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Interaction of a Biosurfactant, Surfactin with a Cationic Gemini Surfactant in Aqueous Solution

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Abstract: The interaction between biosurfactant Surfactin and cationic Gemini surfactant ethanediyl-1,3-bis(dodecyldimethyammoniumbromide) (abbreviated as 12-3-12) was investigated using turbidity, surface tension, dynamic light scattering(DLS) and small angle neutron scattering (SANS). Analysis of critical micelle concentration (CMC) values in Surfactin/12-3-12 mixture indicates that there is synergism in formation of mixed Surfactin/12-3-12 micelles. Although Surfactin and 12-3-12 are oppositely charged in phosphate buffer solution (PBS, pH7.4), there are no precipitates observed at the concentrations below the CMC of Surfactin/12-3-12 system. However, at the concentration above CMC value, the Surfactin/12-3-12 mixture is severely turbid with high 12-3-12 content. DLS and SANS measurements follow the size and shape changes of mixed Surfactin/12-3-12 aggregates from small spherical micelles via elongated aggregates to large bulk complexes with increasing fraction of Gemini surfactant.

Keywords: Surfactin, Gemini surfactant, micelle, surface tension, SANS

1. Introduction

The mixtures of different types of surfactants have attracted significant interest since mixtures provide a synergistic enhancement of performance and functionality which cannot take place in single surfactant systems¹⁻³. Synergism increases with the degree of charge difference⁴⁻⁶ meaning that the higher level of synergism is obtained by mixing anionic and cationic surfactants. There have been plenty of studies of anionic/cationic surfactants mixtures. The behavior and physicochemical properties of mixtures of a highly branched cationic and sodium alkyl sulfate have been widely studied by Yu and co-workers⁷⁻⁹. And, it has been reported that the asymmetrically double-tailed cationic surfactants fail to fit well into a crystal lattice structure and hence minimize precipitation¹⁰. Bergström and co-workers have studied the structures in cationic/anionic surfactant including Gemini systems using the small angle neutron scattering technique¹¹⁻¹³. However, precipitation is a common phenomenon that can occur in all of the anionic/cationic surfactants mixture mentioned above and in most cases precipitation is undesirable because it renders the surfactant ineffective in solution. Therefore, a better understanding of such system is necessary to broaden the horizon for their application.

Surfactin, a biosurfactant produced by various *Bacillus subtilis* strains, is cyclic lipopeptide built from a heptapeptide (Glu-Leu-D-Leu-Val-Asp-D-Leu-Leu) and a β -hydroxy fatty acid with variable chain lengths of 13-15 carbon atoms¹⁴⁻¹⁶ (Figure 1(a)). Surfactin has been receiving attention for industrial, biotechnological, and therapeutical applications^{17,18} because of its high surface activity, which could reduce the surface tension of water to 27 mN/m¹⁷ by that concentration as low as 10^{-5} M. It can be seen that Surfactin has two $-\text{COOH}$ groups in L-Glu1 and L-Asp5. The pK_a values¹⁹ of Asp and Glu are around 4.3 and 4.5, respectively, which means it exists as an anionic molecule in neutral solution.

Gemini surfactants contain two single-chain surfactant moieties joined by a spacer group.²⁰⁻²² The two amphiphilic moieties are close to each other, especially when the spacer group is short. Owing to this, on the one hand, the interaction between the hydrophobic chains is enhanced; on the other hand, repulsion between the hydrophilic

groups (particularly the electrostatic between the ionic head groups) will be greatly reduced due to the chemical bonds connection. This novel class of surfactants has many unique properties that are superior to those of conventional single-chain surfactants, such as remarkably low critical micelle concentration (CMC), much higher surface activity, and better wetting properties. Moreover, it has unusual aggregation morphologies. Since the surfactant micellization is driven by hydrophobic interactions but opposed by the repulsion of charged head groups (for ionic surfactants) and hydration (for nonionic surfactants), Gemini surfactant is more readily to form aggregates. The quaternary ammonium Gemini surfactants are widely investigated about their properties and applications^{23,24}. For the 12-s-12 (12 carbon atoms on the hydrophobic alkyl chain and 's' represents the number of carbon atoms of the spacer) series, at the concentration close to CMC value, spherical micelles are formed. Increasing the surfactant concentration, for the short spacer, such as $s = 2, 3$, elongated rod-like micelles are formed; for the medium length like $s = 4, 6, 8, 10, 12$, spherical micelles are formed, and for the longer spacer, $s = 16, 20$, vesicles are readily to form²⁴.

There are a lot of studies on Surfactin¹⁴⁻¹⁹ and Gemini²⁰⁻²⁴ from various aspects. However, to the best of our knowledge, there is no research about their mixtures. The dynamic interfacial tension between the Surfactin/12-3-12 binary aqueous system and crude oil has been carried out in our group, which revealed that Surfactin/12-3-12 mixtures can reduce the interfacial tension to an ultralow level in alkaline environment (see details in Supporting Information) which can be used in the application in oil recovery. The better understanding of the fundamental physicochemical property of the mixture of Surfactin/Gemini surfactant system is the key point for their practical application. In our previous work, we have investigated the micelle formation and interfacial behavior of Surfactin²⁵ in PBS buffer. A further research²⁶ has also been carried out on the interaction of Surfactin with betaines which revealed that there was a synergistic effect between them, and the configuration of mixed micelles changed with the head-groups of betaines. Then, the interactions among neutral polymer PAM, Surfactin and four betaines in PBS buffer were further

studied. Transition from spherical to rodlike aggregates (micelles) has been observed in solutions of Surfactin and Surfactin/SDDAB (N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate) with addition of 0.8 wt % of PAM²⁷. Wang et al²⁸ studied the interaction between surfactin and cationic surfactant Cetyltrimethylammonium Bromide (CTAB) in mixed micelle, There existed synergism between anionic Surfactin cationic surfactant CTAB, and the mixed system might be able to form vesicle spontaneously at high molar fraction of surfactin. However they did not study the precipitation condition and the aggregates properties (shape and size) of the anionic/cationic mixed surfactant aqueous system. A continuation of the aggregation behavior of Surfactin/12-3-12 mixtures were investigated in present paper by surface tension, small angle neutron scattering and dynamic light scattering, which will broaden the potential application for both Surfactin and Gemini surfactants.

