

# Solubilization of PAH Mixtures by a Nonionic Surfactant

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Enhanced solubilization of naphthalene, phenanthrene, and pyrene in micellar solutions of Triton X-100 was studied for single compounds and their binary and ternary mixtures. Experimental results were obtained for the following conditions: (i) naphthalene, phenanthrene, and pyrene as single compounds at saturation; (ii) naphthalene, phenanthrene, and pyrene as binary and ternary mixtures at saturation; (iii) phenanthrene at saturation in a range of naphthalene concentrations; (iv) pyrene at saturation in a range of naphthalene concentrations. The solubility enhancement of naphthalene was slightly reduced in the presence of phenanthrene and/or pyrene. A synergistic effect on the solubilization of phenanthrene was observed in the presence of different amounts of naphthalene. The solubility of phenanthrene was greatly enhanced in both binary mixtures and in the ternary mixture. The solubility of pyrene was slightly reduced in the presence of naphthalene, remained unaffected in the presence of phenanthrene, and increased significantly in the ternary mixture. The increase in the partition coefficient values is explained by the partitioning of the solubilize at the micellar core–water interface, which changes the interfacial free energy and effectively increases the volume of the core leading to a higher solubilization potential.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed by natural and anthropogenic pyrolysis of organic matter during forest fires, fossil fuel utilization, and chemical manufacture (1–3). Most PAHs are carcinogenic, which causes environmental concerns (4–6). PAH removal from soils and aquifers by natural attenuation mechanisms or traditional remediation efforts such as pump-and-treat is slow due to the low solubility of these compounds in water. It is well-known that surfactants can increase the solubility of a hydrophobic (low water solubility) compound by partitioning it into the hydrophobic cores of surfactant micelles. Numerous studies have investigated the enhanced solubility of a contaminant in the presence of surfactants above their critical micelle concentrations (7–11). Some studies have observed enhanced biodegradation of phenanthrene in the presence of surfactants (12, 13). A few studies have also indicated the potential for using micellar solubilization to clean up residual and sorbed contaminants from soils (14–16).

Much of the work on micellar solubilization of PAH has focused on individual compounds, whereas at a contami-

nated site, PAHs mostly exist in mixtures of many compounds. Only a limited number of studies have been reported where effects of multiple solutes on micellar solubilization of an individual component were examined. Chaiko et al. (17) and Nagarajan et al. (18) investigated the solubilization of binary mixtures of hydrocarbons (benzene and hexane) in anionic and nonionic surfactant systems. They observed selective solubilization in some mixtures and a synergistic effect on the solubilization of hexane in the presence of small amounts of benzene.

In the process of polyoxyethylene surfactants aggregation to form micelles, the net free energy of aggregation has contributions from the following: (i) transfer of hydrophobic moieties from water to a hydrophobic core; (ii) formation of an interface between the hydrophobic core and water; (iii) conformational free energy of the hydrophobic moieties due to constrained location of the headgroups at the aggregate surface; (iv) deformation and mixing free energy of the polyoxyethylene chains; and (v) steric interaction between the headgroups at the aggregate surface (19–21). The magnitudes of the first two contributions are generally much larger than those of the others. Molecular structure of the hydrophobic tail determines physical properties of the liquid-hydrocarbon-like core, including the interfacial tension at the core–water interface (19, 21). This interfacial tension limits the curvature of the core–water interface that can be supported and, thus, the size of the micelle (19–22). A higher curvature and larger interface can be supported by the same free energy change if the interfacial tension is decreased, which can occur by the presence of certain types of solutes at the interface. This was demonstrated by Nagarajan et al. (18) in the presence of two solutes with different hydrophobicities. The less hydrophobic solute (benzene) partitioned at the core–water interface causing the interfacial tension to decrease, which enabled the core volume to increase, leading to a greater solubility of the more hydrophobic compound (hexane). This concept was also supported by Mukerjee and Cardinal (7), who, based on their measurement of the dielectric constant and the polarity parameter of the microenvironment in the micelle, concluded that a large fraction (~88%) of the total solubilized benzene was present at the core–water interface of the micelle.

