



Cosolubilization of phenanthrene and pyrene in surfactant micelles: Experimental and atomistic simulations studies

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ARTICLE INFO

Article history:

Received 8 September 2017

Received in revised form 6 March 2018

Accepted 24 April 2018

Available online 26 April 2018

Keywords:

Surfactant

Phenanthrene

Pyrene

Cosolubilization

Molecular dynamics simulations

ABSTRACT

Solubilization of mixed phenanthrene (PHE) and pyrene (PYR) in Triton X-100 (TX), sodium dodecyl sulfate (SDS) and mixed TX-SDS surfactant solutions were done to observe their cosolubilization effect. Moreover, molecular dynamics (MD) simulations were performed to reveal how polycyclic aromatic hydrocarbons (PAHs) co-exist in the micelle. Cosolubilization of PHE and PYR exhibited synergism along with decreasing synergistic extent with increasing SDS in mixed micelle. MD simulations verified the distribution of PHE and PYR in the shell and core regions of pure SDS and mixed SDS-TX micelles (with molar ratio of 1: 1), which were chosen as the representative systems for simulation study. The movement of PHE and PYR inside the micelle along with their different probability to contact with SDS non hydrogen atoms in pure SDS and mixed SDS-TX solubilization systems suggests the different solubilization sites of the two PAHs inside the micelle leading to their co-existence in the micelle. This study implies the significance of considering cosolubilization effects between PAH mixtures in determining surfactant concentration for environmental remediation.

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1. Introduction

With increasing industrialization and urbanization around the world, there is an increasing demand and consumption of fossil fuels. Incomplete combustion or pyrolysis of the fossil fuels has produced a group of ubiquitous organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) [1,2]. PAHs are a global environmental concern due to their carcinogenic, teratogenic and mutagenic effects on both human and ecosystem [3,4]. Due to their hydrophobicity, PAHs incline to deposit into soil [5]. Surfactant-enhanced remediation (SER) has been studied and assessed as an efficient technology for the decontamination of PAHs from soil [6–9]. Surfactants' solubilization power towards PAHs is one of the main drivers governing SER efficiency. Most studies focused on observing solubilization of individual PAHs into single, binary or ternary surfactant systems [10–15]. However, PAHs exist in complex mixtures in contaminated sites. Previous reports have shown that cosolubilization of mixed organic pollutants in surfactant

micelles exhibits inconsistent effects - synergistic, inhibitive or little impact on each other's solubility [16–20]. At present, researches concerning cosolubilization of mixed low-molecular-weight (LMW, molecules formed by 2- and 3- benzene rings) and high-molecular-weight (HMW, molecules composed of ≥4 benzene rings) PAHs in single and binary surfactant systems are limited.

Cosolubilization effect between mixed PAHs has been related to the solubilization sites of PAHs inside surfactant micelles. Rouse et al. found that, fluorene and phenanthrene (PHE) could compete for a similar locus in the micelle due to their resemble hydrophobicity, thus contributing to their decreasing solubility when coexisted in surfactant solutions [18]. Yang et al. also found that solubilization of naphthalene (NAP) and pyrene (PYR) in micelle shell could reduce micelle-water interfacial tension and increase micelle internal volume to solubilize more NAP and PYR with different solubilization sites [19]. The locus of PAHs inside the micelle can be detected by various experimental techniques such as NMR [21], UV-visible [22] and fluorescence [23] spectroscopy. However, due to the small size of the micelle and the existence of solvents, it is difficult to attain a clear and microscopic view of the distribution of PAHs inside the micelle using the experimental approaches. By using molecular dynamics (MD) simulation approaches, Liang et al. observed that NAP and PYR could dynamically partition in the shell and

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core regions of a micelle formed by 60 sodium dodecyl sulfate (SDS) monomers due to the movement of the two PAHs inside the micelle [24]. Although the distribution of single PAHs inside the micelle has been revealed, how mixed PAHs coexist inside the micelle remains unclear.

Herein, in this study, the solubilization and cosolubilization of mixed LMW and HMW PAHs in pure SDS, Triton X-100 (TX) and their mixed surfactant solutions was firstly investigated. Then pure SDS micelle and mixed SDS-TX micelle (with molar ratio of 1: 1) were selected as representative systems for performing MD simulations of cosolubilization of PAH mixtures to observe the potential mechanisms controlling their coexistence in the micelle. PHE and PYR were chosen as model LMW and HMW PAHs, respectively, due to their wide distribution in urban and coking plant soil [25,26]. This study will further our understanding of cosolubilization mechanisms of PAH mixtures in surfactant micelles.

2. Materials and methods

2.1. Chemicals

PHE and PYR with purities > 98% were purchased from Sigma Aldrich Chemical Company. TX (purity ≥ 99%) and SDS (purity 98%) were chosen as the model nonionic and anionic surfactants, respectively, since

they were widely used in industry and subsurface remediation [27,28]. The two surfactants were also obtained from Sigma Aldrich Chemical Company. Physicochemical properties of PHE, PYR, TX and SDS were listed in Fig. 1. Deionized water was used for preparing surfactant solutions. HPLC-grade methanol (Shanghai Anpel Scientific Instrument Co., Ltd) was used for standard solution preparation and sample dilution.