2. Materials and Experiments

2.1 Materials.

2.1.1 Surfactin. Surfactin was produced by *Bacillus subtilis* TD7 cultured in a laboratory of East China University of Science and Technology^{29,30}. Surfactin isoform (Figure 1(a)) was separated by extraction with anhydrous ether, isolated with normal pressure ODS C18 column and purified by the RP-HPLC (Jasco, Japan). The structure of the isolated lipopeptide was determined by the electrospray ionization-time-of-flight mass spectrometer (ESI-TOF MS/MS) and GC/MS^{29,30}.

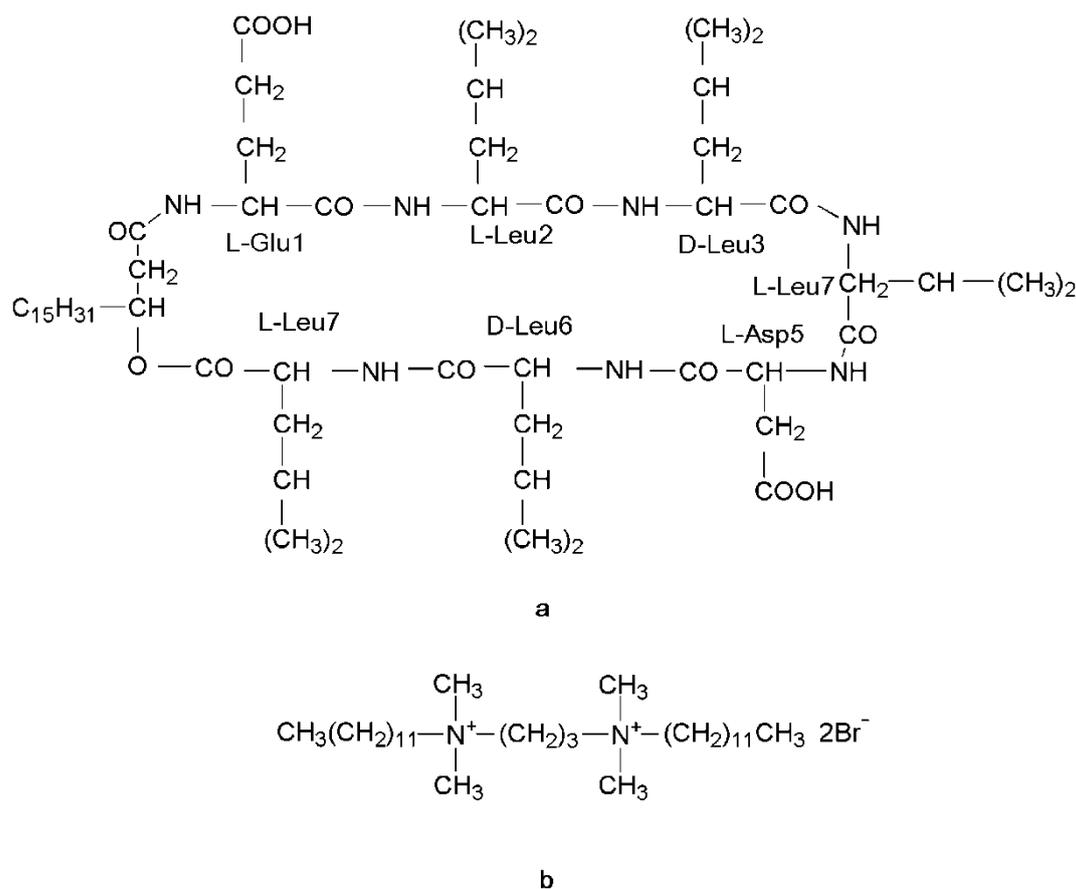


Figure 1. The chemical structure of Surfactin(a) and 12-3-12(b).

2.1.2 Gemini Surfactant. Crude ethanediyl-1,3-bis(dodecyldimethylammonium) bromide (abbreviated as 12-3-12) was obtained from Daochun Chemical Technology Co. Ltd. It was recrystallized at least four times with ethanol and ethyl acetate³¹ then dried under vacuum with low heat at 40°C for 1 day. The purity of 12-3-12 was checked by ¹H NMR. The ¹H NMR Spectra of 12-3-12 and the related analyzing data are presented in Supporting Information, and the impurity content was estimated to be below 2%. The chemical structure of 12-3-12 is presented in Figure 1(b).

2.2 Sample Preparation. First, 10 mM phosphate buffer solution (PBS, pH=7.4, this pH value was chosen to achieve better water solubility for Surfactin) were prepared as the solvent, then high concentration of pure surfactant solutions were prepared by weighing the desired amounts of surfactants and dissolved in the solvent. The mixtures of the desired composition of surfactants were made by mixing high concentration of two pure surfactant solutions with a certain amount and added solvent to a settled volume. The composition of the Surfactin/12-3-12 binary system

is described with $\alpha_{\text{Surfactin}}$, the mole fraction of Surfactin.

$$\alpha_{\text{surfactin}} = \frac{c_{\text{surfactin}}}{c_{\text{surfactin}} + c_{12-3-12}} \quad (1)$$

For SANS experiments, the samples were prepared under the same condition except doubly distilled water was replaced by D₂O (99.9% D, from Sigma-Aldrich). The pD value was mediated by eq2, with proper corrections by Krezel et al^{32,33}.

$$\text{pD} = 0.929 \text{ pH meter trading} + 0.42 \quad (2)$$

2.3 Precipitation Determination. For the series of mixed solutions of Surfactin and 12-3-12, since surfactant solutions can remain supersaturated for long periods of time before precipitation started^{34,35}, therefore, to determine whether there is precipitation formed, all solutions were cooled at 0°C to force precipitation to occur³⁵. The solutions were then placed in a water bath at 25.0 ± 0.1 °C, shaken periodically, and allowed to equilibrate for at least 4 days before measurements. If a solution is outside of the precipitation region, crystals would dissolve so that the solution became isotropic. If crystals remained in solution after equilibration, the initial solution composition was considered to be inside the precipitation region. The presence of precipitate in solution was determined by visual inspection using a high intensity light.