The objective of this research was to obtain experimental results and develop a mechanistic understanding of the effect of the presence of multiple PAHs on the micellar partitioning of individual compounds.

## Materials and Methods

**Materials.** *Contaminant.* PAHs used in this study were naphthalene, phenanthrene, and pyrene. Single-substrate experiments were performed with <sup>14</sup>C-labeled compounds. Multicomponent experiments were conducted with nonradiolabeled compounds. Radiolabeled naphthalene was uniformly labeled with a purity of >98% and an activity of 49.8 mCi/mmol. Radiolabeled phenanthrene was labeled at the ninth carbon with a purity of >98% and an activity of 8.3 mCi/mmol. In the radiolabeled pyrene, 4th, 5th, 9th and 10th carbons were labeled, and the purity and activity were >98% and 32.3 mCi/mmol, respectively. Each radiochemical was obtained from Sigma Chemical Company and mixed with an appropriate amount of nonlabeled compound based on the sensitivity requirements of the individual experiments. Nonlabeled compounds were obtained from Aldrich Chemical Company. The purity of the nonlabeled compounds was 99+, 98%, and 99% for naphthalene, phenanthrene, and pyrene, respectively. Although values reported in the

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**TABLE 1. Micellar Partition Coefficients for Different Solubilization Experiments<sup>a</sup>**

description of the experiments	experiment identifier	$K_{mc,i}$ (L/mg)
naphthalene, present in excess of its apparent solubility limit	naphthalene	naphthalene = $0.0025 \pm 0.00005$
phenanthrene, present in excess of its apparent solubility limit	phenanthrene	phenanthrene = $0.023 \pm 0.0023$
pyrene, present in excess of its apparent solubility limit	pyrene	pyrene = $0.148 \pm 0.016$
naphthalene and phenanthrene, each present in excess of its apparent solubility limit	Nap(s)-Phen(s)	naphthalene = $0.0019 \pm 0.0002$ phenanthrene = $0.044 \pm 0.004$
phenanthrene and pyrene, each present in excess of its apparent solubility limit	Phen(s)-Pyr(s)	phenanthrene = $0.041 \pm 0.005$ pyrene = $0.132 \pm 0.012$
naphthalene and pyrene, each present in excess of its apparent solubility limit	Nap(s)-Pyr(s)	naphthalene = $0.0017 \pm 0.00045$ pyrene = $0.126 \pm 0.013$
naphthalene, phenanthrene, and pyrene, each present in excess its apparent solubility limit	Nap(s)-Phen(s)-Pyr(s)	naphthalene = $0.0022 \pm 0.00013$ phenanthrene = $0.04 \pm 0.003$ pyrene = $0.18 \pm 0.025$
phenanthrene, present in excess of its solubility limit and $8.41 \pm 0.49$ mg/L naphthalene in solution	Nap(8)-Phen(s)	phenanthrene = $0.027 \pm 0.004$
phenanthrene, present in excess of its solubility limit and $19.28 \pm 1.5$ mg/L naphthalene in solution	Nap(19)-Phen(s)	phenanthrene = $0.032 \pm 0.005$
pyrene, present in excess of its solubility limit and $2.44 \pm 0.66$ mg/L naphthalene in solution	Nap(2)-Pyr(s)	pyrene = $0.105 \pm 0.016$
pyrene, present in excess of its solubility limit and $7.82 \pm 0.71$ mg/L of naphthalene in solution	Nap(8)-Pyr(s)	pyrene = $0.105 \pm 0.013$
pyrene, present in excess of its solubility limit and $18.71 \pm 0.95$ mg/L of naphthalene in solution	Nap(19)-Pyr(s)	pyrene = $0.106 \pm 0.014$

<sup>a</sup> Each experiment was conducted in duplicate at eight different surfactant concentrations.

literature for the aqueous solubility of a given PAH may vary, values for the three compounds studied span 3 orders of magnitude. At 20 °C, they have been reported to be 31.3, 1.35, and 0.135 mg/L for naphthalene, phenanthrene, and pyrene, respectively (25), in close agreement with observations from this study.

