



Competitive solubilization of low-molecular-weight polycyclic aromatic hydrocarbons mixtures in single and binary surfactant micelles



Xujun Liang^a, Menglu Zhang^a, Chuling Guo^{a,b,*}, Stéphane Abel^c, Xiaoyun Yi^{a,b}, Guining Lu^{a,b}, Chen Yang^{a,b}, Zhi Dang^{a,b}

^aSchool of Environment and Energy, South China University of Technology, Guangzhou 510006, China

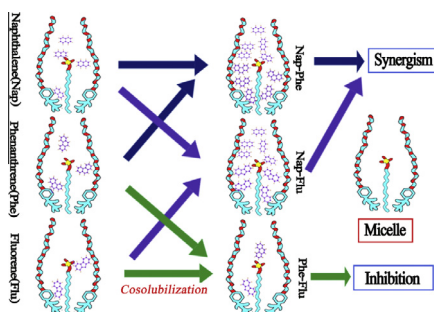
^bThe Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, China

^cCommissariat à l'Energie Atomique et aux Energies Alternatives, DSV/iBiTEC-S/SB2SM/LBMS & CNRS UMR 8221, Saclay, France

HIGHLIGHTS

- Naphthalene and phenanthrene/fluorene had synergistic effect in surfactant micelle.
- Cosolubilization of phenanthrene and fluorene showed inhibitive effect.
- LMW PAHs could solubilize in the micellar shell and core regions.
- Synergism and competition related with amounts of PAHs in micellar shell region.
- Cosolubilization effects were consistent in single and mixed micelle.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study aims to assess mutual interaction among low-molecular-weight polycyclic aromatic hydrocarbons (LMW PAHs), predominant contaminants at petroleum contaminated sites, in nonionic, anionic and their mixed micelles. Cosolubilization effects were evaluated by the molar solubilization ratio, the micelle-water partition coefficient and the deviation ratio. Two conditions existed: (i) naphthalene/phenanthrene and naphthalene/fluorene, with significant different hydrophobicities, showed synergistic effect, a new finding compared to previous observations that no more than one solute's solubility would increase when two solubilizates coexisted, e.g. solubility of naphthalene and phenanthrene in Triton X-100 was increased by 20.8% and 38.5% when cosolubilized, respectively and (ii) phenanthrene/fluorene, with similar hydrophobicity, exhibited inhibitive effect due to competition for the same solubilization sites, i.e. solubility of phenanthrene and fluorene in Triton X-100 was decreased by 36.1% and 6.5% when cosolubilized, respectively. Solubility of PAHs with higher $\log K_{ow}$ gained larger enhancement. Synergism was stronger in bisolutes solubilization system where more PAHs could solubilize in the micellar shell region. Solubility inhibition was more intense to PAHs with lower $\log K_{ow}$. The cosolubilization trends were consistent in single and mixed surfactant systems, whereas the enhancing and suppressive extent, on the whole, were weakened and strengthened with increasing mole ratio of anionic surfactant in the mixed micelles because of reduction in micelle size. This study suggested the significance of considering multi-solutes' interaction to estimate solubilization power of surfactants for selective separation of LMW PAHs from water and soil.

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* Corresponding author at: School of Environment and Energy, South China University of Technology, Guangzhou 510006, China. Tel.: +86 20 39380522.

E-mail addresses: clguoscut@gmail.com, clguo@scut.edu.cn (C. Guo).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), due to their mutagenic and carcinogenic effects on both human and ecosystem [1,2], are a global environmental concern. Most PAHs are formed during incomplete combustion and pyrolysis of fossil fuels and biomass, as well as the coking process [3,4]. Emissions of PAHs are increasing, especially in developing countries such as in China, where emissions of PAHs rose from about 18,000 tons in 1980 to about 116,000 tons in 2003 as a result of growing energy consumption [5]. PAH removal from soils and aquifers by natural attenuation mechanisms or traditional remediation efforts is limited by their poor water solubility.

Micellar surfactant solutions have been studied and assessed as efficient agents for enhancing PAHs' aqueous solubility, and thus increasing PAHs' bioavailability for their biodegradation [6–12]. Most investigations have focused on solubilization of individual compounds in single, binary or ternary surfactant systems [13–19]. PAHs exist, however, in mixtures of many compounds. Reports on cosolubilization of multiple solutes in micellar solutions have shown that the extent of solubilization of mixed solutes differs from their behaviors exhibited in single component systems [20–26]. Rouse et al. [25] found, for instance, that fluorene (Flu) and phenanthrene (Phe) did compete for the same solubilization sites within micelles formed with the anionic surfactant Diphenyloxide Disulfonate with a alkyl moiety of 16 carbon units (C16-DPDS) because of similar hydrophobicity. Recently, Masrat et al. [23] showed that naphthalene (Nap) was inhibited by pyrene to solubilize in nonionic, cationic and anionic micelles, but inhibitive extent followed the order: cationics < nonionics < anionics. These results suggest that the solubilization sites of solutes within micelles and headgroup natures of surfactants may play important roles in influencing the micellar partition of solutes in multi-solute systems.