2.4 Surface Tension Measurements. For CMC measurements, surface tension was measured after the samples were properly mixed by ultra-sonic and equilibrated for 1 day. Measurements were carried out at 25°C by surface tension meter DCAT21 (Dataphysics, Germany) using a Wilhelmy small platinum plate of ca. 4 cm perimeter. The plate was first rinsed with doubly distilled water and then burned to red to make sure there are no surfactants left on the plate. Prior to the measurements, the equipment was tested by determination of a surface tension of double distilled water (72 ± 0.2 mN/m) at 25.0 °C.

2.5 DLS Measurements. DLS measurements were carried out at 25°C with Nano-ZS (Malvern Instruments Ltd. UK), equipped with 4 mW He-Ne laser at $\lambda_0 = 633 \text{ nm}$ as a light source. PAL (Phase Analysis Light Scattering) and LDV (Laser Doppler Velocimetry) were used to measure the size at a scattering angle of 173°.

Samples were kept in quartz cuvette. DLS measurements were made at 0.5 mM surfactant concentration with $\alpha_{\text{Surfactin}}$ ranges from 0 to 1, and each sample was measured for three times. Experimental data are given by the Malvern Zetasizer software.

2.6 Small angle neutron scattering (SANS) Measurements. SANS measurements were performed at SANS1 instrument operated by HZG and TUM at the Meier-Leibniz-Zentrum (FRM2, Garching, Germany)³⁶. The wavelength of the neutron beam was 6 Å with $\Delta\lambda/\lambda=10\%$. A position-sensitive detector with 128×128 pixels and a pixel size of 8 mm was used. These settings allowed us to cover a q range from 0.008 to 0.4 \AA^{-1} . Samples were placed in 1 mm thick quartz cell and measured at $T = 25 \pm 1$ °C. Data have been normalized by water measurements at same geometry and corrected for detector response and electronic noise. The scattering from PBS buffer prepared in D₂O was subtracted as the background. Data reduction has been done by the QtiKWS³⁷ data analysis software. The dispersion of resolution function has been calculated and taken into account for further data analysis.

3. Results and Discussion

3.1 Precipitation Phase Boundary. Since Surfactin and 12-3-12 are oppositely charged in PBS (pH 7.4), it was expected that precipitates will form in their mixtures. In order to evaluate the precipitation potential of these mixtures as well as to ensure that the surface tension studies were conducted in regions without precipitates, turbidity studies were conducted. At a constant $\alpha_{\text{Surfactin}}$ value, the measurements were made at series concentrations to confirm the phase boundaries.

In Figure 2(a), the red line represents the precipitation phase boundary which was determined by visual observation using a high intensity light. The precipitation region was further divided into two parts as dark gray and light grey in Figure 2(a), where the precipitation potential is different between these two parts. In order to better explain the meaning of “dark and light grey” in Figure 2(a), the photos of 0.5 mM Surfactin/12-3-12 solutions at different $\alpha_{\text{Surfactin}}$ values is shown in Figure 2(b). The dark gray represents high turbid solutions ($\alpha_{\text{Surfactin}} = 0.1, 0.2, \text{ and } 0.3$ in Figure 2(b)) which are entirely opaque, while the light gray corresponds to turbid solutions

($\alpha_{\text{Surfactin}} = 0.4, 0.5$, and pure Gemini in Figure 2(b)) which can still transfer light. Besides, the white region means visually clear and transparent solutions ($\alpha_{\text{Surfactin}} = 0.6-1$ in Figure 2(b)).

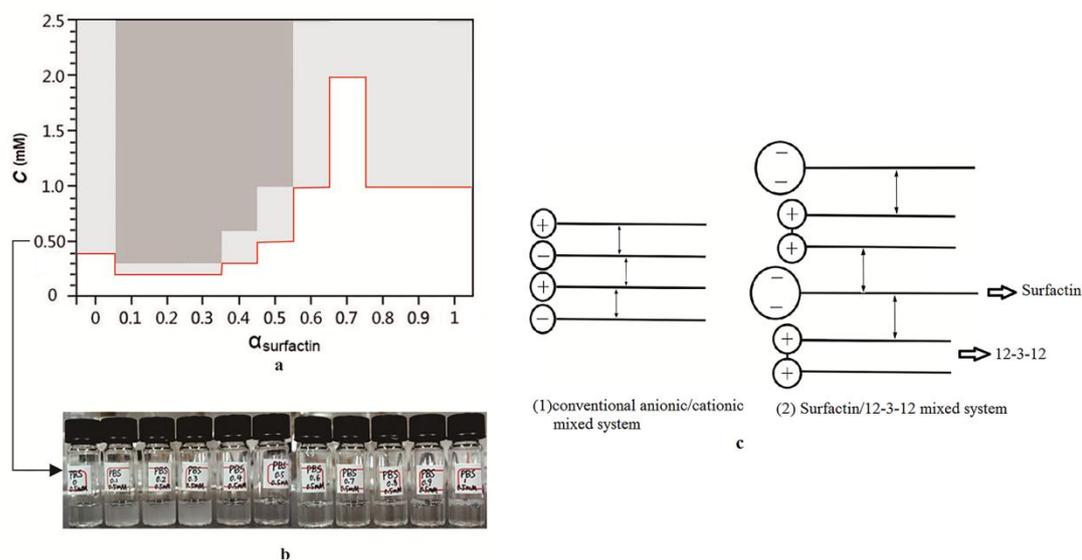


Figure 2. a: The precipitation phase boundary of Surfactin/12-3-12 mixture over a wide range of concentration, b: The photos of 0.5 mM Surfactin/12-3-12 solutions with $\alpha_{\text{Surfactin}}$ ranges from 0 to 1, c: The peptide ring of Surfactin can result in reduced precipitation, c(1) is the precipitation schematic diagram of conventional anionic/cationic mixtures (Adapted from Panswad³⁵).