**Surfactant.** A synthetic, polydispersive, nonionic surfactant, Triton X-100 (octylphenol polyoxyethylene), was obtained from the Aldrich Chemical Company. The solution contained <3% poly(ethylene glycol) and was used without further purification. The hydrophilic moiety of the surfactant consists of a polyoxyethylene (POE) chain with an average of 9.5 oxyethylene units per molecule. The hydrophobic moiety consists of a phenol group attached to an alkyl chain of eight carbons. The critical micelle concentration (cmc) of the surfactant was measured as 43 mg/L (12). Different cmc values for Triton X-100 have been reported in the literature that are attributed to impurities and general variability of the POE chain-length distribution in polydispersive surfactants.

**Analytical Procedures.** Radiolabeled compounds were analyzed using a Packard Tri-carb 1900TR liquid scintillation counter. The disintegration per minute (dpm) data for each compound were converted to concentration of carbon using a standard curve prepared from the stock solution of known concentration and radioactivity.

A Hewlett-Packard high-pressure liquid chromatograph (HPLC) with UV and fluorescence detection was used to quantify the nonradiolabeled PAH compounds. A HP Spherisorb ODS 2, 5  $\mu$ m, 125  $\times$  4 mm column was used for the HPLC under the following operational conditions: flow rate = 1.5 mL/min; temperature = 30 °C; injection volume = 10  $\mu$ L; mobile phase = acetonitrile:water, using an uniform gradient from 40:60 to 80:20 during the run time of 10 min. Naphthalene was detected with a diode array UV detector at 220 nm for the concentration range of 0.75–31 mg/L. Fluorescence detection (excitation 218 nm and emission 357 nm) was used for concentration below 0.75 mg/L. The detection limit for naphthalene was 0.01 mg/L. Phenanthrene was detected using the fluorescence detector with

excitation at 248 nm and emission at 395 nm. The detection limit for phenanthrene was 0.002 mg/L. The fluorescence detector was also used for pyrene with excitation at 230 nm and emission at 387 nm. The detection limit was 0.001 mg/L.

**Experimental Procedures.** A series of 15-mL centrifuge tubes were spiked with a solution of the respective PAH, dissolved in methanol. The mass of the PAH added was in excess (about four times) of the apparent solubility (as defined by eq 1), and the presence of an excess amount was visually confirmed at the end of each experiment. Methanol was then allowed to evaporate, after which 10 mL of Triton X-100 solutions of varied concentrations was added to each tube. Tubes were placed in a rotary shaker for 7 days at 20 °C. Different incubation times showed no difference after a 12-h incubation period; a 7-day incubation period was therefore considered to be sufficient to reach equilibrium conditions. At the end of the incubation period, the tubes were centrifuged at 600g for 30 min. Duplicate samples (0.5 mL) were drawn from the supernatant of each tube. The pipet tips were presaturated with the corresponding PAH before drawing the sample. The samples from the single-compound experiments were analyzed for radioactivity in a liquid scintillation counter to quantify the PAH concentration in solution. The samples from the multicomponent experiments were quantified using the HPLC. The combination of the solutes in the experiments conducted are listed in Table 1.

### Effect of Solubilities on the Micellar Size

The equilibrium apparent concentration of a hydrophobic compound in an aqueous surfactant solution can be expressed as

$$C_{app} = C + C_{mic} = C + S_{mc}K_{mc}C \quad (1)$$

where  $C_{app}$  is the apparent concentration of hydrophobic compound in solution (mg/L);  $C$  is the dissolved concentration of the compound in the aqueous phase (mg/L);  $C_{mic}$  is the concentration of the compound in the micellar phase

expressed as an equivalent concentration in the water phase (mg/L);  $K_{mc}$  is the equilibrium partition coefficient of the compound between the aqueous phase and the micellar phase (L/mg); and  $S_{mc}$  is the surfactant concentration in the micellar form (mg/L), which can be estimated as

$$S_{mc} = \begin{cases} S - cmc & \text{for } S > cmc \\ 0 & \text{for } S \leq cmc \end{cases} \quad (2)$$

where  $S$  is the total concentration of the surfactant in solution (mg/L) and  $cmc$  is the critical micelle concentration of the surfactant (mg/L).