According to the survey results of Sanchez-Trujillo et al. [27], low-molecular-weight (LMW) PAHs (i.e. molecules formed by 2- and 3- benzene rings), were more abundant than high-molecular-weight (HMW) PAHs (i.e. molecules composed of ≥ 4 benzene rings), at petroleum contaminated sites, especially naphthalene, phenanthrene, fluorene, anthracene, indicating that LMW PAHs may play an important role in evaluating enhanced solubilization efficiency. So far, there are no systematic reports on the cosolubilization effects of LMW PAHs within surfactant micelles. Thus, it's important to investigate the interaction between LMW PAHs in single surfactant micelles. Furthermore, due to the formation of mixed micelles and reduction of surfactants' adsorption losses [28–30], nonionic and anionic surfactants are generally combined for surfactant-enhanced solubilization of PAHs. The mixed micellar structure may have dramatic influences on solubilization behavior of LMW PAHs in micelles. To our knowledge, this study is the first report on solubilization of mixed LMW PAHs in combined nonionic and anionic micelles. The specific objectives were to investigate (i) the effects of solute properties and (ii) mixing mole ratios of nonionic/anionic surfactants on the cosolubilization effects.

2. Materials and methods

2.1. Chemicals

Nap, Phe and Flu were chosen as representative LMW PAHs. Triton X-100 (TX100) and Sodium Dodecyl Sulfate (SDS) were selected as the nonionic and anionic surfactant since they are widely used in industry and subsurface remediation [31,32]. TX100 (purity $\geq 99\%$), SDS (98% purity), Nap (purity $\geq 99\%$), and Phe (purity $\geq 98\%$) were obtained from Sigma Aldrich Chemical

Company. Flu (98% purity) was purchased from Adamas Reagent Co. Ltd. Molecular properties of selected PAHs are presented in Table 1. HPLC-grade methanol was obtained from Shanghai Anpel Scientific Instrument Co., Ltd. All solutions were prepared with Milli-Q[®] water except for the ¹H NMR experiments, which used D₂O (Cambridge Isotope Laboratories, 99.9% purity).

2.2. Measurement of surface tension and critical micelle concentration

Surface tension of TX100, SDS and their mixtures were measured at 25 °C by the Wilhelmy plate technique with a QZBY-1 model tensiometer (Fangrui Instrument Co., Ltd., Shang Hai). The mixing mole ratios of TX100/SDS were set at 4/1, 1/1 and 2/3. The plotted surface tension value was taken when stable readings were obtained for a given surfactant concentration, as indicated by at least three consecutive measurements having nearly the same value. Critical micelle concentration (CMC) values of the surfactant systems were determined as the inflection points by plotting surface tension values versus logarithm of the surfactant concentration shown in Fig. 1.

2.3. Solubilization experiments

Appropriate amounts of Nap, Phe and Flu were added to a series of 30 ml borosilicate vials. The mass of the PAHs added was in excess of their apparent solubility, and the presence of an excess amount was visually confirmed at the end of each test. 20 ml of surfactant solutions of varying concentrations were put into each tube for solubilization. Except for the pure SDS surfactant solutions with concentrations of 10, 20, 30, 40 and 50 mM, concentrations of other surfactant systems were 2, 4, 6, 8 and 10 mM. The surfactant solutions added were all above their CMC. Each treatment was conducted in triplicate. The vials, after being sealed with screw caps having Teflon-lined septa in order to prevent any loss, were shaken on a reciprocating shaker for 48 h at 150 rpm and 25 °C. After equilibration, the tubes were centrifuged at 4000 rpm for 1 h to separate the solid and aqueous phases. An adequate volume of the supernatant was taken to a volumetric flask and diluted with methanol for HPLC analysis. The surfactant concentration in all diluted samples was suitably low to avoid interference during UV detection of the PAHs. Combinations of the solutes in each of the experiments are listed in Table 2. Solutions of the standard curves were prepared by dissolving a mixture of Nap, Phe, and Flu in methanol.

2.4. Analytical methods

Standard solutions and diluted enhanced solubilization samples were analyzed on an Agilent HPLC equipped with a diode array detector and an Agilent Eclipse XDB-C18 column (5 μm , 4.6 \times 150 mm). The HPLC was run with a mobile phase of methanol–water (v/v, 70/30) at a flow rate of 1.2 ml min⁻¹. The three PAHs were well separated, as shown in Fig. 2. Retention time of Nap, Phe and Flu is about 6.43, 14.20 and 15.49 min. Surfactants in the samples were low enough to avoid interference during PAHs detection. According to the peak intensity in Fig. 2, the UV detector was set at 263, 263 and 250 nm for Nap, Flu and Phe, respectively.

2.5. ¹H NMR experiments

NMR analyses were performed on various surfactant solutions contacted with excess amounts of the PAHs, modified from Bernardes [34]. Solubilization processes were the same as that described above. After equilibration, 3 ml of the surfactant solution was then removed from the vials and centrifuged, and 600 μl of the supernates were transferred to 5-mm NMR tubes. Proton NMR chemical

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