It was reported that pure 12-3-12 aqueous solution of concentration close to 1 wt% (16mM) was still clear by visual observation at 25 °C³⁸. However, it can be seen from Figure 2(a) that the 0.4 mM 12-3-12 solution is turbid when it was dissolved in 10mM PBS buffer. This result means that there are big aggregates formed in 12-3-12 solution. Therefore, PBS buffer should have some effect on the aggregation behavior of 12-3-12. The negatively charged hydrogen phosphates and dihydrogen phosphates will screen the positive charges on the head groups of 12-3-12 and weaken the electrostatic repulsion between 12-3-12 molecules, thus large aggregates of 12-3-12 formed in PBS buffer. Figure 2(a) also shows that the solution in the high 12-3-12 content region is more turbid and the region of dark grey is much larger than that in the high Surfactin content region. In aqueous solution the peptide ring of Surfactin shows a “horse-saddle” topology³⁹, the two negatively charged amino acid residues

Glu and Asp constitute a minor polar domain. On the opposite side, Val residue extends down, facing the fatty acid chain, making up a major hydrophobic domain. When mixed with 12-3-12, the hydrophobic domain of Surfactin sterically hindered the interaction between oppositely charged head groups and tail–tail interaction (see in Figure 2(c)). In Panswad's work³⁵, extended anionic surfactants (a novel class of surfactants that have groups of intermediate polarity such as polypropylene oxides (PO) or ethylene oxides (EO) inserted between the hydrocarbon tail and the hydrophilic head group) have the similar property when mixed with cationic surfactants.

So there are no precipitates formed in Surfactin/12-3-12 mixture at low surfactant concentration. The CMC values of Surfactin/12-3-12 mixture presented in Table 1 with different $\alpha_{\text{Surfactin}}$ values, which were determined by surface tension measurements as shown in Figure 3. It can be found that all CMC values are smaller than the surfactant concentrations suggested by the precipitation phase boundary in Figure 2(a). And it is interesting that the precipitates region reduced with the increase of $\alpha_{\text{Surfactin}}$ value. This excellent property can mitigate the main disadvantage of mixed anionic and cationic surfactant systems which is their tendency to form precipitates⁴⁰. The precipitation happening in the anionic/cationic surfactant system is unfavorable for their applications, such as detergency performance and subsurface remediation of oil contamination^{40,41}.

3.2 Interaction between Surfactin and Gemini (12-3-12). Since the precipitation phase boundary of Surfactin/12-3-12 mixture has been studied, the synergism between them was expected and further studied. The surface tension (γ) as a function of total surfactant concentration with different molar fractions of Surfactin is presented in Figure 3. The relevant results obtained from the analysis of surface tension data are summarized in Table 1.

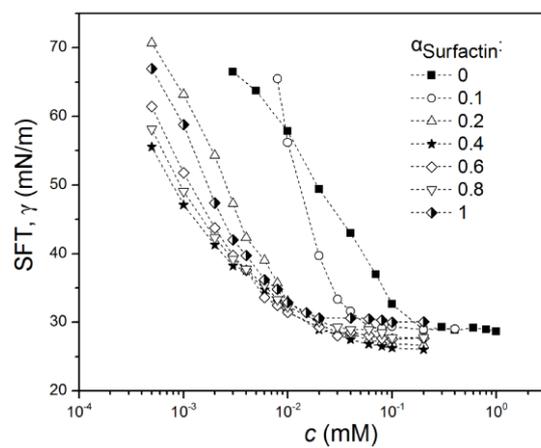


Figure 3. Surface tension isotherm of Surfactin/12-3-12 system in 10 mM PBS medium at 25°C.

Table 1. CMC and γ_{CMC} Values of Surfactin/12-3-12 system

| $\alpha_{\text{Surfactin}}$ | $\text{CMC}_{\text{exp}} \times 10^2$ (mM) | $\text{CMC}_{\text{ideal}} \times 10^2$ (mM) | γ_{CMC} (mN/m) (± 0.03) |
|-----------------------------|---|---|--|
| 0 | 18.9 \pm 0.3 | 18.9 \pm 0.3 | 30.43 |
| 0.1 | 3.75 \pm 0.01 | 6.91 \pm 0.02 | 30.39 |
| 0.2 | 1.21 \pm 0.02 | 4.23 \pm 0.03 | 30.15 |
| 0.4 | 1.14 \pm 0.01 | 2.38 \pm 0.02 | 29.77 |
| 0.6 | 1.05 \pm 0.03 | 1.66 \pm 0.05 | 28.91 |
| 0.8 | 1.06 \pm 0.01 | 1.27 \pm 0.03 | 30.32 |
| 1 | 1.03 \pm 0.03 | 1.03 \pm 0.03 | 30.97 |

Figure 3 presents the surface tension results of pure Surfactin, 12-3-12, and their mixtures at $\alpha_{\text{Surfactin}} = 0.1, 0.2, 0.4, 0.6$ and 0.8 . Compared with that of pure Surfactin and 12-3-12, the γ_{CMC} values of Surfactin/12-3-12 mixtures are smaller, all also in the surface tension decreasing region before CMC, a lower surfactants concentration is needed to reach the same surface tension.

Table 1 shows that the CMC of 12-3-12 is 1.89×10^{-1} mM in 10mM PBS (pH=7.4). Shang et al⁴² has reported that the CMC of 12-3-12 in aqueous solution is 9.21×10^{-1} mM, while its CMC decreased to 1.16×10^{-1} mM when 5mM NaBr was added in the system, which is close to our result. The surface activity of 12-3-12 changes remarkably when Surfactin is added to pure 12-3-12 solution. When $\alpha_{\text{Surfactin}}$ value is 0.1, The CMC value is reduced to 3.75×10^{-2} mM (Table 1) by one order of magnitude compared with that of pure 12-3-12. With $\alpha_{\text{Surfactin}}$ increases to 0.8, the CMC value gradually decreases and approaches to that of pure Surfactin. The lower γ_{CMC} and CMC values show that the mixture of Surfactin and 12-3-12 has better ability and efficiency in reducing surface tension than the individual surfactant.