Equation 1 does not account for the fact that dissolved surfactant monomers can also enhance the apparent solubility of hydrophobic compounds. Results from this research, where for all experiments several measurements were conducted at surfactant concentrations below  $cmc$ , have shown that for these PAHs and surfactant combination this effect could be neglected.

The mole fraction of a constituent in the micellar phase can be computed as

$$x_i = \frac{C_{mic}^{*i}}{S_{mc}^* + \sum_{i=1}^n C_{mic}^{*i}} \quad (3)$$

The quantity  $x_i$  represents the mole fraction of the  $i$ th solubilize in the micelle where  $n$  solutes are present. This mole fraction accounts for the surfactant monomers and hydrophobic compounds in micelles and not water molecules. The asterisk represents concentrations expressed as moles per liter. This quantity can provide an understanding of the hydrophobic microenvironment inside the micellar core and the validity of the dilute solution approximations which dictates the interaction between the solutes.

The solubilized concentration of the compound in the micelle ( $C_{mic}$ ) is expressed above as an equivalent concentration in the water. It may be noted that the true concentration of the PAH in the micelles will be much larger. The relative volume contribution by each PAH in the micellar core is the ratio of the volume of the PAH solubilized to the volume of the hydrophobic moieties of surfactant in micellar form. This quantity reflects the increase in the micellar core volume due to the solubilization of a solute of low solubility in its core. The volume increment due to each solute can be computed as follows:

$$\eta_i = \frac{v_i(C_{app}^{*i} - C^{*i})}{v_{alkyl}(S - cmc)} \quad (4)$$

where  $v_i$  is the molar volume of the  $i$ th component in the micelle (L/mol),  $v_{alkyl}$  is the volume of alkyl chain per mole of surfactant (L/mol),  $\eta_i$  is the volume fraction of the  $i$ th component in the micelle. The above volume fraction was estimated assuming that excess volumes from nonideal molecular interactions are negligible. The specific volume of one alkyl chain in the micellar core of Triton X-100 was reported to be  $363 \text{ \AA}^3$  (21), which leads to a hydrophobic (alkyl) volume of  $0.22 \text{ L/mol}$  of surfactant. The liquid molar volumes of naphthalene, phenanthrene, and pyrene were taken from Daubert and Danner (24) as 0.13, 0.16, and 0.17 L/mol, respectively.

Since  $C$  (the solubility limit at saturation),  $cmc$ ,  $C_{app}$ , and  $S$  are all measured experimentally, the quantities  $K_{mc}$ ,  $x_i$ , and  $\eta_i$  can be computed from the experimental data.

## Results

**Solubilization of Naphthalene.** Enhanced solubilization of naphthalene by Triton X-100 above its  $cmc$  was studied under

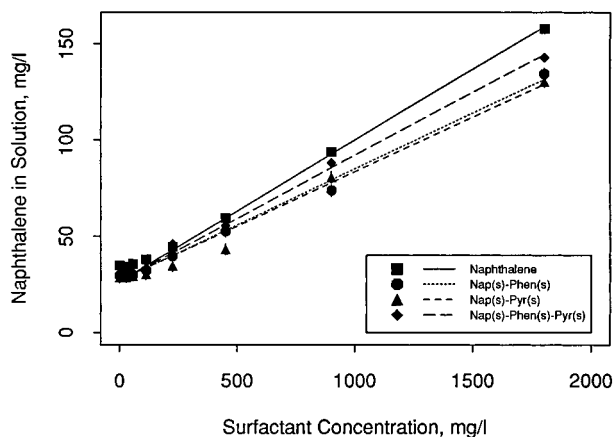


FIGURE 1. Enhanced solubility of naphthalene by Triton X-100. Symbols represent experimental values, and lines represent linear regression.

the following conditions: (a) naphthalene, present in excess of its solubility limit; (b) a mixture of naphthalene and phenanthrene, each present in excess of its respective solubility limit; (c) a mixture of naphthalene and pyrene, each present in excess of its respective solubility limit; (d) a mixture of naphthalene, phenanthrene, and pyrene, each present in excess of its respective solubility limit.

