton X-100 molecules have greater interfacial activity.

APU 1000 nanoparticles had a lower surface tension at the same concentrations and greater decrease in surface tension, compared to APU 700-2, which is identical with the order of enhanced solubility of phenanthrene in APU solutions. APU nanoparticles used in this study were synthesized with the different UAN chains having different chain length of polyethylene oxide (PEO) and polypropylene oxide (PPO) segment, so that these nanoparticles have different hydrophilic/hydrophobic balances, resulting in different affinity with phenanthrene. APU 1000 nanoparticles, having the longer PPO and PEO chains solutions, show the greater degree of decrease in surface tension than APU 700-2.

### 3.2. Sorption of phenanthrene on aquifer sand

Phenanthrene aqueous solution, and Triton X-100 or APU nanoparticles were simultaneously added to scintillation vials containing aquifer sand and mixed for 2 days (Protocol II) to measure the distribution of phenanthrene between the aquifer sand and aqueous phase. Results were expressed as the  $K_d$  value of phenanthrene and plotted in Fig. 4 as a function of concentration of Triton X-100 or APU nanoparticles in aqueous phase. In the absence

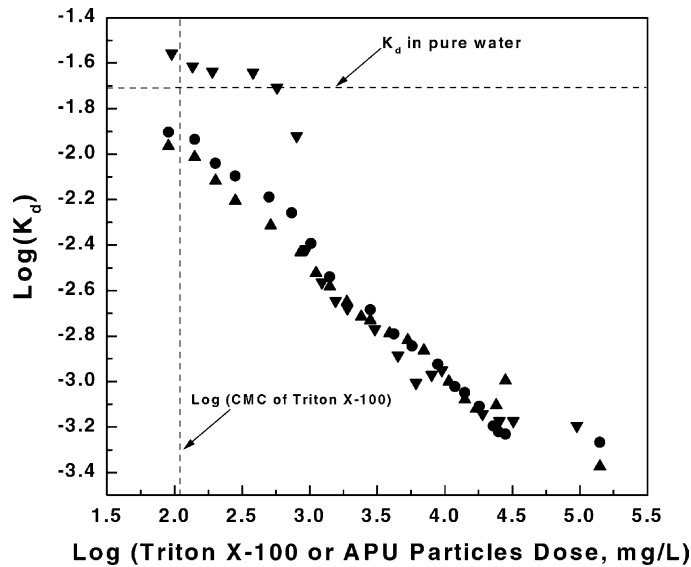


Fig. 4. Distribution of phenanthrene between soil and aqueous pseudophase containing Triton X-100 or APU nanoparticles: (●) APU 700-2; (▲) APU 1000; and (▼) Triton X-100.

of APU nanoparticles or Triton X-100 in the aqueous phase, the  $\log(K_d)$  of phenanthrene is  $-1.7037$  l/g, which was determined based using Protocol I. This value indicates the distribution of phenanthrene between pure water and aquifer sand. The sorption behavior of phenanthrene onto aquifer sand in the presence of Triton X-100 and APU nanoparticles can be divided into two regions according to their concentrations.

In the low concentration region (93–600 mg/l),  $\log(K_d)$  values in Triton X-100 solutions are larger than that in pure water ( $-1.7037$  l/g), indicating that the sorption of phenanthrene onto the aquifer soil is increased by Triton X-100 existing at aqueous phase. For APU 700-2 and 1000 nanoparticles, however,  $\log(K_d)$  values are smaller than  $-1.7037$  l/g, indicating that APU 700-2 and APU 1000 nanoparticles can reduce the sorption of phenanthrene onto the aquifer sand at relatively low concentrations. Although CMC of Triton X-100 is 112.5 mg/l, Triton X-100 could reduce sorption of phenanthrene when the concentration is greater than 574 mg/l that is five times greater than its CMC. In high concentration region (700–14,000 mg/l) that is much greater than CMC of Triton X-100, APU nanoparticles and Triton X-100 exhibited almost same values of  $K_d$  at this concentration.

