The Solubilization Capability of Polycyclic Aromatic Hydrocarbons Enhanced by Biosurfactant Saponin Mixed With Conventional Chemical Surfactants

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Water solubilities of anthracene and phenanthrene were measured by adding a plant-derived biosurfactant Saponin and/or synthetic surfactants correspondingly below and above their critical micelle concentrations (CMCs). The results showed that the solubilities of anthracene and phenanthrene in water were greatly enhanced following a linear fashion if adding Saponin, TX100 and Brij35, respectively. The enhancing solubility capacities for Polycyclic aromatic hydrocarbons (PAHs) followed the order as: Saponin > Brij35 > TX100 at the concentrations below their CMC. It also proved that biosurfactant Saponin exhibited much higher enhancement efficiency for PAHs solubilization than the synthetic ones at the concentrations below the CMC. However, the solubility enhancement efficiencies of surfactants above the CMC turned to be the following order as Brij35 > Saponin > TX100. Furthermore, this study has confirmed that PAHs are synergistically solubilized in the mixed biologic-synthetic surfactant solutions, especially at the low surfactant concentrations.

Synergistic effect of a prepared mixed-surfactant solution on different PAH compounds also appeared to be linear related to the surfactant concentrations. The synergistic power of mixed surfactants were examined as Saponin-Brij35 > Saponin-TX100 while the efficiencies of synergistic solubilization ranged from 27% to 137%. The noted solubilization for the single and mixed surfactants could be attributed to the formation of single and mixed micelles, the lower CMC of the single and mixed surfactant solutions, and the increase of the solubilization ratio or micellar partition coefficients.

Keywords: biosurfactant, micelles, PAHs, Saponin, solubilization

1. INTRODUCTION

PAHs are widespread contaminants in soil and sediment. Some of them have raised public particular concern due to the persistent, toxic, mutagenic and carcinogenic characteristics of PAHs (Zedeck, 1980) and their potential threat and toxicity to human health (Wei et al., 2010). Some of them are on the U.S. Environmental Protection Agency's list of priority pollutants. Petrogenic sources are a major origin of anthropogenic PAHs in the environment. Crude and refined petroleum contain petrogenic PAHs, and are also important sources of PAHs. Furthermore, PAHs are more abundant in heavy petroleum products (e.g., diesel engines of motor vehicles make a considerable contribution to both gaseous and particulate air toxics in the urban atmosphere; Karavalakis et al., 2011). Once produced,

PAHs can be widely dispersed into the environment by atmospheric transport or through stream pathways, and eventually accumulate in soils and aquatic sediments. The existing levels of these compounds in the environment are taken into the special consideration and regulated by government agencies. Bioremediation is a cost-effective approach for decontamination of PAH-contaminated sites and has been extensively used (Xia et al., 2006). However, PAHs with three or more rings have low solubility in water and strong sorption to soils or sediments (Yang et al., 2008), which limits the site bioremediation polluted with PAHs. The remediation of hydrophobic organic contamination in the soil-water systems is dependent on desorption of the contaminant from the soil surface and the subsequent incorporation of pollutants into the bulk aqueous phase (Achten et al., 2011). Once in the bulk aqueous phase, engineered treatment systems may be used to affect remediation.

It is well known that surfactants can increase the solubility of hydrophobic organic compounds (HOCs) by partitioning them into the hydrophobic cores of surfactant micelles, thus surfactant-enhanced remediation has been suggested as a promising technology for the removal of sorbed HOCs (Whang et al., 2008). Being the typical HOCs, PAHs possess certain hydrophobicity and can increase desorption of PAHs from soil particles into the aqueous phase and increase bioavailability of PAHs to microorganisms, in which one effective way is to add surfactants at sufficiently high concentrations to form micelles and solubilize the PAHs (Li and Chen, 2002). With higher aqueous phase concentrations, more organic compounds can potentially be removed by microbial degradation (Lee et al., 2001; Doong and Lei, 2003). Because chemical surfactants may have issues of toxicity, low bio-degradability, and may be recalcitrant in the environment, biosurfactants have been considered to be a better choice. Biosurfactants not only have beneficial effects on physical properties of soil, but also have a role in controlling both the fate of environmental pollutants and the biogeochemistry of organic carbon in the global ecosystem (Kingsley and Turgay, 2004).

Saponin, a class of nonionic biosurfactants derived from plants, is glycosidic compound present in many edible and inedible plants. In an early study, Saponin as a washing soap has not cited any toxic effects on human skin and eyes (Roy et al., 1997). Some studies investigated the removal of heavy metals from contaminated soils by Saponin (Chen et al., 2008; Mulligan, 2009), but few scientific researches have reported the enhanced solubilization of Saponin for HOCs and little information is available about the solubilization properties of Saponin-conventional surfactant systems for HOCs (Mulligan, 2005, 2009), which restricted the application of Saponin in the remediation of petroleum-contaminated soils.