Figure 1 shows solubility enhancement of naphthalene for the above-mentioned conditions at different surfactant concentrations. The error bars represent the standard deviation of two different samples from each of two parallel experiments and are in most cases smaller than the symbols. Table 1 lists the respective values of micelle-water equilibrium partition coefficients ( $K_{mc}$ ). The mean value of the partition coefficient of naphthalene is slightly lower for the binary mixtures and the ternary mixture than for the single compound. The differences between mean partition coefficient values for naphthalene as a single compound and in the binary mixtures were found to be significant at a 95% confidence level using a  $t$ -test.

**Solubilization of Phenanthrene.** Solubilization of phenanthrene in the micellar solution of Triton X-100 was studied under the following conditions: (a) phenanthrene only, present in excess of its solubility limit; (b) naphthalene and phenanthrene each present in excess of its respective solubility limit; (c) phenanthrene present in excess of its solubility limit and  $8.41 \pm 0.49$  and  $19.28 \pm 1.5$  mg/L naphthalene in the solution; (d) phenanthrene and pyrene, each present in excess of its respective solubility limit; (e) naphthalene, phenanthrene, and pyrene, each present in excess of its solubility limit. Figure 2 shows enhanced solubility of phenanthrene at different surfactant concentrations for the conditions a, b, d, and e mentioned above. The error bars represent the standard deviation of two samples from each of two parallel experiments. An increase in the partition coefficient value for phenanthrene was observed in the presence of naphthalene and/or pyrene. All of these increases were significant at a 95% confidence level based on the results of  $t$ -tests. The increased partition coefficient value was as much as 90% over that of the single compound phenanthrene partition coefficient value. Figure 3 illustrates the enhanced solubilization of phenanthrene as a function of the surfactant concentrations in the presence of different amounts of naphthalene (conditions a–c). The error bars are the standard deviation of four different samples from two parallel experiments. The mean value of the partition coefficient of phenanthrene increases from a minimum when naphthalene is absent to a maximum when the naphthalene is present at saturation. Each increment was found to be

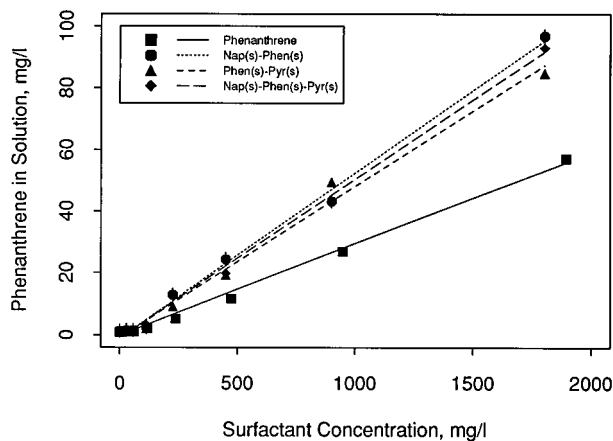


FIGURE 2. Enhanced solubility of phenanthrene by Triton X-100. Symbols represent experimental values, and lines represent linear regression.

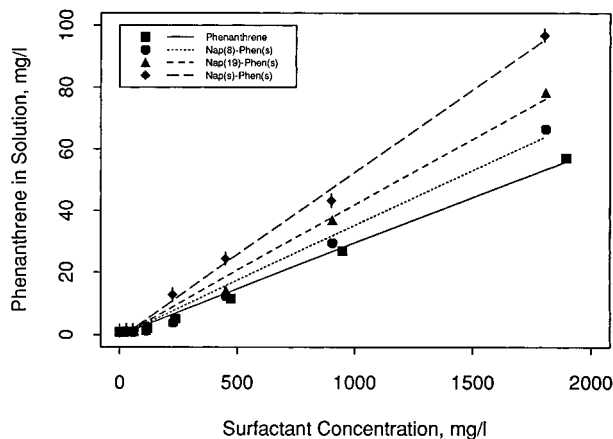


FIGURE 3. Enhanced solubility of phenanthrene by Triton X-100 in the presence of different amounts of naphthalene. Symbols represent experimental values, and lines represent linear regression.

