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Efficiency of single and mixed Gemini/conventional micelles on solubilization of phenanthrene

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ABSTRACT

Water solubility enhancement of phenanthrene (PHE) by a cationic Gemini surfactant (CG), four cationic and nonionic conventional surfactants (Brij35, TX 100, CPC and DTAB) as well as their equimolar binary combinations (CG/Brij35, CG/TX100, CG/CPC and CG/DTAB) have been studied and compared. Their solubilization efficiency and relationship between the structure and the solubilizing capacity towards PHE have been quantified in terms of the critical micelle concentration (CMC), the molar solubilization ratio (MSR) and the micelle–water partition coefficient (K_m). The ideality/nonideality of the mixed micelles has been discussed in light of Clint, Rubingh, Edwards and Treiner's approaches. It has been observed that both CG and equimolar binary surfactant systems remarkably enhanced the water solubility of PHE. The solubilizing capacity of CG/nonionic surfactants is particularly higher than their corresponding conventional surfactant while the contrary results have been shown by CG/cationic surfactants. This may be attributed to the "complement–counteract" effect between the micellar core solubilization and the micelle–water interface adsorption. The interaction between the Gemini and the conventional surfactants with the same chain length becomes more intense regardless of the positive or the negative effect. These results demonstrate and suggest that CG/nonionic mixed surfactants with the same chain length are more appropriate to employ for soil and water remediation.

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1. Introduction

The contamination of soils and water by polycyclic aromatic hydrocarbons (PAHs) which are bio-accumulative, resistant to degradation, and possess toxic properties has become a widespread environmental concern [1]. Various ways such as chemical [2], physical [3], biological [4], and their combined methods [5] have been made to develop efficient technologies to remedy PAHs contaminated soils and groundwaters. The main principle of such remedy strategies is their significant capabilities of desorbing organic compounds from contaminated subsurface. Among them, in situ surfactant-enhanced remediation (SER) has been developed to be a more powerful remediation method [6] due to the outstanding solubility enhancements of organic compounds by partitioning them into the hydrophobic cores of surfactant micelles. Numerous peer-reviewed studies have shown that the enhanced solubility of a contaminant in the presence of surfactants occurs above their critical micelle concentrations (CMC) [7]. Besides, surfactants can

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promote microbial remediation of PAHs in soil and water by affecting the accessibility of PAHs to microorganisms [8,9]. Recently, mixed surfactants were shown to be of great interest in scientific and industrial application due to their efficient solubilization, suspension, dispersion and transportation capabilities [10]. There are numerous reports on the solubilization of PAHs by conventional single/mixed surfactants systems. Zhou and Zhu [11] have reported the potential capacity of anionic–nonionic mixed surfactants to enhance the solubility of pyrene in water. Dar et al. [10] have concluded that cationic–nonionic mixtures has better solubilization capacity for PAHs than pure cationic, nonionic and cationic–cationic mixtures. Paria and Yuet [12] found a negative deviation solubilization of naphthalene from the ideal value by various ionic–nonionic mixed surfactant systems.

However, most of previous studies related to partitioning of PAHs in micellar dispersion were reported on the use of conventional surfactants having single monomers with a single hydrophobic tail and a single hydrophilic head group. A more recent and innovative surfactant to aid the removal of contaminants from soil is Gemini surfactant. It is the family of surfactant molecules consisting of two hydrophobic chains and two hydrophilic headgroups connected through a relatively short (rigid or flexible) spacer group [13]. Gemini surfactants have attracted considerable attention, since they have lower CMC values, much greater efficiency in reduc-

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Table 1

The formula and physicochemical properties of the selected surfactants.