Even though Triton X-100 exhibited much greater solubility enhancing performance and interfacial activity than APU 700-2 and APU 1000 nanoparticles (see Figs. 2 and 3), in the low concentration region, APU nanoparticles exhibited a greater reduction of phenanthrene sorption compared to Triton X-100. In the higher concentration region, APU nanoparticles and Triton X-100 showed almost the same reduction of phenanthrene sorption. This result can be interpreted in terms of microstructural difference between Triton X-100 and APU nanoparticles.

### 3.3. Microstructural difference of APU nanoparticles and surfactant micelles

The surfactant can exist in a soil/aqueous phase as a dissolved monomer or aggregate of monomers called micelles [7,9–11,25], i.e. aqueous pseudophase of surfactants consists of the micelles and dissolved monomers of surfactants in water. When the concentration of surfactant is equal to or greater than its CMC, surfactant molecules form micelles via aggregation of surfactant monomers. At surfactant concentrations less than CMC, surfactant monomers completely dissolve in the aqueous phase.

Unlike surfactant molecules that completely dissolve in water below its CMC, UAN chains can not be dissolved in water but are just dispersed in water to form nano-aggregates (APU nanoparticles) even at extremely low concentrations, because whole UAN chains are insoluble in water. As illustrated at Fig. 1, UAN chains have hydrophobic polypropylene oxide (PPO)-based segment and hydrophilic polyethylene oxide (PEO) segment at the same chain. Water is a good solvent for PEO segments in UAN chains but is not a solvent for PPO chains. On contacting water, water-soluble PEO segments in UAN chains are microphase separated from hydrophobic segment and oriented toward water phase to form outer layer. Hydrophobic PPO-based segments are associated with each other to form hydrophobic interior, leading to form micelle-like nano-sized aggregates of UAN chains (APU nanoparticles) (Fig. 5). Finally, this aggregate structure of APU nanoparticles is permanently locked-in by chemical cross-linking reaction.

As illustrated in Fig. 3, as the concentration of the Triton X-100 from the base case of no Triton X-100 increases in the aqueous solution, the surface tension of the solution is abruptly changed and remains constant with concentration, whereas surface tension of APU solutions decreases linearly. This result indicates that unlike Triton X-100, UAN chains do not have a critical concentration to form nano-aggregates like micelles (APU nanoparticles). This result can be interpreted as being due to water insolubility of UAN chains. In other words, Unlike Triton X-100 completely dissolving in water below CMC, UAN chains cannot be dissolved in water but are just dispersed in water to form APU nanoparticles even at extremely low concentrations in aqueous solutions.

In our previous paper, the water solubility of UAN chains was examined using an ultrafiltration method [20]. APU aqueous solutions were ultra-filtrated to separate dissolved UAN chains from APU aqueous solutions. Permeated solutions collected from APU solutions of various concentrations were examined by UV-Vis spectrometer, but no UAN chain was detected in any permeated solutions, indicating that there was no dissolved UAN chain in water. As a result, one can conclude that APU aqueous pseudophase consists of dispersed nano-sized particles only even at extremely low concentration.

Fig. 6 shows the sorption of APU nanoparticles and Triton X-100 molecules onto the aquifer sand at various concentrations. In the low concentration region (93–600 mg/l), the sorption of Triton X-100 onto aquifer sand is much higher than the sorption of APU 700-2 and APU 1000 nanoparticles, i.e. 30–40% of the Triton X-100 molecules are sorbed, whereas 7–14% of APU nanoparticles are sorbed onto aquifer materials. At higher concentrations (>700 mg/l), the sorption of Triton X-100 is also slightly greater than that of APU nanoparticles. This result is mainly due to the cross-linking nature of APU nanoparticles.