statistically significant at a 95% confidence level using a *t*-test. Table 1 lists the micellar partition coefficient values for phenanthrene ( $K_{mc}$ ) for these experiments. While the presence of naphthalene or pyrene or both results in a significant increase in the partition coefficient value, the difference in the maximum values between these two cases is not statistically significant at a 95% confidence level.

**Solubilization of Pyrene.** Enhanced solubilization of pyrene by Triton X-100 was studied under the following conditions: (a) pyrene only, present in excess of its solubility limit; (b) naphthalene and pyrene, each present in excess of its respective solubility limit; (c) pyrene present in excess of its solubility limit and  $2.44 \pm 0.66$ ,  $7.82 \pm 0.71$ , and  $18.71 \pm 0.95$  mg/L naphthalene in the solution; (d) phenanthrene and pyrene, each present in excess of its respective solubility limit; (e) naphthalene, phenanthrene, and pyrene, each present in excess of its respective solubility limit. Figure 4 illustrates pyrene solubility enhancement by Triton X-100 above its cmc as a single compound and in the presence of naphthalene and/or phenanthrene. The error bars represent the standard deviation of four different samples from two parallel experiments. Table 1 lists the micellar partition coefficients ( $K_{mc}$ ) for all the experiments involving pyrene. The reduction in the pyrene partition coefficient value in the presence of naphthalene is statistically significant at a 95% confidence level but insignificant in the presence of phenanthrene. The reduction in the partition coefficient of pyrene in the presence of naphthalene was found to be insensitive to the amount of naphthalene present in the system. A

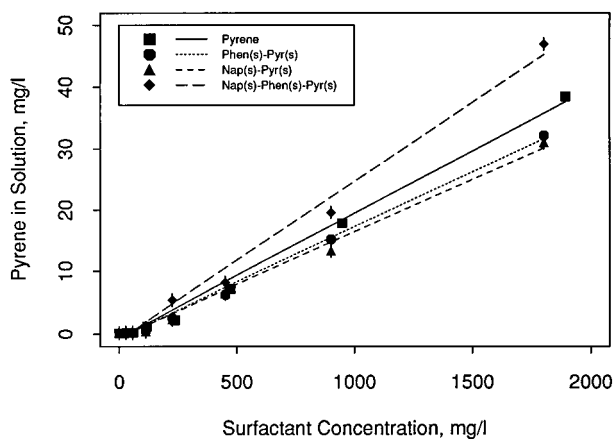


FIGURE 4. Enhanced solubility of pyrene by Triton X-100. Symbols represent experimental values, and lines represent linear regression.

significant increase (of about 40%) in the pyrene solubility was observed when naphthalene and phenanthrene both were present at saturation (Figure 4), and the increase was statistically significant at a 95% confidence level.

## Discussion

Mole fractions the individual PAHs in micelles were computed using eq 3, and the results are illustrated in Figure 5. The contributions of different solutes in a micellar core to the core volume were computed using eq 4, and the results are shown in Figure 6. The contributions of each compound to the core volume follow closely the trend of the mole fractions for the different experiments. The volume contribution ( $\eta_i$ ) may be used to visualize the composition of the micellar core. For a surfactant solution without solubilizates, the quantity ( $\eta_i$ ), which is the volume of the solubilizates in the micelle normalized to the surfactant concentration, is zero.

In our experiments with binary and ternary mixtures, we observed the following results: (i) A decrease in partition coefficient values in some binary mixtures. (ii) No effect on the partition coefficient values in some binary mixtures. (iii) An increase in partition coefficient values in some binary mixtures and in the ternary mixture.

