



Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed micelles composed of a photoresponsive surfactant and a conventional non-ionic surfactant



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ABSTRACT

Surfactant-enhanced remediation is a powerful technology for soil clean-up. However, some drawbacks, such as its high cost and the secondary contamination caused by flushing agents, have hampered this technology and its commercial application has been largely limited to North American and European countries. The aim of this work is to introduce a novel reversible solubilization system composed of the photoresponsive surfactant 4-butylazobenzene-4'-(oxyethyl)trimethylammonium bromide (AZTMA) and the commercial non-ionic surfactant Tween80 for the solubilization of organic contaminants. The solubilization behavior of the AZTMA/Tween80 surfactant system toward polycyclic aromatic hydrocarbons (PAHs) has been studied. Critical micelle concentration (CMC) values indicate that the mixed system has a synergism in mixed micelle formation, and that the interaction parameter (β) is -2.85 when the mole ratio is 2:8. AZTMA is also predicted to be low biologic toxicity by the CMC and surface tension. The synergistic effect on molar solubilization ratio (MSR) and micelle-phase/aqueous-phase partition coefficient K_{mc} values is related to the composition and concentration of the mixed system and follows the order pyrene > phenanthrene > acenaphthene, and these parameters are much higher than those for the single surfactants. After irradiation with UV light, more than 65% of the PAHs could be separated from the mixed micelles, and the cumulative release efficiencies of selected PAHs are consistent with the results of solubilization experiments. All of these features demonstrate that mixed AZTMA/Tween80 should be preferable to single surfactants for soil remediation, avoiding the issues associated with chemical flushing agents and decreasing remediation costs.

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1. Introduction

The hazardous contaminants polycyclic aromatic hydrocarbons (PAHs) show a tendency to persist and accumulate in soils and groundwater and are of great environmental concern [1–3]. It is known that the solubility of PAHs may be significantly enhanced by the hydrophobic tails of surfactant micelles [4]. Thus, surfactant-enhanced remediation (SER) has been suggested as an efficient technology for removing PAHs from soil or groundwater [5,6]. However, the practical application of SER technology has been curbed by some limiting factors, such as the large amount of flushing/washing agent used and its loss in the remediation process, for example by adsorption onto the subsurface matrix,

partitioning into sediments, and the loss during the recovery procedure [7–9]. Hence, it appears to be vitally important to bring forth new ideas for improving SER.

Recently, there has been increasing interest in photoresponsive surfactants by virtue of their unique physical and chemical properties [10–13]. Eastoe and co-workers have systematically studied such amphiphilic molecules containing photoresponsive groups, and they discovered that light can be employed as an external stimulus to cause changes in these surfactants, such as *cis*–*trans* isomerization, photocission, dimerization, polymerization, or polarity reversal [14]. Naturally, these physical and chemical changes could affect the surface activity, solubilization efficiency, microemulsion separation, viscosity, and aggregation structure of the surfactants [15]. As a consequence, owing to their controllability, the development and application of photoresponsive surfactants is an appealing and maturing field of colloid science, and they have been widely implemented in fields such as electronics [16], nanomaterials [17], medicine [18], and life sciences [19].

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Previous investigations have shown that 4-butylazobenzene-4'-(oxyethyl)trimethylammonium bromide (AZTMA), an azobenzene-modified cationic photoresponsive surfactant, could undergo *trans*–*cis* photoisomerization under the stimulation of light [20]. During the photoisomerization process, the surface chemical properties of AZTMA may change accordingly [21,22]. Therefore, we envisaged that it should be possible to regulate the solubility of contaminants in AZTMA solution through reversible control of the formation and disintegration of micelles by light. In other words, the separation and reclamation of a surfactant could be achieved.

In our previous study [23], a novel principle based on AZTMA termed reversible surfactant-enhanced remediation was expounded and we described successful control of the uptake and release of PAHs using AZTMA, which undergoes significant changes upon light irradiation and a solubilization–release cycle of PAHs by AZTMA micelles was achieved. Unlike with some other reversible surfactants, the relevant properties of AZTMA can be reversibly controlled by light alone, without the addition of a third substance or the involvement of a specific reaction site.

However, as a cationic surfactant, the cationic groups of AZTMA tend to bind to anionic sites in soil. Because of this, the potential for the application of AZTMA for soil remediation may be questionable. Actually, however, cationic surfactants have been used in SER applications. As mentioned by Xu et al. [24], the presence of a non-ionic surfactant reduced the amount of cationic surfactant adsorbed. Dar et al. [25] also indicated that a cationic–non-ionic surfactant mixture could enhance the retention of PAHs compared with the individual surfactants, which might improve the processing efficiency of SER. Currently, most surfactant-based practical applications employ mixed surfactants, which give good results [26]. For these reasons, AZTMA still has the potential to be applied in SER.