Below CMC, 100% of Triton X-100 molecules exist not as micelles but as monomeric molecules, whereas APU aqueous pseudophase phase consists of nano-sized particles only

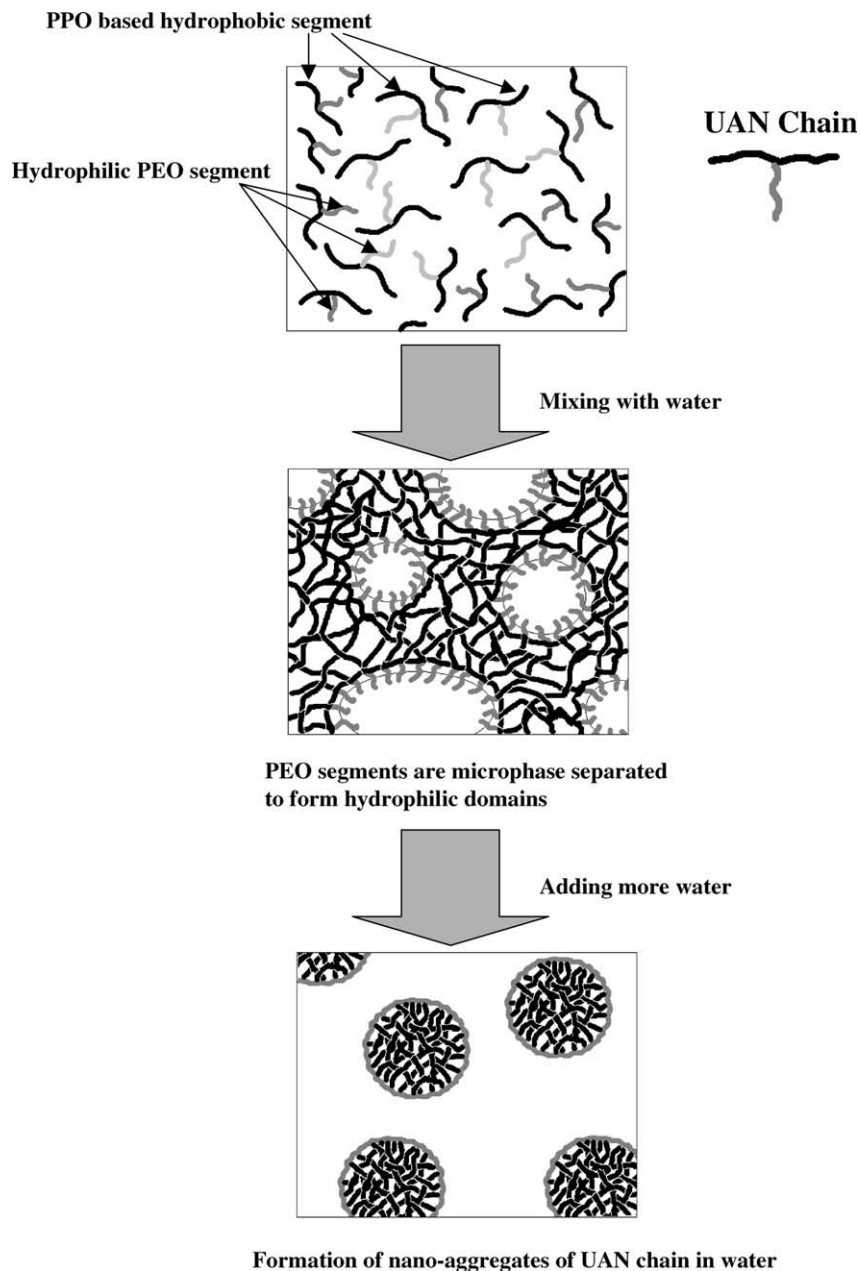


Fig. 5. Schematic presentation of formation of nano-aggregates of UAN chains (APU nanoparticles).