If the solutes compete with each other for a location in the interior of the micelle, it will lead to a decrease in the solubility of one solute in the presence of others (17). This effect may explain result (i), which was observed for the partition coefficient value of naphthalene in naphthalene-phenanthrene and naphthalene-pyrene mixtures. More hydrophobic compounds such as phenanthrene and pyrene likely displaced naphthalene from micelle cores and thus reduced the apparent naphthalene solubility.

If the contribution of an individual solubilizate to the core volume remains constant, which apparently is more likely to occur for the more hydrophobic compounds, then the solubility enhancement is relatively unaffected by the presence of less hydrophobic solubilizates (result ii). This is clearly shown for the case of pyrene in the presence of naphthalene ranging from 2 to 19 mg/L, where the contribution of pyrene to the core volume as well as its  $K_{mc}$  remains constant, even though the total core volume increases as the amount of naphthalene increases (Figure 5 and Table 1, respectively).

Less hydrophobic compounds can be solubilized at the interfacial region of a hydrophobic core (7), which reduces the interfacial tension between the liquid-hydrocarbon-like core and water (17-19). Recent evidences also suggest that less hydrophobic compounds such as benzene participate in hydrogen bonding (26) with water, which presumably facilitates solubilization at the interface. The reduced

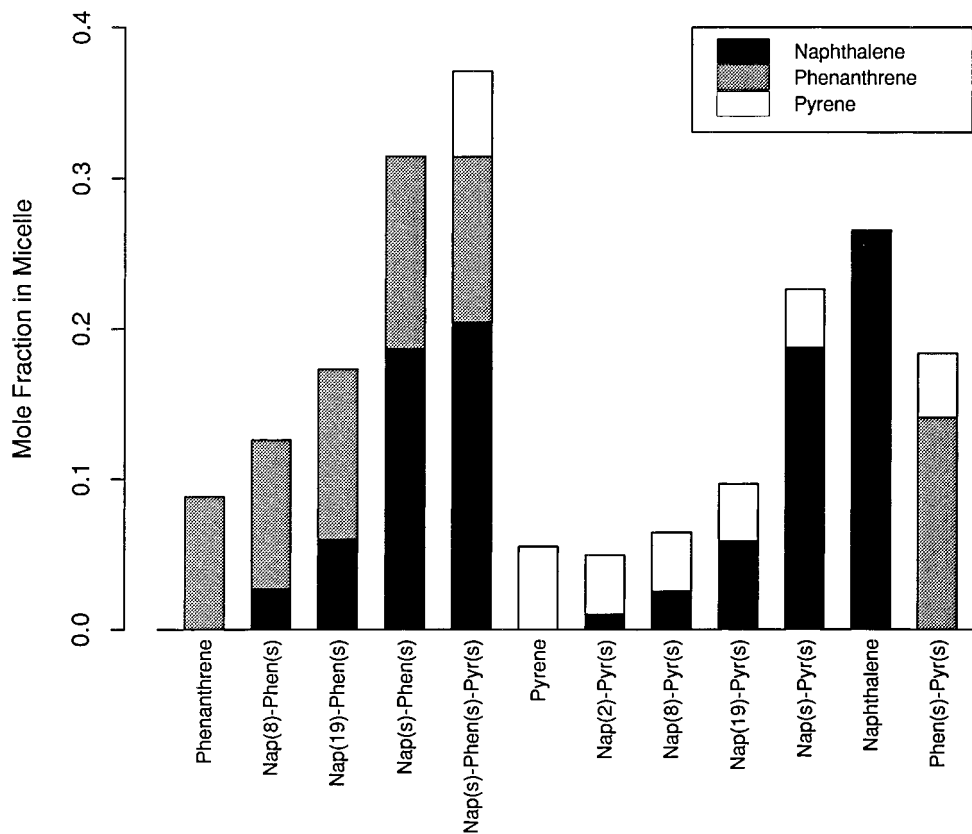


FIGURE 5. Mole fraction of solutes in Triton X-100 micelles. Heights of individual shades represent mole fractions of individual compounds. Total height of vertical bars represents total mole fraction of the solutes in micelles.

