Micellar and Interfacial Behavior of Mixed Systems Containing Anionic-nonionic Gemini Surfactant

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Abstract. The Anionic-nonionic Gemini Surfactant oxalamide polyoxyethylene lauryl ether(9)succinate sodium sulfonate(OPLES-9) was synthesized. It was mixed with the anionic surfactant sodium lauryl sulfate(SDS) and the nonionic surfactant dodecanol polyoxyethylene(9) ether (AEO9) respectively in different ratios to enhance application performance. The experimental results showed that the surface performance of the mixed systems was more superior to the relevant single surfactants. The mixed critical micelle concentration (CMC) of the binary surfactant systems was determined by surface tension measurement. Critical micelle concentration of mixed system reached the minimum 0.146mmol·L⁻¹ when the molar fraction of OPLES-9 to SDS was 1:1. Critical micelle concentration of OPLES-9/AEO9 mixed system reached the minimum 0.259mmol·L⁻¹ when the molar fraction of OPLES-9 to AEO9 was 0.9:1.

1. Introduction
Most of surfactants are used in the form of mixtures in practical application, therefore, surfactant mixtures became an important subject in industrial production. A mixed surfactant system often can show a unique performance, for example, lower surfactant tension and better wettability. The surfactant mixtures can achieve the excellent properties [1-7].

The anionic-nonionic Gemini surfactant—oxalamide polyoxyethylene lauryl ether(9)succinate sodium sulfonate(OPLES-9, for short) has shown interesting applications in detergents, cosmetics, pesticides, and medicine because of its good dermatological compatibility and biodegradability. The mixed system properties of OPLES-9 and sodium lauryl sulfate (SDS, for short), OPLES-9 and dodecanol polyoxyethylene(9) ether (AEO9, for short) were studied in this paper. The aim is to provide a theoretical basis for the practical application of the mixed system of OPLES-9/SDS and OPLES-9/AEO9.

2. Experiments

2.1 Materials and Apparatus
Materials: The anionic-nonionic Gemini surfactant—OPLES-9 (lab-synthesized surfactant) is analyzed by FT-IR, mass spectrometry, elementary analysis, and is consistent with the target product. SDS(reagent grade, Shenyang Xinhua Reagent Factory), AEO9(reagent grade, Shenyang Xinhua Reagent Factory), the water of the experiment is ultrapure water(lab-synthesized water).

Apparatus: K100 Surface tensiometer(KRUSS,Germany),BP2MKII Dynamic surface

IOP Conf. Series: Materials Science and Engineering 729 (2020) 012071 doi:10.1088/1757-899X/729/1/012071
2.2 Synthesis of oxalamide polyoxyethylene lauryl ether(9)succinate sodium sulfonate

OPLES-9 was synthesized through the first step amidation, then through the second step esterification, followed by the third step sulfonation according to the Scheme 1. Fig.1 and Fig.2 are IR and mass spectrum of Oxalamide lauryl polyoxyethylene ether(9) succinate sodium sulfonate.

Scheme 1: Synthesis of oxalamide lauryl alcohol polyoxyethylene ether succinate sodium sulfonate

Fig. 1 IR of Oxalamide lauryl polyoxyethylene ether(9) succinate sodium sulfonate

Fig. 2 Mass spectrum of Oxalamide lauryl polyoxyethylene ether(9) succinate sodium sulfonate

Fig. 1 and Fig. 2 show that the synthesized product is the target product.

2.3 Determining mixed proportion

The anionic-nonionic Gemini surfactant OPLES-9 was selected for compounding with SDS and AEOs, separately. Mixed proportion was selected 0:1, 1:10, 3:10, 5:10, 7:10, 9:10, 1:0 (mole:mole) respectively.

2.4 Physicochemical Characterization

Equilibrium surface tension(γ)of mixed systems of OPLES-9/SDS, OPLES-9/AEOs was measured by K100 automatic surface tensiometer under 25°C, respectively. The equilibrium surface tensions were
taken after the change in surface tension was less than 0.1 m N m\(^{-1}\) every 5 min. The CMC and \(\gamma_{\text{cmc}}\) was obtained from the breakpoint of the curve of surface tension versus the logarithm of molar concentration.

3. Results and Discussion

3.1 The surface chemistry of the mixed systems of OPLES-9/SDS and OPLES-9/AEO\(_9\)
Surface tension(\(\gamma\)) of mixed systems of OPLES-9/SDS and OPLES-9/AEO\(_9\) was measured, respectively. Fig. 3 shows the curve of surface tension(\(\gamma\)) to the total concentration (lgC) of the mixed systems. As shown in figure 3, the surface tension of the mixed system of OPLES-9 and SDS is lower than that of OPLES-9. The surface tension of the mixed system of OPLES-9 and AEO\(_9\) is also lower than that of OPLES-9.