Surfactant	Structure	MW	CMC _{exp} ^a (mM)
CG	$C_{12}H_{25}N^{+}(CH_{3})_{2}(CH_{2})_{2}-N^{+}(CH_{3})_{2}C_{12}H_{25}\cdot 2Br-$	614.67	0.8 (0.81) [22]
TX 100	$C_8H_{17}C_6H_4(OCH_2CH_2)_{9.5}OH$	628	0.2 (0.21) [11]
Brij35	C ₁₂ H ₂₅ (OCH ₂ CH ₂) ₂₃ OH	1200	0.065 (0.061) [8]
CPC	CICH ₂ (CH ₃) ₂ COCl	155.02	1.02 (0.99) [23]
DTAB	$C_{12}H_{25}(CH_3)_3NBr$	308.4	15.0 (14.0) [24]

^a Error limits of CMC_{exp}s are $\pm 4\%$.

ing surface tension and unusual aggregation morphologies [14]. They have been generating growing interest owning to their superior performance in applications.

What is noteworthy is that the solubilization capabilities of surfactants are selective. The amount and structure of surfactants, even the type of contaminants could also be expected to influence the efficient solubility of pollutants in surface and ground water. It is meaningful to explore new surfactant systems and develop more practical soil and water remediation methods. However, few reports of solubilization towards organic compounds by single or mixed Gemini surfactant systems are available [15] and most present research activities on Gemini surfactant are mainly focused on their synthesis and characterizations [16,17].

In this work, we have investigated the solubilization of PHE in selected single and equimolar CG/nonionic and CG/cationic mixed surfactant systems. The theories of Clint [18], Rubingh [19], Edwards et al. [20] and Treiner et al. [21] were used to analyze and compare the experimental results to understand the synergism and antagonism in solubilization capabilities of multi component surfactant systems. The experimental results of this study will be useful to find out and predict the solubilization properties of mixed Gemini/conventional surfactant systems.

2. Materials and methods

2.1. Materials

The nonionic surfactants (Brij35 and TX 100) and cationic surfactants (CPC and DTAB) with purity > 99% were all purchased from Sigma-Aldrich. Gemini surfactant (CG) N1-dodecyl-N1,N1,N2,N2tetramethyl-N2-octylethane-1,2-diaminium bromide was obtained from Chengdo Organic Chemicals Co., LTD., Chinese Academy of Science, with a purity of 98%. The molecular structures and properties of selected surfactants are given in Table 1. Phenanthrene, the three-ring PAH, was selected as the representative contaminant in this study and purchased from Sigma-Aldrich; the purity of compound is greater than 98%. The water solubility of PHE is 5.61×10^{-6} M at 25 °C and the octanol-water coefficients $(Log K_{ow})$ is 4.46. The stock solutions of surfactant were prepared by dissolving the weighed amount of the relevant surfactants in deionized water. Different concentration levels of surfactant solutions were made by diluting the stock solution in the appropriate amount of deionized water.

2.2. Surface tension measurements

Surface tension measurements were performed by a model 70545 surface tensionmeter manufactured by CSC Scientific Company, INC. This instrument operates on the DuNouy principle, in which a platinum ring is suspended from a torsion balance, and the force (in mNm⁻¹) necessary to pull the ring free from the surface film is measured. A concentrated stock solution of the single as well as mixed surfactant was added to a known amount of water and allowed to equilibrate for approximately 3 h. Then the surface tension values were measured until constant surface tension values

ues indicated that equilibrium had been reached. The accuracy of measurements was within $\pm 0.1 \text{ mNm}^{-1}$. The values of CMC were determined as the concentration at sharp breaks in the plot of surface tension (γ) versus the logarithm values of surfactant solutions (Log C_t) over a wide concentration range shown in Fig. 1.

2.3. Solubilization experiments

Batch experiments for solubilization of PHE in nine different single and equimolar mixed surfactant systems were carried out subsequently. Each contaminant–surfactant system involved seven to twelve batch experiments with surfactant solutions having a range of concentrations above the CMC. For each batch test, excess amount of PHE was separately added to each vial containing a series of 10 ml single or equimolar mixed surfactant solutions to ensure maximum solubility. The sample vials were sealed with a screw cap fitted with a Teflon lined septum to prevent any volatiliza-



Fig. 1. Plots of the surface tension (γ) versus the total surfactant concentration (C_t) of single and binary surfactant combinations: (a) single and equimolar binary Gemini and nonionic conventional surfactant; and (b) single and equimolar binary Gemini and cationic conventional surfactant.

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