In this study, we investigated and compared the solubilization aspects of PAHs enhanced by single biosurfactant Saponin and mixed Saponin-conventional surfactant systems, and elucidated the causes for synergistic solubilization of PAHs in mixed Saponin-conventional surfactant solutions. Because Saponin does not have any environmental issues and shows the greater bioavailability, it is considered as a better solubilizer than conventional surfactants (Sun et al., 2006). The work presented herein will provide a potential methodology for safe remediation of petroleum-contaminated soils through the flushing approach by using Saponin and the mixed surfactant solutions.

2. MATERIALS AND METHODS

Analytical grade anthracene and phenanthrene were selected as representative PAHs to model hydrophobic organic contaminants and obtained from Shanghai Chemical Company, China. Their properties are listed in Table 1

Surfactants used in experiment were obtained either directly from the manufacturer or through a distributor, all of which were used without further purification. Saponin was obtained from Sigma Chemical Company meanwhile Triton X-100 (TX100) and Brij35 were purchased from Shanghai

TABLE 1
Characteristic of the Selected Reagents

Reagent	Molecular Weight	Solubility,[a] mol L^{-1b}	Log K$_{ow}$ [a]	CMC, mg L^{-1}	ST[b]
Anthracene	178.2	3.0×10^{-7}	4.45	—	—
Phenanthrene	178.2	6.6×10^{-6}	4.46	—	—
TX100	625	—	—	165	32.69
Brij35	1198	—	—	74	27.53
Saponin	1650	—	—	145	29.32
Saponin-Brij35	—	—	—	63	25.82
Saponin-TX100	—	—	—	140	28.41

[a]Solubility and Log K$_{ow}$ reported by Dar et al. (2007). [b]Surface tension (mN m^{-1}).

Chemical Company. The formula and properties of surfactants are shown in Table 1. The biosur-factant used in the study was a plant product because it is a glycolipid that is the most commonly isolated type of biosurfactant. Deionized water was used for all the tests.

Single- and mixed-surfactant solutions with the different total concentrations were prepared in flasks, respectively. A series of 20 mL of single or mixed surfactant solutions with the different concentrations and composition were placed into 25 mL Corex centrifuge tubes with Teflon cap liners before PAHs was separately added to each tube in an amount slightly more than required to saturate the solution. Duplicate tests were prepared for each surfactant concentration in meantime, the samples were then equilibrated on a reciprocating shaker for 48 h at 25 ± 1°C. The samples were subsequently centrifuged at 5,000 rpm for 1 h to separate the undissolved PAH. A 5 mL aliquot of the supernatant was then carefully withdrawn with a volumetric pipette and diluted to 10 mL in flasks with 5 mL of methanol when the rest was surfactant-water solution. The concentration of solubilized PAH was determined spectrophotometrically with a Shimadzu spectrophotometer (ModelUV-1650). The UV wavelengths were set at 254.4 and 250.8 nm for anthracene and phenanthrene, respectively. The surfactant concentration was kept constant in both standard and experimental solutions to eliminate the effects of surfactants on determining PAHs. All of the solubility measurements were carried out in triplicate while the typical error in the measurements was less than 5%.

The critical micelle concentrations (CMC) values of single-surfactant and mixed-surfactant so-lutions at 25 ± 1°C were determined as the concentration at sharp breaks in the plots of the surface tension versus the logarithm of surfactant concentration. Surface tensions of single-surfactant and mixed-surfactant solutions over a wide concentration range were determined with a Model 20 ten-siometer (Fisher Science Instrument Co., USA). Surfactant solutions of varying concentrations were made and allowed to equilibrate for approximately 5 h before measurements were completed. The plotted surface tension value was taken when stable reading were obtained for a given surfactant concentration as indicated by at least three consecutive measurements until nearly having the same value. The CMC values and the basic characteristics of the selected surfactants in this study are shown in Table 1.