![Fig. 3 Representative plot of surface tension curves lg surfactant concentration for different mole fraction of the OPLES-9 and other surfactants](image)

The calculation shows that \(\gamma_{\text{cmc}}\) of OPLES-9/SDS system is slightly greater than that of OPLES-9/AEO\(_9\) system. The reason may be that sulfuric acid group in SDS has stronger hydration than that of hydroxyl group in AEO\(_9\) to form stronger hydration layer and more adsorption of water molecules on the surface. SDS molecules are repelled by more adsorption of water molecules when they continue to spread into the surface area, which results in the \(\gamma_{\text{cmc}}\) of OPLES-9/SDS system is slightly greater than that of OPLES-9/AEO\(_9\) system. The regular solution theory(RST) is a medium to understand the interaction between surfactant molecules in mixed system. The regular solution theory is used to solve the surfactant molecules interacting with each other in the mixed system since the regular solution theory is applied to the ideal mixed system successfully by Clint [8] and to the nonideal mixed system by Rubingh [9].

The interaction parameters \(\beta\) (\(\beta^\sigma\) and \(\beta^m\)) of the mixed system and the properties of the single surfactant can be used to determine whether there is synergistic effect in the mixed system.

1. Judgment criteria of ability of reducing surface tension:

\[
\beta^\sigma < 0 \quad \beta^\sigma - \beta^\sigma(0) \quad |\sigma^\sigma - \sigma| \quad \left|\frac{n}{C_j^{\sigma}} \frac{C_j^{\sigma}}{C_j^{\sigma}}\right|
\]

2. Judgment criteria of efficiency of reducing surface tension:

\[
\beta^\sigma(0) \quad \left|\ln \frac{C_j^{\sigma}}{C_j^{\sigma}} \right| \sigma^\sigma
\]

3. Judgment criteria of forming micellar power:

\[
\beta^\sigma(0) \quad \left|\ln \frac{C_j^{\sigma}}{C_j^{\sigma}} \right| \sigma^\sigma
\]

The calculated data is shown in table 1.
Table 1 Composition and interaction parameters of the OPLES-9/SDS and OPLES-9/AEO₉ mixed system at 298K

| α<sub>SDS</sub> | x₁<sup>α</sup> | β<sub>αSDS</sub> | x₁<sup>σ</sup> | β<sub>αSDS</sub> | β<sub>σ</sub>-β<sub>αSDS</sub> |
|-----------------|-------------|-----------------|-------------|----------------|-----------------|
| 0.1             | 0.185       | -4.549          | 0.239       | -4.868         | -0.319          |
| 0.3             | 0.279       | -4.191          | 0.298       | -3.452         | 0.739           |
| 0.5             | 0.340       | -4.083          | 0.369       | -3.299         | 0.784           |
| 0.7             | 0.373       | -2.282          | 0.441       | -2.971         | -0.689          |
| 0.9             | 0.537       | -1.343          | 0.583       | -2.509         | -1.166          |
| α<sub>AEO₉</sub> |             |                 |             |                |                 |
| 0.1             | 0.170       | -6.621          | 0.292       | -10.235        | -3.614          |
| 0.3             | 0.213       | -5.746          | 0.331       | -9.438         | -3.692          |
| 0.5             | 0.261       | -5.670          | 0.341       | -7.389         | -1.719          |
| 0.7             | 0.286       | -4.464          | 0.386       | -7.469         | -3.005          |
| 0.9             | 0.300       | -1.749          | 0.435       | -4.357         | -2.608          |

Synergy parameter β<sub>m</sub> and β<sub>σ</sub> are an important index of the synergistic effect of mixed surfactant system. β<sub>m</sub> < 0 means that two components of mixed system are attracted each other. β<sub>σ</sub> = 0 expresses that mixed system is the ideal mixture solution in the micelle or surface layer. β<sub>σ</sub> > 0 means that two components of mixed system are repelled each other.

Table 1 shows that both β<sub>m</sub> and β<sub>σ</sub> value are negative, and β<sub>m</sub> is $\beta_m = \frac{C_m}{C_0} - 1.31$ in the OPLES-9/SDS system and β<sub>σ</sub> is $\beta_{\sigma} = \frac{C_\sigma}{C_0} - 2.86$ in the OPLES-9/AEO₉ system, which indicates that OPLES-9/SDS and OPLES-9/AEO₉ system all meet the conditions of reducing surface tension efficiency and synergistic effect.

α₁ is 0.3-0.5, β<sub>σ</sub>-β<sub>m</sub> > 0 and $\beta_{\sigma} - \beta_m = -0.55$ in OPLES-9/SDS system, which indicates that synergistic effect shows decreasing effect when the surface tension decreases to a maximum. α₁ is 0.7-0.9, β<sub>σ</sub>-β<sub>m</sub> < 0 in OPLES-9/SDS system, which indicates that surface tension reduction efficiency shows increasing effect. Synergy parameters are $\beta_{\sigma} - \beta_m = -0.70$ in OPLES-9/AEO₉ system, which indicates that surface tension reduction efficiency always shows increasing effect.