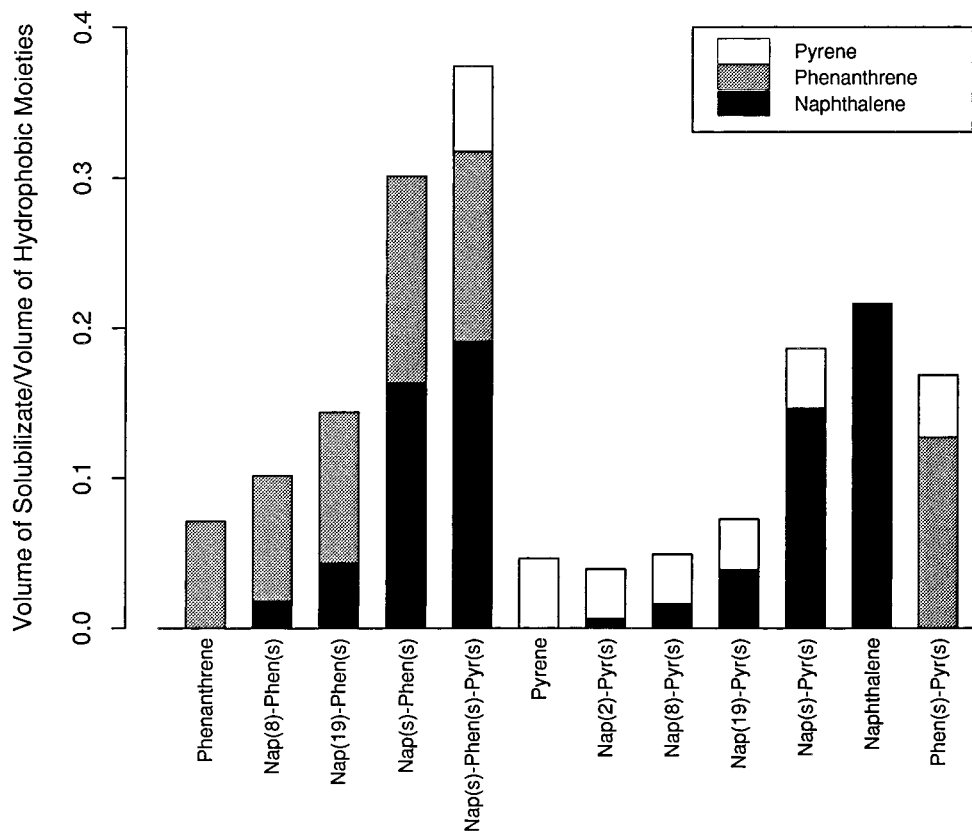


FIGURE 6. Core volume contribution by solutes in Triton X-100 micelles. Heights of individual shades represent volume contribution by individual compounds. Total height of vertical bars represents total volume contribution by the solutes in micelles.

interfacial tension can support a larger core volume for the same interfacial energy (18, 19, 22).

Dielectric constant and polarity parameter values of the microenvironment of naphthalene in sodium dodecyl sulfate

micelles were found to be comparable to those of *p*-xylene, ethylbenzene, and Triton X-100 (7) and slightly less than that for benzene. Given these similarities between Triton X-100 and naphthalene, one would expect naphthalene to be solubilized at the interfacial region of the hydrophobic core. This would explain the increased partition coefficient of phenanthrene in the binary and ternary mixtures. The partitioning of naphthalene at the core-water interface in a micelle is proportional to the amount of naphthalene present in the solution (7). This might explain the proportional increase in the core volume contribution (Figure 6) and the partition coefficient values for phenanthrene (Table 1) as a function of naphthalene concentration. The core volume reaches its maximum for the ternary mixture (Figure 6). It is important to state that the relation between changes in micellar core volume and solubilization is not based on direct measurements and is conjecture.

Using simple binary and ternary PAH mixtures, it was demonstrated that the single-component micellar partition coefficient cannot be used to predict the multicomponent micellar solubilization. In the presence of less hydrophobic solutes that partition at the interface of the liquid-hydrocarbon-like core of the micelle, the solubility of the more hydrophobic solute is likely to increase. In some cases, this increase may amount to as much as 90%.

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