3. RESULTS AND DISCUSSION

3.1 Water Solubility Enhancements of PAHs by Single Surfactants

The solubility enhancements of the two PAH components in the aqueous biosurfactant and synthetic surfactant solutions at various concentrations are illustrated in Figure 1, in which each datum
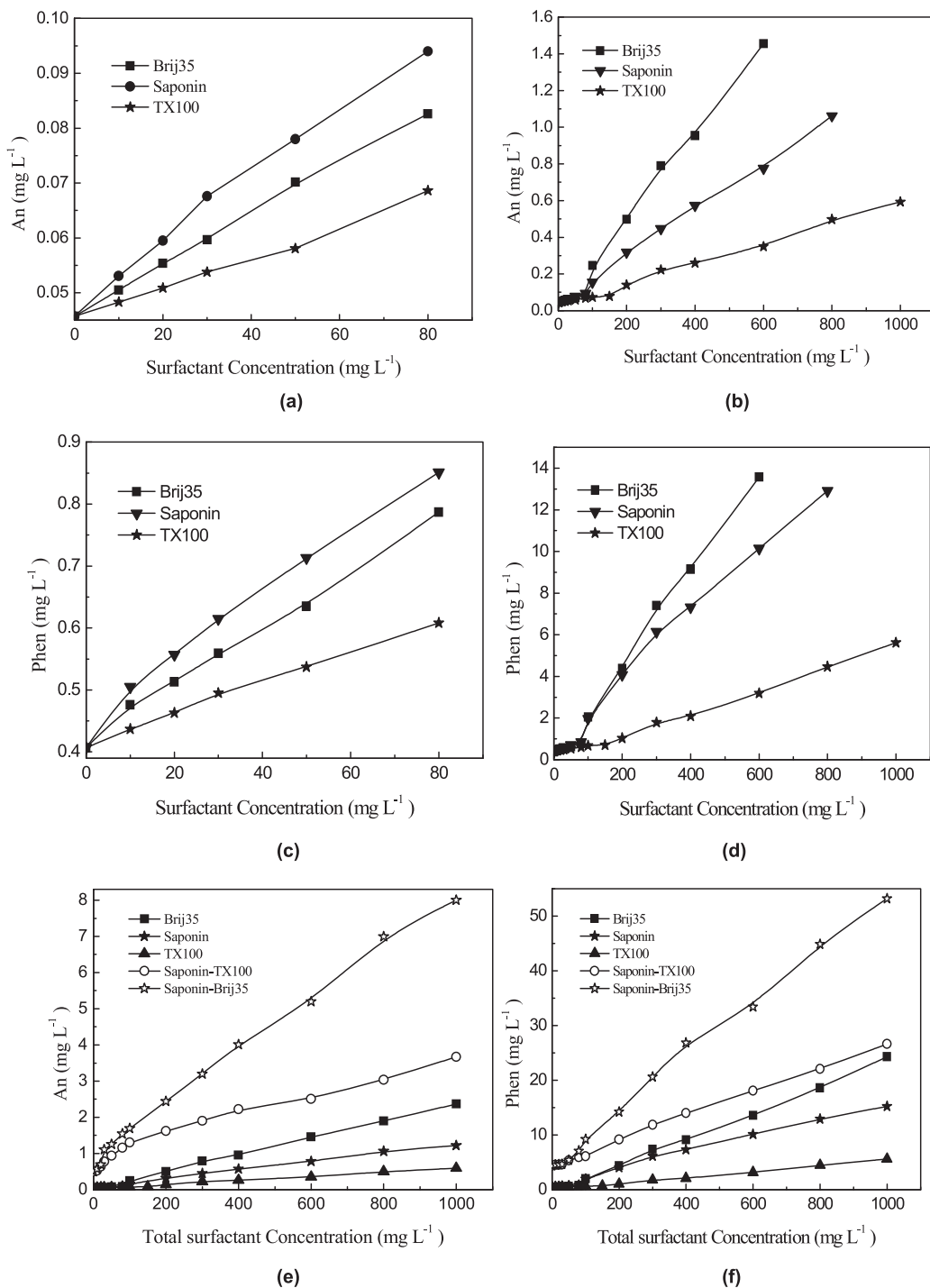
FIGURE 1   Variation of solubility of An and Phen with the surfactant concentration (C_t) of single and mixed surfactant combinations (a and c are below the CMC; b, d, e, and f are above the CMC).

represents the average concentration obtained from three independent experiments. The standard deviations associated with each mean concentration were less than 5% of the mean on average.