The regular solution theory (RST) is applied to obtain $\text{CMC}_{\text{ideal}}$ values for the mixed Surfactin/12-3-12 systems, and the $\text{CMC}_{\text{ideal}}$ values were calculated according to Eq. 3⁴³. Here 1 and 2 refers to Surfactin and 12-3-12, respectively. Parameters α_1 is the molar fraction of Surfactin, f_1 and f_2 are the activity coefficients of Surfactin and

12-3-12 in mixed micelles (for ideal mixing $f_1 = f_2 = 1$), respectively.

$$\frac{1}{\text{CMC}_{\text{ideal}}} = \frac{\alpha_1}{f_1 \text{CMC}_1} + \frac{(1 - \alpha_1)}{f_2 \text{CMC}_2} \quad (3)$$

The experimental CMC values (Table 2) are always lower than the values expected for ideal mixing, indicating that there is synergism pointing to the formation of mixed micelles in Surfactin/12-3-12 solution.

The strong synergistic behavior is also supported by negative values of Molecular Interaction Parameter β^m calculated with Eq. 4 and 5 according to the Regular Solution Theory⁴⁴.

$$\frac{(X_1^m)^2 \ln [(\alpha_1 C_{12}^m / X_1^m C_1^m)]}{(1 - X_1^m)^2 \ln [(1 - \alpha_1) C_{12}^m / (1 - X_1^m) C_2^m]} = 1 \quad (4)$$

$$\beta^m = \frac{\ln(\alpha_1 C_{12}^m / X_1^m C_1^m)}{(1 - X_1^m)^2} \quad (5)$$

Where α_1 is the mole fraction of Surfactin in solution, X_1^m is the mole fraction of Surfactin in the mixed micelle. C_1^m , C_2^m and C_{12}^m is the CMC values of pure Surfactin, pure 12-3-12 and mixture respectively. The conditions for synergism to exist in the mixture are as follows: (a) β^m is negative; (b) $|\beta^m| > |\ln(C_1^m / C_2^m)|$. In Table 2, the values of β^m , and $|\ln(C_1^m / C_2^m)|$ obtained for different compositions of Surfactin/12-3-12 system are summarized. It can be seen that the average negative values of the interaction parameter β_{ave} for Surfactin/12-3-12 mixtures support the synergism between Surfactin and 12-3-12.

For conventional anionic/cationic mixtures, the β^m values are reported to be in the range of -10 to -20 by Rosen⁴⁵, while the values report here are in the range of -2 to -6. Although Surfactin and Gemini mixtures show lower synergism than conventional surfactant mixtures, this unique combination actually has better ability in practical application due to the less precipitation potential (see Fig. 2(a) and discussion). Wang²⁸ and co-workers have investigated the synergism of Surfactin/CTAB mixtures using the surface tension method over a wide range of mole fraction which means the precipitation is not heavy enough to be obstacle to CMC measurement, the β^m values of the mixtures are in the range of -1 to -3 which also show much lower

synergism than conventional anionic/cationic mixtures. Therefore, we can speculate that Surfactin can reduce precipitation when mixed with not only 12-3-12 but also other kinds of cationic surfactants due to its special structure.

Table 2. Molecular Interaction and Synergism Parameters for Surfactin/12-3-12 mixtures.

| α_1 | β^m | X_1^m | $ \ln(C_1^m / C_2^m) $ |
|-----------------------|-----------|---------|------------------------|
| 0.1 | -2.68 | 0.5795 | |
| 0.2 | -5.77 | 0.5982 | |
| 0.4 | -4.54 | 0.6885 | 2.91 |
| 0.6 | -4.04 | 0.7654 | |
| 0.8 | -3.28 | 0.8695 | |
| $\beta_{ave} = -4.06$ | | | |

Prof. Maeda⁴⁶ suggested a new approach which is based on the phase separation model and describes the thermodynamic stability of mixed micelle using Gibbs energy of micellization. The values of ΔG_M , B_0 , B_1 , and B_2 were also calculated and discussed (presented in Support Information). Negative B_1 values indicate that with an increasing molar fraction of Surfactin, the chain-chain interaction initially gets stronger then becomes weak. The ΔG_M values also reveal that mixed micelles are more stable than pure surfactant micelles.

3.3 Structure Study of the Aggregates in Bulk Phase

3.3.1 Dynamic Light Scattering (DLS). DLS was performed to determine the size distribution of the aggregates, as shown in Figure 4 by the volume size distribution. Measurements were made at a constant total surfactant concentration of 0.5 mM. For pure 12-3-12, it can be seen that large aggregates around 200 nm are mainly formed in PBS, which is consistent with the turbidity shown in figure 2(a). For Surfactin/12-3-12 mixtures, at higher 12-3-12 content region ($\alpha_{\text{Surfactin}} = 0.1, 0.2,$ and 0.3), large size aggregates with hydrodynamic r around 400 nm are mainly formed in Surfactin/12-3-12 solution. That is why the Surfactin/12-3-12 solutions at this composition are obviously turbid. With the increasing amount of Surfactin ($\alpha_{\text{Surfactin}} =$

0.4 and 0.5), the size distribution of aggregates also appears the bimodal distribution, most aggregates are around 30 nm, and there remains some amount of large aggregates around 400nm. Thus, the Surfactin/12-3-12 solution ($\alpha_{\text{Surfactin}} = 0.4$ and 0.5) is clear and transparent. When $\alpha_{\text{Surfactin}}$ is 0.6, there are only small micelles around 6 nm in Surfactin/12-3-12 solution. At higher Surfactin content region ($\alpha_{\text{Surfactin}}$ value between 0.7 and 0.9), the size of Surfactin/12-3-12 aggregate is reduced to about 3 nm. For pure Surfactin solution, micelles around 4 nm are mainly formed, which is similar to the result reported by Zou²⁵.