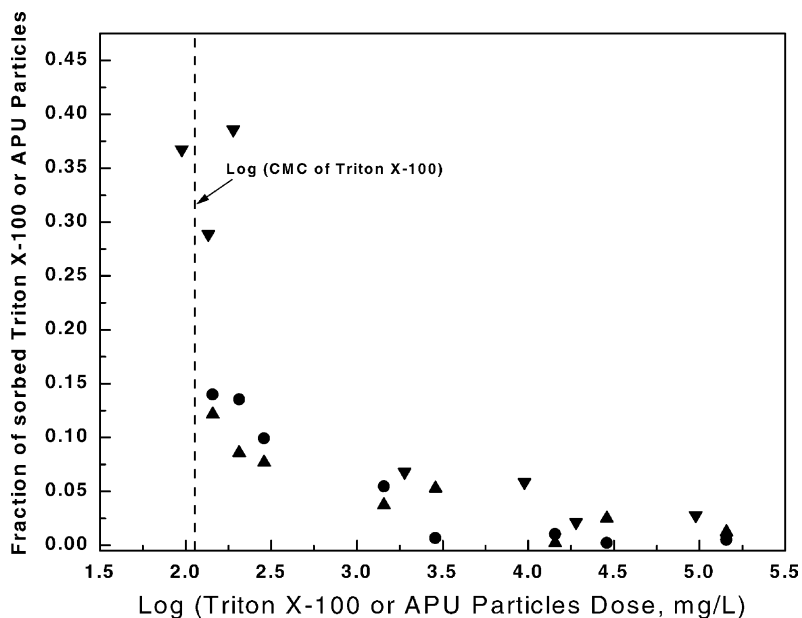


Fig. 6. Sorption of Triton X-100 and APU nanoparticles onto aquifer sand as a function of Triton X-100 or APU nanoparticle dose: (●) APU 700-2; (▲) APU 1000; and (▼) Triton X-100.

at this concentration. On contact aquifer sand, monomeric molecules of Triton X-100 can be easily adsorbed onto the aquifer sand, whereas sorption of APU nanoparticles can be largely hindered due to their aggregated structure. At higher concentrations, even though Triton X-100 can form aggregates (Micelles) at aqueous phase, Triton X-100 exhibits greater sorption onto the aquifer material than APU 700-2 and APU 1000 nanoparticles. This result can be explained by the chemically cross-linked microstructure of APU nanoparticles. Surfactant micelles formed by physical association of monomeric molecules tend to break up on contacting with a soil or solid. However, APU nanoparticles, nano-aggregates of UAN chains, can not be easily destroyed because this aggregated structure is permanently locked in by chemical cross-linking reaction. As a consequence, APU nanoparticles can be remain intact due to their chemically cross-linked structure, yielding the lower degree of sorption of APU 700-2 and APU 1000 nanoparticles.

It can be postulated that in the low concentration region, a greater reduction of phenanthrene sorption onto aquifer material in APU nanoparticle solutions is mainly due to a much lower degree of APU nanoparticle sorption onto aquifer material. That Triton X-100 and APU nanoparticles exhibited almost the same degree of reduction of phenanthrene sorption in the high concentration region can be also interpreted in terms of a lower degree of APU nanoparticle sorption. Consequently, it can be tentatively concluded that a relatively lower degree of sorption onto aquifer material causes APU nanoparticle to effectively reduce phenanthrene sorption onto aquifer material, regardless of their lower solubilizing efficiency and interfacial activity.

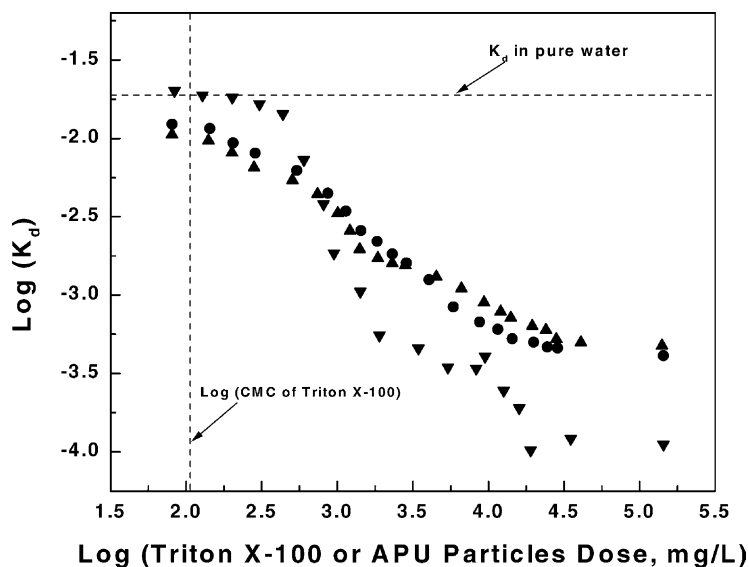


Fig. 7. Desorption experiments of sorbed phenanthrene from aquifer soil in the presence of TX-100 or APU nanoparticles: (●) APU 700-2; (▲) APU 1000; and (▼) Triton X-100.