According to the conventional phase-separation model for surfactants in aqueous solution, surfactants are assumed to exist in monomeric state below the CMC (Jafvert et al., 1994). Above the CMC, the concentration of monomers remains constant at CMC while the excess surfactant leads to the formation of pseudophase micelles. A general expression for the solubility enhancement of a solute by surfactants can be written as Eq. (1) in terms of the concentrations for monomers and micelles and the corresponding solute partition coefficients (Kile and Chiou, 1989),

$$\frac{S_w^*}{S_w} = 1 + X_{mn} K_{mn} + X_{mc} K_{mc} \tag{1}$$

where S_w^* is the apparent solute solubility at the total stoichiometric surfactant concentration of X ($X = X_{mn} + X_{mc}$), S_w is the intrinsic solubility in "pure water," X_{mn} is the concentration of the surfactant as monomers ($X \leqslant$; CMC, $X_{mn} = X$; $X >$ CMC, $X_{mn} =$ CMC), and X_{mc} is the concentration of the surfactant in micellar form ($X \leqslant$ CMC, $X_{mc} = 0$; $X >$ CMC, $X_{mc} = X -$ CMC). K_{mn} is the partition constant of the solute between monomers and water, and K_{mc} is the corresponding partition constant of the solute between micelles and water. The separation of the concentration terms (X_{mn} and X_{mc}) accounts for differences in the partition efficiency of the solute with monomers and micelles.

In this study, the water solubility enhancement of anthracene and phenanthrene by Saponin, TX100 and Brij35 at surfactant concentrations extending from far below CMC to significantly above CMC is shown in Figure 1. In these signal-surfactant systems, the apparent solute solubility (S_w^*) versus the total concentration of surfactant seemed to be bilinear, giving a straight line with slope of K_{mn} from $X = 0$ to $X =$ CMC, followed by another straight line with slope of K_{mc} at $X \geqslant$ CMC. The water solubility of anthracene and phenanthrene was greatly enhanced by all the surfactants above the CMC when the apparent aqueous solubility increases with increasing surfactant concentration. The observed difference in solubility enhancement by surfactants above and below CMC was a result of the different abilities of micelle and monomer to concentrate anthracene and phenanthrene by partitioning interactions. The equations of aqueous solubility enhancements of anthracene and phenanthrene by biosurfactant and synthetic surfactant solutions with corresponding K_{mn} and K_{mc} values are shown in Table 2. From Figure 1 and Table 2, it can be seen that the sequence of the solubility enhancement for PAHs by surfactants below the CMC was shown as: Saponin > Brij35 > TX100. The measured K_{mn} values were 1.414×10^4 for Saponin, 1.072×10^4 for Brij35, and

TABLE 2
The Measured K_{mn}, K_{mc} Values of Surfactants and $\triangle S\%$ of Mixed Saponin-TX100, Saponin-Brij35 solutions (Saponin 200 mg L^{-1})

PAHs	Surfactant	K_{mn}	K_{mc}	$\triangle S\%$ (A)[a]	$\triangle S\%$ (B)[b]
Anthracene	Saponin	1.414×10^4	2.963×10^4	—	—
	Brij35	1.072×10^4	5.521×10^4	—	—
	TX100	5.430×10^3	1.127×10^4	—	—
	Saponin-Brij35	1.058×10^5	2.398×10^5	136.6	42.20
	Saponin-TX100	2.135×10^4	9.578×10^4	94.79	26.95
Phenanthrene	Saponin	9.958×10^3	2.841×10^4	—	—
	Brij35	6.681×10^3	3.368×10^4	—	—
	TX100	2.563×10^3	5.452×10^3	—	—
	Saponin-Brij35	1.464×10^4	8.247×10^4	—	—
	Saponin-TX100	1.129×10^4	3.700×10^4	—	—

[a]$\triangle S\%$ (anthracene). [b]$\triangle S\%$ (phenanthrene).

5.43×10^3 for TX100, respectively. However, The extent of solubility enhancement by surfactants above the CMC follow the order as: Brij35 > Saponin > TX100. The corresponding K_{mc} values were 5.521×10^4 for Brij35, 2.963×10^4 for Saponin, 1.127×10^4, for TX100, respectively. As S_w^*/S_w was usually adopted as a solubility enhancement factor, apparent solubilities of PAHs in 600 mg L^{-1} of Saponin solution were about 31.86, which was 33.37 times higher than the water solubilities for anthracene and phenanthrene, respectively. In general, the large solubility enhancements and sharply rising slopes for anthracene and phenanthrene were recognized as the surfactant concentrations exceeded the CMC values of Saponin, Brij35, and TX100. The observed difference in solubility enhancement effect by surfactants above and below their CMCs could be considered as a result of the difference in the ability of micelles and monomers to concentrate anthracene and phenanthrene by partitioning interactions. At a given total surfactant concentration, biosurfactant Saponin below CMC appeared to be the better solubilizing agent than synthetic surfactant solutions as indicated by its higher K_{mn} values. In comparison with K_{mn} values, the remarkably greater K_{mc} values indicate that micelles were far more effective to solubilize PAHs because of the wider extent of the organic environment in a pseudophase state.