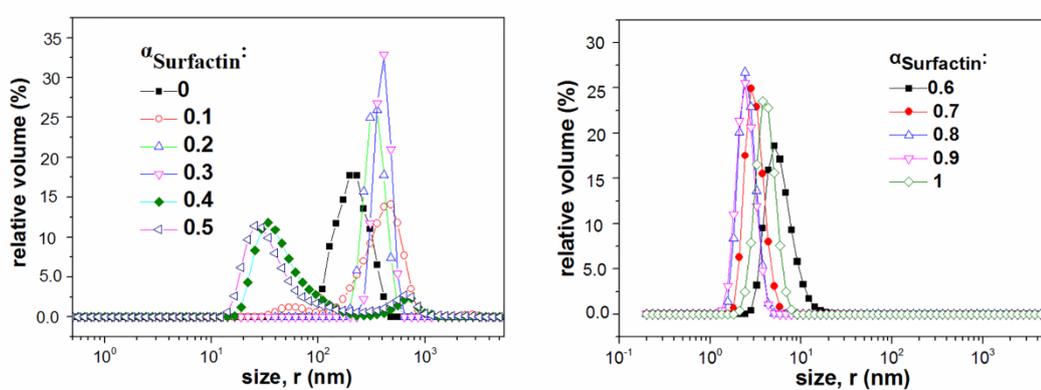


Figure 4. Volume Size Distribution of Surfactin/12-3-12 Aggregates at different $\alpha_{\text{Surfactin}}$ values.

The DLS results indicate that large aggregates are formed in Surfactin/12-3-12 solution at high 12-3-12 content, and the smaller micelles start to form at high Surfactin content. This result agrees well with the phenomenon observed in Figure 2(a), where the severely turbid solution shade into clear and transparent ones with the increasing molar fraction of Surfactin.

3.3.2 Small Angle Neutron Scattering (SANS) measurements. DLS measures the hydrated size of particles (particles plus water), whereas SANS points to the “dry size”.⁴⁷ So SANS measurements were performed to further confirm the size and shape changes of Surfactin/12-3-12 aggregates with $\alpha_{\text{Surfactin}}$ values. Here the measurements were made at a constant total surfactant concentration of 0.5 mM. As shown in Figure 2, the Surfactin/12-3-12 solution is turbid when $\alpha_{\text{Surfactin}}$ is in the range of 0 to 0.5. Therefore, the SANS measurements were only performed for pure

Surfactin and Surfactin/12-3-12 mixtures with $\alpha_{\text{Surfactin}}$ between 0.6 to 0.8 . The SANS results are presented in Figure 5.

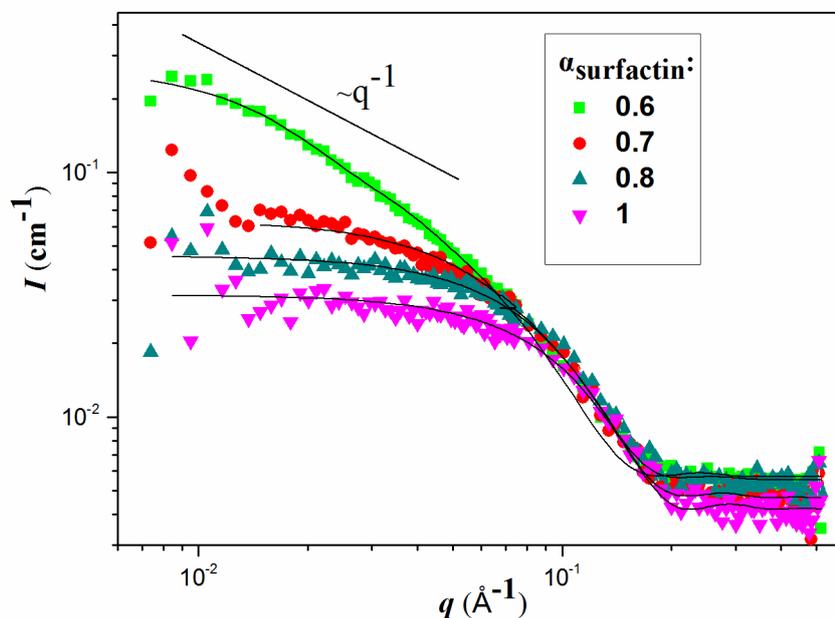


Figure 5. The SANS results of Surfactin/12-3-12 mixtures at different $\alpha_{\text{Surfactin}}$ values. Solid lines are fits according to the models described in the text below.

At constant concentration the scattering intensities $I(q)$ are proportional to the volume square of aggregates and the contrast between neutron scattering length densities of the aggregates and the solvent⁴⁷. Figure 5 reveals that the scattering intensity decreases with the increase of $\alpha_{\text{Surfactin}}$ value. This result is consistent with the above results in Section 3.2 that there is synergetic interaction between Surfactin and Gemini, where the interaction parameters between Surfactin and 12-3-12 decrease in the same $\alpha_{\text{Surfactin}}$ range . We have performed the data analysis by employing the Indirect Fourier Transformation (IFT) method developed by Glatter⁴⁸ and using the version reported by J. S. Pedersen⁴⁹.