#### 3.4. Desorption of phenanthrene on aquifer sand

The concentration of phenanthrene in the aqueous phase was measured to determine the change of phenanthrene distribution between the aqueous phase and the aquifer sand before and after adding APU nanoparticles or Triton X-100 (Protocol III). The results of the experiments were plotted in Fig. 7 as a function of the concentration of APU nanoparticles or Triton X-100. For APU and Triton X-100 solutions, the  $K_d$  values of phenanthrene decrease with an increase of APU or Triton X-100 concentration, indicating that sorbed phenanthrene on the soil is extracted and dissolved in the aqueous pseudophase. Like phenanthrene distribution behavior in aquifer material/APU and Triton X-10 solutions, the desorption behavior of sorbed phenanthrene can be divided into two regions.

In the low concentration region, when one adds Triton X-100 to water/aquifer material sorbing phenanthrene, the logarithms of  $K_d$  are either increased or slightly decreased compared to the  $K_d$  value in pure water. This result indicates that in this concentration region, Triton X-100 molecules do not extract sorbed phenanthrene. Rather they cause an increase of the sorption of phenanthrene from aqueous phase to aquifer sand.

However, APU nanoparticles resulted in a decrease of  $K_d$  value, indicating that APU nanoparticles can extract sorbed phenanthrene in this concentration region. In higher concentration regions, APU and Triton X-100 solutions exhibited almost the same  $K_d$  values, indicating that APU nanoparticles and Triton X-100 have the same extraction efficiency, even though Triton X-100 has a stronger affinity for phenanthrene than APU nanoparticles. This result may be attributed to a much lower degree of APU nanoparticle sorption on aquifer sand.

At surfactant concentrations less than CMC, surfactant monomers can extract sorbed HOC but most of surfactant monomers are easily sorbed onto the soil. These sorbed surfactants on a soil increase the soil's organic carbon content and solubilize HOCs as well as, resulting in an enhanced sorption of HOC onto the soil [9,11,25–27]. In addition, the CMC of the surfactant in soil/water system is much greater than its CMC in pure water, due to high degree of surfactant sorption onto the soil. As a consequence, the surfactant can effectively extract sorbed hydrophobic pollutant only at concentrations much greater than its CMC in pure water. Consequently, Triton X-100 could extract sorbed phenanthrene from aquifer material only when the concentration is greater than 312 mg/l which three times greater than its CMC.

However, unlike Triton X-100, APU nanoparticles could extract sorbed phenanthrene and exhibit greater extraction efficiency at this low concentration. This result can be also interpreted as due to microstructural difference between APU nanoparticles and Triton X-100 molecules. As noted earlier, APU nanoparticles can be formed at extremely low concentrations and have a relatively low degree of sorption onto the aquifer material, due to the chemically cross-linked structure of APU nanoparticles. As a consequence, APU nanoparticles could extract sorbed phenanthrene with a relatively smaller dose compared to Triton X-100 solutions, even though Triton X-100 has a better solubilizing performance for phenanthrene compared to APU nanoparticles.

#### 4. Conclusions

Triton X-100 has a stronger affinity for phenanthrene and better phenanthrene solubilizing performance than APU nanoparticles. However, APU nanoparticles exhibited better extraction performance and had a greater reduction of phenanthrene sorption in low concentration regions. Also these two aqueous solutions portrayed relatively small differences in extraction efficiency of phenanthrene in the higher concentration region. So, it can be concluded that the soil washing performance strongly depends not on the affinity with phenanthrene but on the degree of sorption of interfacial agents onto the aquifer sand.

The price of UAN chains could be more expensive than that of commercialized surfactants. This higher cost, however, would be compensated by better extraction performance at a relatively low concentration, and low degree of sorption of APU nanoparticles onto the soil. Furthermore, according to our previous report, 100% of the applied APU nanoparticles could be recovered through a membrane separation process. In situ extraction of sorbed phenanthrene using APU nanoparticles will be studied in future work to investigate possible application of APU nanoparticles in real field.

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