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Reversible solubilization of typical polycyclic aromatic hydrocarbons by a photoresponsive surfactant

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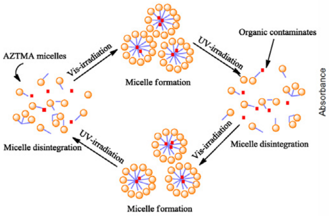
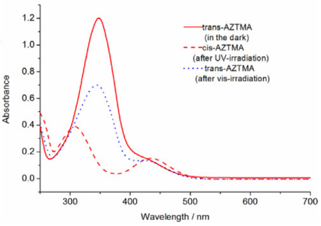
HIGHLIGHTS

- A novel principle for reversible surfactant-enhanced remediation was explicated.
- The feasibility of this principle for organics-polluted soil was preliminarily verified.
- Photoresponsive surfactant AZTMA was suitable for reversible solubilizing PAHs.
- Solubilization-release cycle of PAHs by AZTMA manipulated promptly under UV–vis irradiation.

GRAPHICAL ABSTRACT





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ABSTRACT

For the purpose of surfactant-enhanced remediation (SER) as a means of removing polycyclic aromatic hydrocarbons (PAHs) from polluted soils, a new method of reversibly solubilizing PAHs has been developed based on modulating the surface activity of the photoresponsive surfactant 4-butylazobenzene-4′-(oxyethyl)trimethylammonium bromide (AZTMA). AZTMA undergoes reversible isomerization between *trans* and *cis* isomers upon irradiation with ultraviolet (UV) and visible lights. The considerable disparity in critical micelle concentrations (CMCs) between *trans*- and *cis*-AZTMA implies that the surface activity of this surfactant may be easily manipulated. Kinetic studies have indicated that the solubilization mechanism of PAHs by AZTMA is similar to that of the conventional surfactants and can be described by an adsorption–desorption model. The molar solubilization ratios (MSRs) of pyrene, phenanthrene and acenaphthene in 10 mmol L^{-1} *trans*-AZTMA solution were 0.66×10^{-2}, 3.92×10^{-2} and 5.02×10^{-2}, respectively, much higher than those with *cis*-AZTMA. More than 70% of the solubilizate in *trans*-AZTMA solution could be released through irradiation with 365 nm UV light at an appropriate surfactant concentration. The presented results provide a theoretical foundation for reversible surfactant-enhanced remediation (RSER) based on a photoresponsive switchable surfactant.

1. Introduction

The contamination of soil by toxic and hazardous organic pollutants is a worldwide environmental problem. Polycyclic aromatic hydrocarbons (PAHs) are of particular concern owing to their long-term persistence in soil and adverse effects on human health [1]. Various physical, chemical, and biological technologies, as well as combinations thereof, have been evaluated for their removal. However, PAHs are very difficult to degrade because they adsorb strongly to soils or sediments. As a consequence, remediation of PAH-contaminated soil is often geared towards desorption of the PAHs [2,3]. It is well known that surfactants can improve the mass-transfer of PAHs from the solid phase or a non-aqueous phase

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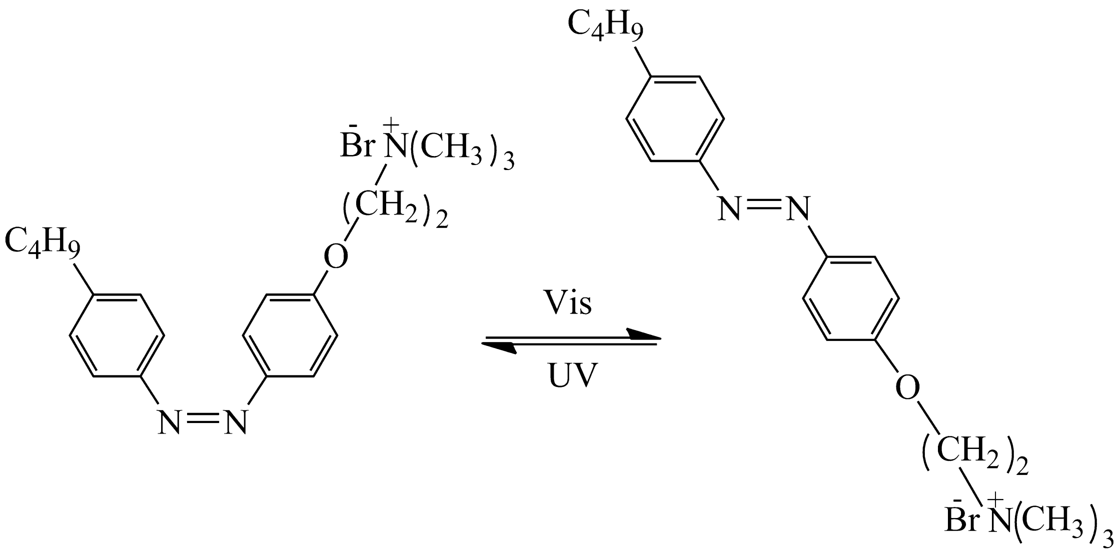