2.2. Solubilization experiments

Solubilization experiments were done according to the previous report [17]. Briefly, an excess amount of solid PHE and PYR with single or binary combinations were weighted to 30 mL borosilicate vials. Then, 20 mL of surfactant solutions with TX/SDS molar ratio of 5/0, 4/1, 1/1, 2/3 and 0/5 were added to each vial. Surfactant concentrations for pure SDS solubilization systems were set as 10, 20, 30, 40 and 50 mM, whereas the other solubilization systems were 2, 4, 6, 8 and 10 mM. The surfactant concentrations set were all above their CMC [17]. Afterwards, the vials were equilibrated on a reciprocating shaker for 48 h at 150 rpm and 25 °C. Then, the vials were centrifuged at 4000 rpm for 1 h to separate the solid and aqueous phases, and an adequate volume of the supernatant was taken and diluted with methanol for HPLC analysis. Standard solutions were prepared by dissolving mixed PHE and PYR in methanol and stored at 4 °C for further use.

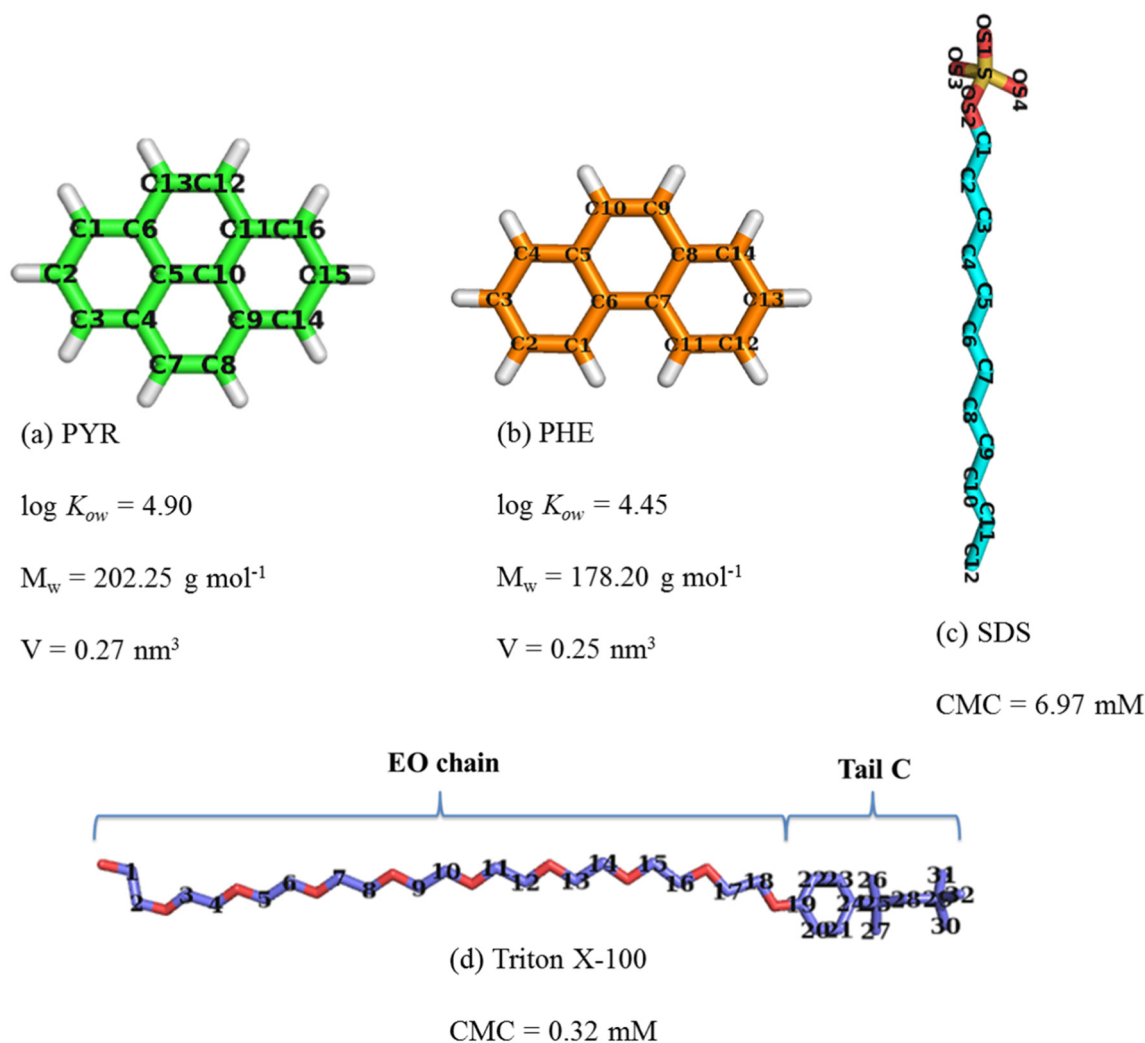


Fig. 1. Physicochemical properties and carbon numbers of (a) pyrene (PYR), (b) phenanthrene (PHE), (c) SDS, and (d) Triton X-100 (TX). The proton atoms of SDS and TX are removed for clarity in numbering the carbon atoms. The physicochemical properties of PHE and PYR are cited from Ref. [29]. V means the molecular Voronoi volume of PHE/PYR in our simulations, which is computed with the *trjVoronoi* program [30,31]. CMC means the critical micelle concentration of SDS and Triton X-100, which were cited from Ref. [17].

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