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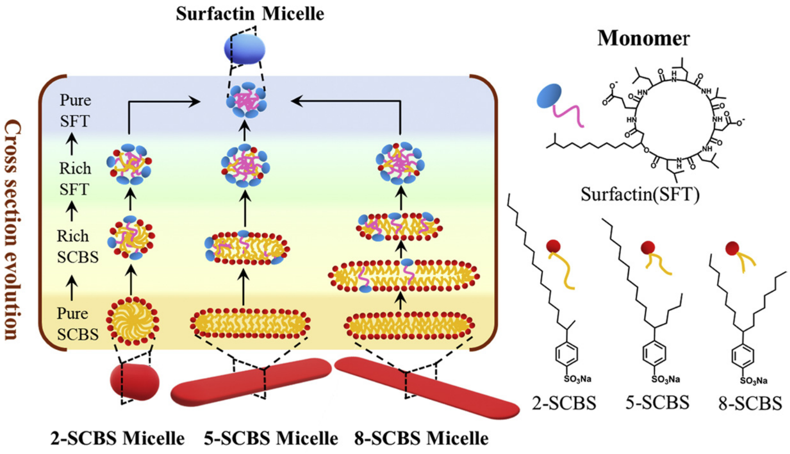
# Micellization in binary biosurfactant/synthetic surfactant systems: Effects of temperature and hydrophobic group structure of alkyl benzenesulfonate

Lingling Kong[a], Hongze Gang[a,*], Zijun Wang[b], Tianfu Li[b], Charl J. Jafta[c,1], Dan Fei[a], Ruqiang Ye[a], Bozhong Mu[a,d,*]

[a] State Key Laboratory of Bioreactor Engineering and Applied Chemistry Institute, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, PR China
[b] China Institute of Atomic Energy, Beijing 102413, PR China
[c] Helmholtz-Zentrum Berlin fur Materialien und Energie, Lise-Meitner-Campus, Berlin, 14109, Germany
[d] Shanghai Collaborative Innovation Center for Biomanufacturing Technology, Shanghai 200237, PR China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Micellization mechanism of biosurfactant/synthetic surfactant systems is essential in predicting their industrial applications. Biosurfactant, [Glu1,Asp5]-C15 surfactin, mixing with three isomers of sodium cetyl benzenesulfonate (SCBS) with benzenesulfonate attached at the 2nd, 5th, 8th carbon on the alkyl chain (abbreviated as 2-SCBS, 5-SCBS, and 8-SCBS), constituted the binary biosurfactant/synthetic surfactant systems in this work. Effects of mixing ratios, temperature, and hydrophobic structures of SCBS on micellization process were investigated by surface tensiometry, steady state fluorescence measurements, dynamic light scattering, and small angle neutron scattering. The results showed that at 60 °C synergism in micellization occurred in surfactin/2-SCBS and surfactin/5-SCBS binary systems, while antagonism appeared in surfactin/8-SCBS binary systems. Molecular interaction in mixed micelle at 60 °C turned from strong attractive to strong repulsive with the benzenesulfonate moving from the end to the middle of the alkyl chain. Surfactin exhibited weak interaction

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[*] Corresponding authors at: State Key Laboratory of Bioreactor Engineering and Applied Chemistry Institute, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, PR China.
*E-mail addresses:* ganghz@ecust.edu.cn (H. Gang), bzmu@ecust.edu.cn (B. Mu).
[1] Current address: Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

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with both 5-SCBS and 8-SCBS at 25 °C. Mixed surfactin/2-SCBS micelles were formed in spherical cylinders with more hydrophobic core and within 66 Å. Mixed surfactin/5-SCBS micelles and mixed surfactin/8-SCBS micelles showed similar morphology evolutions at 25 °C, long elliptical cylinders transformed into small spherical cylinder by reducing both length and radius ratio of cross section with increasing surfactin mole fraction.

## 1. Introduction

Biosurfactants are surface-active components that produced by a variety of animals, plants, and microorganisms [1,2]. Compared with conventional synthetic surfactants, biosurfactants possess the superior properties of biodegradability [3], low toxicity [4,5] and effectiveness in enhancing biodegradation [6,7] and solubilization of low solubility compounds [8,9]. Among the family of biosurfactants, surfactin (SFT)[2], mainly produced by *Bacillus subtilis* strains, remains the main representative of lipopeptide family and is also one of the most powerful ones [10]. Its critical micelle concentration (CMC)[3] can be as low as around 0.01 mM [11–15] and the surface tension of water can be reduced to around 27 mN/m from 72 mN/m [11,14,15]. SFT molecule has a linear alkyl chain ranged from 12 to 17 carbons and a cyclic peptide moiety consisted of seven amino acid residues [16–18]. Two carboxyl groups in Glu1 and Asp5 make SFT serve as anionic surfactant when pH value is above 6 for pKa values of SFT are 4 and 6 in solution and subsurface, respectively [19]. Besides, SFT was found to be able to maintain its surface activities stably in wide temperature range from 30 °C to 120 °C and pH from 5 to 12 [13,20]. Excellent abilities for working in extreme environment make SFT very potential in many industrial application areas, especially in harsh conditions, like enhancing petroleum recovery [21]. However, the relatively high cost and low yield of biosurfactants limit their wider applications.