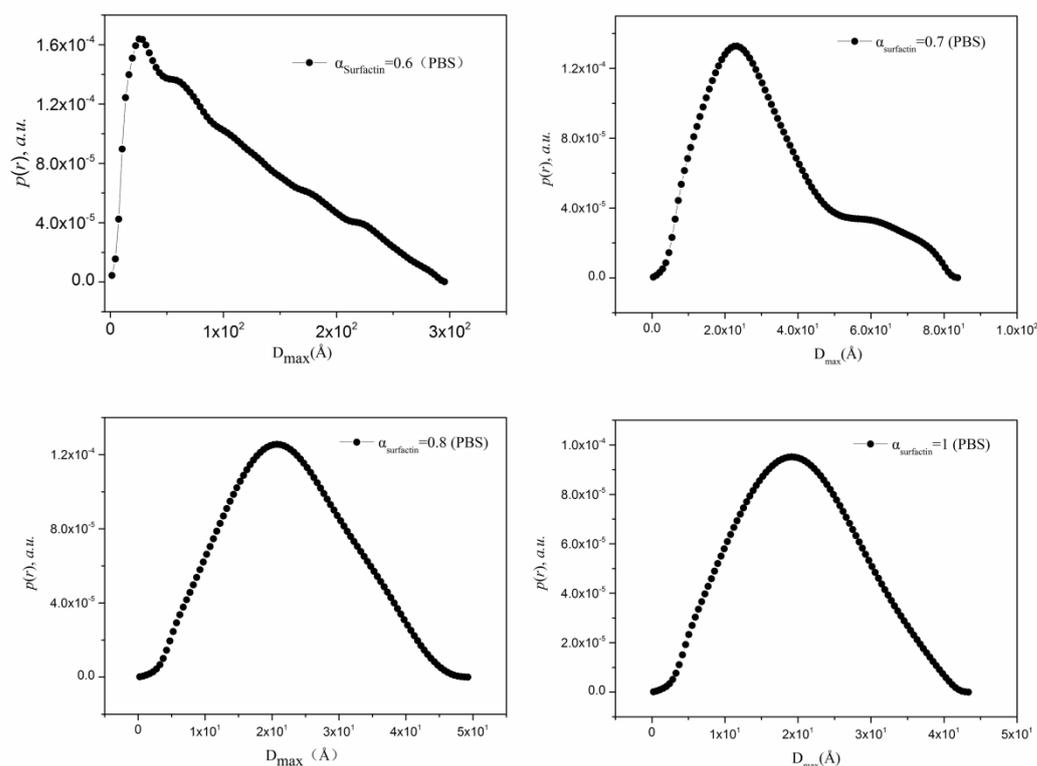


Figure 6. $P(r)$ function obtained from the corresponding scattering curves in Figure 5.

The $p(r)$ functions for $\alpha_{\text{Surfactin}} = 0.6-1$ were presented in Figure 6. The estimation of the micelle diameter D_{max} was obtained from the maximum distance of $P(r)$, and all the fitted data are listed in Table 3. $p(r)$ function for $\alpha_{\text{Surfactin}} = 0.6$ in Figure 6 reveals that large aggregates form in the system. Table 3 shows that radius of gyration R_g for $\alpha_{\text{Surfactin}} = 0.6$ is 87Å , which is highest among these systems and with the DLS results. The slope of scattering curve around -1 and shape of $p(r)$ function of $\alpha_{\text{Surfactin}} = 0.6$ indicates that unspherical (elongated) aggregates form in the solution. The overall size of aggregates is too large for measured q range and it is possible to estimate that length of aggregates is larger than 300Å . The data have been analysed by IFT in approximation of infinitely long cylinder. In this case the information about cross section properties as pair distance distribution function of cross section $p_{\text{CS}}(r)$ and diameter of cross section approximately 50Å have been obtained. When $\alpha_{\text{Surfactin}} = 0.7$, $p(r)$ function shows that both spherical micelles (symmetric part) with $D_{\text{max}} = 50\text{Å}$ and rod like micelles with length of 80Å are formed ($p(r)$ with larger D_{max} of 100Å for

$\alpha_{\text{Surfactin}} = 0.7$ was also calculated and shown in supporting info). Besides, the shape of $P(r)$ function of $\alpha_{\text{Surfactin}} = 0.8$ and 1 change to symmetric shows that the aggregates shape is close to spherical.

To confirm assumption from shape of $p(r)$ function the direct modelling has been performed^[50]. At high Surfactin content the model fitting has been done with model of elliptical object with semi axis of a, b, b (model fits are shown as lines in Fig. 5) . The parameters $a = b = 20 \pm 1 \text{ \AA}$ for $\alpha_{\text{Surfactin}} = 1$, $a = 20 \pm 1 \text{ \AA}$ and $b = 26 \pm 1 \text{ \AA}$ for $\alpha_{\text{Surfactin}} = 0.8$ were obtained. At $\alpha_{\text{Surfactin}} = 0.6$ the fit with model of cylinders with length of $280 \pm 10 \text{ \AA}$ and radius of cross section of $20 \pm 1 \text{ \AA}$ shows some deviation in intermediate q range which can point on presence of small amount of small spherical aggregates. For the most complicated case of $\alpha_{\text{Surfactin}} = 0.7$, it is possible to fit data with mixture of volume fraction 0.33 of cylinders of length $80 \pm 5 \text{ \AA}$ and cross section radius of $20 \pm 1 \text{ \AA}$ and volume fraction 0.67 of spherical objects of radius $20 \pm 1 \text{ \AA}$. Due to limited q range and SANS data measured only at one scattering contrast the fit parameters should be consider with caution.

The shape of the surfactant aggregates in solution could be predicted by the critical packing parameter (cpp) which is defined as $\text{cpp} = V_c/A l_c$, where V_c is the alkyl chain molecular volume, l_c is the extended chain length, and A is the areas per molecule. The value A was measured to be $0.78 \pm 0.04 \text{ nm}^2$ for 12-3-12⁵¹ and $1.47 \pm 0.05 \text{ nm}^2$ for Surfactin⁵² by Neutron reflectometry. The variables l_c and V_c can be calculated by Tanford's formula, eqs 6 and 7.⁵³

$$l_c = (0.154 + 0.127n_c)\text{nm} \quad (6)$$

$$V_c \approx (0.0274 + 0.0269n_c)\text{nm}^3 \quad (7)$$

where n_c is the number of methylene groups on the hydrocarbon chain of the surfactant. For Gemini surfactants, the hydrocarbon tail chains cannot extend beyond a certain length l_c , and each tail must occupy a certain volume V_c .⁵⁴ Surfactants with the cpp value of less than 1/3 are supposed to form spherical micelles. When the cpp value is between 1/3 and 1/2, it indicates that the surfactant is to form rod-shaped micelles, whereas when the cpp value is between 1/2 and 1, it generally corresponds to a monolayer or multilayer vesicles. The cpp value is 0.142 ± 0.05 for surfactin which

is below $1/3$, suggesting that they form spherical micelles in solution. While the value is 0.514 ± 0.027 for 12-3-12 which is close to $1/2$, it indicates that they form rodlike micelles or vesicles in solution. In a word, The c_{pp} value for 12-3-12 is much bigger than Surfactin, If the surfactant composition at interface is nonuniform, with each dominating in regions of preferred curvature, then the spherical Surfactin micelles can be deformed into rod-like micelles as 12-3-12 is increasingly added to the system (see in figure 7).