Hence, in the present study, we have evaluated the synergistic surfactant-enhanced solubilization of three typical carcinogenic PAHs (pyrene, phenanthrene, and acenaphthene) from aqueous solutions by a mixed surfactant system composed of the photoresponsive cationic surfactant AZTMA and the conventional non-ionic surfactant Tween80. The applicability of AZTMA/Tween80 micelles as carriers for the insoluble PAHs for the photochemical control of contamination release has also been evaluated. In addition, we have studied the mixing mechanism of AZTMA and Tween80 in aqueous solutions and explain the chemical reasons for the improved solubilization capacity of the mixed surfactant system.

2. Materials and methods

2.1. Materials

The photoresponsive surfactant AZTMA was obtained from our previous synthetic work. The synthesis and purification steps of AZTMA were similar to those described by Hayashita et al. [27]. The non-ionic surfactant Tween80 was purchased from Aladdin (Jingchun Chemical Co., Shanghai, China). Pyrene, phenanthrene, and acenaphthene with a purity of 98% were obtained from Aldrich Chemical Company. Their physicochemical properties are shown in Table SI-1.

2.2. Surface tension measurements

A surface tensiometer (Fangrui Co. Ltd., Shanghai, China) was employed for measurements of the surface tensions of single and mixed surfactant solutions. The values from the surface tensiometer were each measured three times to ensure that the surface ten-

sion was constant, and the experimental temperature was kept at 25 °C. Because the structure of AZTMA in aqueous solution could be affected by light irradiation, all processes were performed in the dark.

2.3. Solubilization experiments

The enhanced solubilities of pyrene, phenanthrene, and acenaphthene were monitored in a series of surfactant solutions at concentrations of 0–10 mmol/L. Excess PAHs were added to 40 mL Teflon-lined Corex centrifuge tubes containing 20 mL of the surfactant solution. These tubes were then continuously vibrated on a reciprocating shaker for 24 h at 25 °C to ensure maximum solubilization, and then the mixtures were filtered through 0.45 µm syringe-driven filters to separate the undissolved substrates. To reduce the effects of surfactant on determining the solubilities of PAHs, the solubilized PAHs were extracted with hexane. Next, the supernatant was collected and analyzed for pyrene, phenanthrene, and acenaphthene by UV/Vis spectrophotometry (Shimadzu UV-2600) at 334, 251, and 228 nm, respectively. A blank cuvette containing hexane was prepared to achieve a baseline for quantitative analysis of the PAHs. Note that the solubilization process had to be shielded from light to prevent inactivation of the surfactant.

2.4. Evaluation of the reversible properties of the AZTMA/Tween80 mixed solutions

An XPA-7 photochemical reactor (Xujiang Co. Ltd., Nanjing, China) with a 500 W mercury-xenon lamp was employed to evaluate the reversible properties of AZTMA/Tween80 in aqueous solution. By the use of optical filters, UV (365 nm) and visible light (≥ 420 nm) could be selected as appropriate external stimuli. 0.1 mmol/L of mixed surfactant solution was monitored spectrophotometrically in a quartz cuvette with an optical pathlength of 10 mm.

2.5. Photochemical control of the release of PAHs

After dissolution of PAHs, the mixed AZTMA/Tween80 solutions were irradiated with UV light (365 nm) in the XPA-7 photochemical reactor for 2 h at 25 °C to ensure attainment of the photostationary state. The apparent solubility of the PAHs was then measured in a similar manner as described in Section 2.4. The cumulative release efficiencies of pyrene, phenanthrene, and acenaphthene from mixed micelles could be calculated based on the concentration differences of surfactant solutions before and after irradiation.

3. Results and discussion

3.1. Surface activity of AZTMA/Tween80 mixed solutions

The concentration dependence of the equilibrium surface tensions of Tween80 and AZTMA/Tween80 mixed solutions at 25 °C are shown in Fig. 1. The initial mole fractions of *trans*-AZTMA in the mixed surfactant systems were 0, 0.2, 0.3, 0.4, 0.5, 0.8, and 1, respectively. As shown in Fig. 1, the mixed surfactant system displayed lower surface tension values than Tween80 alone when the mole fraction of AZTMA was 0.2 and 0.3, indicating that the addition of cationic AZTMA could change the surface properties of non-ionic Tween80 solution to some extent. The CMC values based on the inflection points of the surface tension curves of individual and mixed surfactants are presented in Table 1. As expected, the CMC of the mixed system reached a minimum when the mole

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