3.2 Synergistic Solubilization of PAHs by Mixed-surfactant Systems

Water solubility enhancements of anthracene and phenanthrene by mixed surfactants of Saponin-TX100 and Saponin-Brij35 were determined and compared with those by single surfactants. The results are shown in Figure 1 and Table 2. In these mixed-surfactant systems, the concentration of Saponin was kept at 200 mg L^{-1}. It can be concluded from Figure 1 that the apparent water solubilities of PAHs in mixed-surfactant solutions were higher than those in single-surfactant solutions at the comparable surfactant concentrations. For example, synergistic solubilization of anthracene by using Saponin-TX100 and Saponin-Brij35 at the concentration 800 mg L^{-1} could relatively increased by 6.1 and 3.6 times, respectively, in comparison with the single synthetic surfactant solutions. The sequence of synergistic solubilization for different mixed-surfactant solutions followed the order as: Saponin-Brij35 > Saponin-TX100. These data illustrated the potential capacity of mixed surfactants to apparently enhance the water solubility of anthracene. The synergistic power of biologic-synthetic mixing surfactants on different PAHs was increased with K_{mc} increase of PAHs, and the relevant effects for PAHs with mixed biologic-synthetic surfactants are shown in Table 2. The synergistic solubilization of solutes by a mixed-surfactant solution at a given surfactant concentration may be expressed as

$$\triangle S\% = \frac{S_w - S_{w1} - S_{w2}}{S_{w1} + S_{w2}} \times 100 \tag{2}$$

where, $\triangle S$ is the synergistic solubilization of a solute by a biologic and synthetic surfactant mixture; S_w is the apparent water solubility of the solute at a given surfactant concentration in the mixed-surfactant solution; S_{w1} and S_{w2} are the apparent water solubility of the solute at the same surfactant concentration of the Saponin and synthetic-surfactant solutions. The $\triangle S$ of PAHs in Saponin-Brij35, Saponin-TX100 mixed-surfactant solutions are shown in Table 2. These data proved the potential capacity of mixed surfactants for enhancing water solubility of PAHs. The synergistic power of the mixed surfactants was ranked as Saponin-Brij35 > Saponin-TX100 when the efficiencies of synergistic solubilization were up to 27–137%.

In the mixed surfactant systems, the solubility enhancements of anthracene and phenanthrene and the CMCs of the synthetic surfactants decreased sharply because of the formation of mixed micelles (Zhu and Feng, 2003; Dar et al., 2007; Radulovic et al., 2009). For example, CMCs were reduced from 165 to 140 mg L^{-1} for TX100, and from 74 to 63 mg L^{-1} for Brij35 in the

solutions containing Saponin 200 mg L^{-1}. It was evident that the micelle concentration in mixed-surfactant mixtures was considerably increased over that in single-surfactant systems. Moreover, the K_{mc} values in mixed-surfactant systems may also be increased. The combined data on CMCs and K_{mc} indicated that the synergistically enhanced water solubility of anthracene and phenanthrene by mixed-surfactant solutions is caused by an increase in K_{mc} and a decrease in the CMC of the mixed-surfactant solutions (Zhu and Chiou, 2001). For Saponin-Brij35 and Saponin-TX100 mixed surfactant solutions, the increase of K_{mc} value was coupled with a decrease of the CMC value.

4. CONCLUSIONS

The study revealed the solubilization capabilities of biosurfactant Saponin and its mixed solutions with conventional surfactant solutions for enhancing the solubility of PAH compounds, anthracene and phenanthrene. As the solubilization capacity could be evaluated with the ratio of S_w^*/S_w and K_{mn}, K_{mc} values, the experimental data in this study proved that the utilization of Saponin and mixed solution of Saponin with conventional surfactant could significantly enhance the solubilization of PAHs. Saponin showed the prominent advantage to promote the solubilization of PAHs at low surfactant levels, which was significantly greater than by single synthetic surfactant for Brij35 and TX100. It can strongly be suggested that utilization of biosurfactant would be more practical and effective than the synthetic surfactants in the remedial flush of contaminated sites. Furthermore, the binary combinations of Saponin with Brij35 and TX100 appeared to be more efficient in solubility enhancement if mixed with the biosurfactant Saponin. The synergism noted for the mixed surfactants could be attributed to both CMC decrease of surfactant solutions and an increase of the partition coefficients K_{mc} between micelle and aqueous phase, which thus reduced the level of surfactant pollution and remediation expenses. As a result, Saponin-synthetic mixed surfactants can be a better choice for the application of surfactant enhanced flushing technology in remediation of PAH contaminated soils.

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