Alkyl benzenesulfonate is one of the important conventional anionic surfactants and takes large and essential part in cleaning and laundry detergents [22,23]. It shows effective surface activity and low cost, but suffers from the increasing pressure for unfavorable environmental impact [23]. In recent years, blends of biosurfactant and synthetic surfactants have potentially provided a way on reducing cost and producing superior properties by maximizing their advantages but minimizing disadvantages.

Micelle formation in surfactant solution always governs many important phenomena, such as detergency, solubilization, *etc.* [24–26] and also affects interfacial properties at various interfaces. Hence, a fundamental understanding of micellization in biosurfactant/conventional surfactant is essential. Micellization properties within binary ionic surfactant systems depend on molecular interactions, which was proposed to be the balance of several factors, mostly hydrophobic interaction and electrostatic interaction. Hydrophobic interaction was suggested to drive surfactant molecules to form mixed micelles for decreasing the free energy in binary ionic surfactants systems [27,28]. Different charged polar heads of surfactants express various electrostatic interactions. Therefore, among the micellization investigations containing SFT and synthetic surfactant, SFT always shows strong synergistic effect in mixing with cationic surfactants by hydrophobic interaction together with electrostatic attractions within opposite charged polar heads. Micellization synergetism were found in SFT mixing respectively with cetyl trimethyl ammonium bromide [11] and cationic gemini surfactant, ethanediyl-1,3-bis(dode-cyldimethylammonium bromide) [14]. In both of the binary SFT/cationic surfactant systems, mixed micelles transformed into larger morphology micelles, such as, vesicles and cylinders, in certain mixing ratios, with no precipitates observed. Interactions between zwitterionic surfactant and SFT were more complex as attractive and repulsive electrostatic interactions coexisted. High micellization synergistic interaction of betaine with SFT was reported as a result of the optimum alkyl chain length and the polar head structure of zwitterionic surfactant [15]. Longer separation between positive and negative charge centers in betaine provided less internal electrical overlap, then induced stronger electrostatic attraction with SFT. Though surfactants with same charges display repulsive effects within their polar heads, but weak synergism in monolayer adsorption and micellization were found in cationic-cationic surfactant systems, which might mainly be attributed to the hydrophobic effects [29,30]. By means of hydrophobic interactions, SFT could spontaneously insert into lipid membrane accompanied by a conformation change of peptide cycle and form ion-conducting pores, especially in the presence of calcium [31,32]. Synergistic effect on improving specific biological activities were discovered from the mixture of SFT and Iturin A, another microbial lipopeptide [33,34].

Up to now, researches on systems of SFT and synthetic anionic surfactants are limited, especially the hydrophobic structure effects in micellization. In this work, we focus on the micellization of a typical lipopeptide, [Glu1,Asp5]-*iso*-C15 SFT, and frequently-used alkyl benzenesulfonate. Three isomers of sodium cetyl benzenesulfonate (SCBS)[4] which has a benzenesulfonate group attached at the 2nd, 5th, 8th carbon in the alkyl chain were chosen to further investigate the effects of hydrophobic group structure of SCBS on mixed micelle formation. CMCs of binary SFT/SCBS systems were first calculated from the measurements of surface tension. Next, micelle microenvironment properties, water penetration and anisotropy of molecule arrangement in micelle, were characterized through the movement of fluorescent probes. In the end, dynamic light scattering and small angle neutron scattering further gave the information of micelle size distributions and morphology. All these will broaden the knowledge about micellization mechanism of binary biosurfactant/synthetic surfactant systems.

## 2. Material and methods

### 2.1. Chemicals

Surfactin (> 95%) was extracted from the fermentation broth of *Bacillus subtilis* as previously reported[35] and its chemical structure is shown in Fig. 1(a). Sodium cetyl benzenesulfonate (> 95%) isomers (2-SCBS, 5-SCBS, and 8-SCBS) were supplied by Lanqi company (Fig. 1(b)–(d)).

Fluorescence probes pyrene (Py)[5], and 1,6-diphenyl-1,3,5-hexatriene(DPH,[6] mass purity ≥98%) were purchased from Sigma-Aldrich.

All the surfactant solutions were prepared using PB buffer (phosphate buffer, 10 mM, pH = 7.4).

### 2.2. Surface tension studies

The surface tensions (γ) of SFT, SCBSs and their mixtures were measured by DCAT 21 tensiometer (Dataphysics, Germany) with the plate method. Experimental temperatures were controlled at 60 °C for all SCBS/SFT binary surfactant systems, and at 25 °C for 5-SCBS/SFT and 8-SCBS/SFT mixtures (due to the good solubility of 5-SCBS and 8-SCBS at room temperature).

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[2] SFT: Surfactin.

[3] CMC: Critical micelle concentration.

[4] SCBS: Sodium cetyl benzenesulfonate.

[5] Py: Pyrene.

[6] DPH: 1,6-diphenyl-1,3,5-hexatriene.