Fig. 1. Photoisomerization of AZTMA.

liquid (NAPL) to the aqueous phase by decreasing the interfacial tension and accumulating the hydrophobic compounds in micelles [4,5]. A variety of researches have also indicated the potential of using micellar solubilization to clean up residual and adsorbed contaminants from soils [5–8]. Surfactant-enhanced remediation (SER) has been proposed as a promising technology for the treatment of organic-contaminated soil [5,9,10]. Numerous studies have demonstrated that SER is very effective for the removal of PAHs from soil [11–16]. Demonstration projects around the world have been carried out to show that SER technology has great potential for the remediation of soil and groundwater [16–20].

Generally, during the SER process, after completing its specific function, the surfactant has to be separated from the solubilization system for reuse. Otherwise, there may be negative effects on the environment caused by its direct emission and costs would be high. Hence, the recycling efficiency of the surfactant must be taken into account in contaminated soil remediation. If the formation and disintegration of molecular assemblies could be reversibly controlled by external stimuli, it might be possible to regulate the solubilization and release of contaminants. In this way, the reuse of a surfactant could be achieved. It has been reported that switchable surfactants can be reversibly controlled through the formation and disruption of vesicles by external stimuli, including photochemical means [21,22], electrical potential [23–26], the presence of gases [27,28], and so on. In our previous studies, a nonionic switchable surfactant FPEG was synthesized and the hydrodynamic diameter and aggregation number of its micelles could be reversibly controlled by an electrochemical approach [29]. Li et al. [30] verified that a ferrocene-modified amphiphilic molecule Fc14 could efficiently solubilize VOCs, and that contaminants in the micelles could be easily separated after solubilization.

In the present study, we have sought a surfactant for which the micelles could be reversibly and rapidly controlled without the addition of a third substance. For this purpose, a photoswitchable surfactant seemed to be a good choice. In order to obtain an appropriate switchable surfactant that could be conveniently regulated, azobenzene-modified cationic 4-butylazobenzene-4′-(oxyethyl)trimethylammonium bromide (AZTMA) was synthesized. This molecule has good photoresponsive characteristics, with *trans*–*cis* photoisomerization occurring under irradiation with UV or visible light, and its surface chemical properties change accordingly [31,32]. As reported previously [33], the release of an oily substance, ethylbenzene, could be reversibly controlled by the change in the molecular structure of AZTMA. Therefore, we envisaged reversible surfactant-enhanced remediation (RSER) based on this switchable surfactant. In the process of soil remediation, the ion-exchange capacity of AZTMA may limit the potential significance of this technology. However, Zhang et al. [34] found that the use of cationic–nonionic mixed surfactant could decrease the adsorption of cationic surfactant, and cationic surfactants can be used for soil remediation when mixed with other surfactants [35]. Furthermore, Matsumura et al. [31] reported that the formation and disintegration of mixed micelles of AZTMA and other surfactants could be regulated by light. Hence, AZTMA appeared to have good prospects for the proposed technique. However, owing to their lower solubility in water, the mechanism of solubilization of PAHs using photoresponsive amphiphilic molecules containing azobenzene groups has rarely been expounded. Understanding of the water solubility enhancement of organic pollutants by switchable surfactants and the release efficiency of organic compounds following contaminant solubilization in surfactant micelles might allow extending of the scope of contaminant remediation.

In this study, due to their ubiquity and persistence in the environment, three typical PAHs (pyrene, phenanthrene, and acenaphthene) with various water solubilities have been employed as target pollutants. Experiments have been carried out to expound the mechanism of solubilization of PAHs using AZTMA and to ascertain whether this azobenzene-modified surfactant might be used in SER. The applicability of light-driven release of pollutants contained by AZTMA micelles has also been investigated. The photoisomerization of AZTMA is illustrated in Fig. 1.

2. Materials and methods

2.1. Materials

The photosensitive surfactant AZTMA was synthesized and purified according to the procedures similar to those described by Hayashita et al. [36]. The identity of the cationic surfactant with an azobenzene moiety in its hydrophobic group was verified by NMR analysis in $CDCl_3$ solution. The physicochemical properties of the target solubilizates pyrene, phenanthrene, and acenaphthene (98% pure, Aldrich Chemicals) are shown in Table SI-1.