Table 3. The fitted results of SANS Data for the Surfactin and 12-3-12 Mixtures

| $\alpha_{\text{Surfactin}}$ | D_{max} (Å) | $I(0)$, (cm^{-1}) | R_g , (Å) |
|-----------------------------|----------------------|-------------------------------|-------------|
| 0.6 | 300 | 0.28 ± 0.01 | 87 ± 4 |
| 0.7 | 85 | 0.060 ± 0.001 | 26 ± 1 |
| 0.8 | 50 | 0.038 ± 0.001 | 17 ± 1 |
| 1 | 44 | 0.027 ± 0.001 | 16 ± 1 |

Thus it is summarized that at low Gemini ($\alpha_{\text{Surfactin}} = 0.8-1$) content there are spherical aggregates around 44 Å in diameter. With increase of Gemini these aggregates expand and transform to short elongated aggregates ($\alpha_{\text{Surfactin}} = 0.7$). With further increase of Gemini part of aggregates in elongated form ($\alpha_{\text{Surfactin}} = 0.6$).

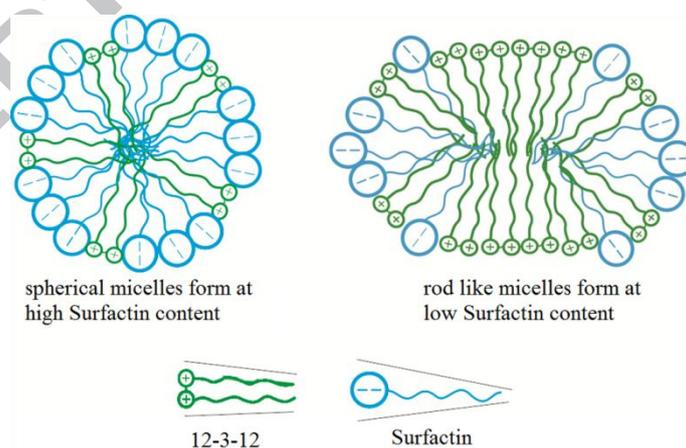


Figure 7. Sketch of the mixed surfactants micelles in the bulk solution.

Conclusions

Surfactin, a biosurfactant has large potential applications in industrial, biotechnological, and therapeutical fields^{17,18} due to its high surface activity and less

toxic. To minimize the cost of using biosurfactant Surfactin, there are a number of studies on Surfactin/synthetic surfactants mixtures in recent years. These synthetic surfactants include anionic Sodium Dodecylbenzenesulphonate (SDOBS)⁵⁵, ampholytic Betaines²⁶ and cationic CTAB²⁸. However, the precipitation condition and the aggregates properties (shape and size) of such Surfactin/ cationic surfactants system were still unclear.

In the present work, we study the precipitation phase boundary and micellar properties of binary systems formed by Surfactin and Cationic Gemini surfactant 12-3-12. Precipitation phase boundary of mixed Surfactin and 12-3-12 were evaluated to ensure that the surface tension measurements are in regions without precipitate. At high concentrations, the solutions are turbid, but with the increasing molar fraction of Surfactin ($\alpha_{\text{Surfactin}}$) turbidity weakened. The CMC analysis shows that the mixtures exhibit synergism in the formation of Surfactin/12-3-12 mixed micelles. DLS and SANS results indicated that in the high 12-3-12 content region larger aggregates were formed, and with the increasing of $\alpha_{\text{Surfactin}}$, micelles of smaller size were formed, so the system became more stable. Besides elongated micelles are formed at $\alpha_{\text{Surfactin}}=0.6$, mixture of elongated and spherical micelles at $\alpha_{\text{Surfactin}}=0.7$ and only spherical micelles at $\alpha_{\text{Surfactin}}=0.8, 1$.

It is interesting to note that Surfactin may have the capability to reduce precipitation when mixed with cationic surfactants due to the peptide ring. The results of Wang⁴⁵ also support the conjecture which has been discussed in section 3.2. In addition, the asymmetrically double-tailed cationic surfactants¹⁰ and extended anionic surfactants³⁵ have been reported to have the similar property to minimize precipitation when mixed with opposite-charged surfactants. It is worth mentioning that Surfactin/12-3-12 mixtures can reduce the interfacial tension to an ultralow level in alkaline environment (see details in Supporting Information). These fundamental physicochemical properties are favorable to the use of Surfactin/Gemini mixture in daily chemical and oil chemistry field.

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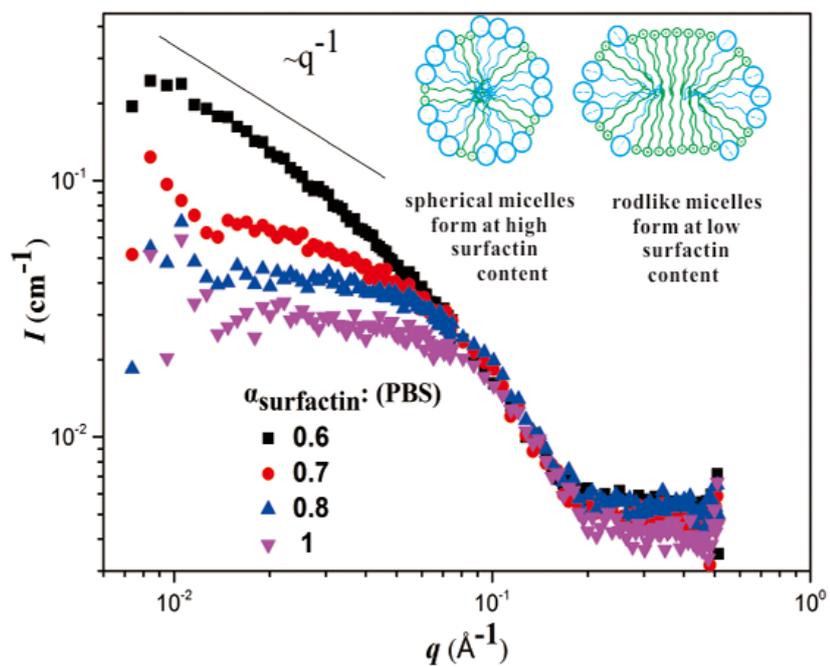
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ACCEPTED MANUSCRIPT

Graphical abstract



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Interaction of a Biosurfactant, Surfactin with a Cationic Gemini Surfactant in Aqueous Solution

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