The reasons why synergistic effect in OPLES-9/AEO₉ system is better than that of OPLES-9/SDS system are as follows. Firstly, electrostatic stability of OPLES-9/AEO₉ system is increased by AEO₉ molecule weakening the repelling effect between OPLES-9 molecules when OPLES-9 and AEO₉ form mixed micelle. Second, because oxygen molecules in AEO₉ and water molecules can form hydrogen bonding and AEO₉ shows the characteristics of weak cationic surfactants in aqueous. Therefore, there is stronger interaction force between the OPLES-9 and AEO₉ molecules than that of OPLES-9 and SDS molecules. Micelles of OPLES-9 and AEO₉ are more likely to form and surface adsorption layer is close [10-12].

3.2 Thermodynamic properties of micelles of mixed systems

The mixed thermodynamic function is calculated using the hypothetical data given by the regular solution theory(RST) in order to obtain additional information about the mixed system. The mixed excess entropy ($S^E$) is considered to be zero and the entropy of mixed system is equal to the entropy of
the ideal case \( S^M = S^{ideal} \) by RST theory. Therefore, the relationship between excess free energy \( (G^E) \), excess enthalpy \( (H^E) \) and mixed enthalpy \( (H^M) \) must be considered.

\[
G^E = H^E = \Delta H_M = RT \sum_i f_i \ln f_i \quad (1)
\]

Excess free energy \( (G^E) \) represents the deviation degree of the actual state and ideal state \( (G^E = G^M - G^{ideal}_M) \). The value of \( G^E \) is related to the interaction parameter \( \beta_{12} \) according to the RST theory. For the two component system, \( G^E \) is as follow.

\[
G^E = RT \beta_{12} x_1 (1 - x_1) \quad (2)
\]

Expression of the ideal mixed free energy is

\[
\Delta G^{ideal}_M = \Delta S^{ideal}_M = RT \sum_i x_i \ln x_i \quad (3)
\]

The RST proposed by Rubingh [7] is more commonly used in calculation of micelle. According to the RST, the relationship between the activity coefficient \( f_i \) and the interaction parameter \( \beta_{12} \) is as follow.

\[
f_1 = \exp(\beta_{12}(1 - x_1)^2) \quad (4)
\]

\[
f_2 = \exp(\beta_{12}x_2^2) \quad (5)
\]

\( x_1 \) represents the mole fraction of component 1 (OPLE-9) in the mixed micelle. \( \beta_{12} \) is the interaction parameter of OPLES-9 and SDS, OPLES-9 and AEO9, which illustrates the deviation degree of the real solution to the ideal solution in the two components system.

Expression of real mixed free energy is

\[
\Delta G^\text{real}_M = RT \sum_i x_i \ln f_i \quad (6)
\]

The entropy value can be calculated by the following formula.

\[
T \Delta S_M = \Delta H_M - \Delta G^\text{real}_M \quad (7)
\]

The calculated data is shown in table 2.

| \( x_1 \) | \( f_1 \) | \( f_2 \) | \( \Delta G^M \) | \( \Delta H_M \) | \( T \Delta S_M \) |
|---|---|---|---|---|---|
| αSDS | 0.1 | 0.198 | 0.051 | 0.832 | -3.043 | -1.801 | 1.242 |
| | 0.3 | 0.280 | 0.113 | 0.715 | -3.570 | -2.100 | 1.470 |
| | 0.5 | 0.342 | 0.170 | 0.614 | -3.878 | -2.281 | 1.597 |
| | 0.7 | 0.374 | 0.410 | 0.722 | -2.968 | -1.368 | 1.640 |
| | 0.9 | 0.539 | 0.751 | 0.672 | -2.533 | -0.823 | 1.710 |
| αAEO9 | 0.1 | 0.169 | 0.012 | 0.825 | -3.460 | -2.322 | 1.138 |
| | 0.3 | 0.212 | 0.030 | 0.770 | -3.686 | -2.395 | 1.291 |
| | 0.5 | 0.260 | 0.046 | 0.679 | -4.142 | -2.713 | 1.429 |
| | 0.7 | 0.284 | 0.105 | 0.694 | -3.753 | -2.264 | 1.489 |
| | 0.9 | 0.299 | 0.426 | 0.855 | -2.429 | -0.909 | 1.520 |

From Table 2, it can be seen that \( \Delta G^M \) is all negative value, which indicates that the micellation of the mixed system is a spontaneous process. \( \Delta G^M \) value of mixed system of OPLES-9/SDS and OPLES-9/AEO9 both reach the minimum when the mole ratio of OPLES-9 and SDS, OPLES-9 and AEO9 is equal. The reason for the increase in entropy value is explained as follow. On the one hand, the regular water structure is destroyed around the carbon chain by the hydrophobic groups escaping.
water phase. On the other hand, the degree of freedom is increased by hydrophobic group transferring to inside the micelles of liquid hydrocarbons.

4. Conclusion
Critical micelle concentration of mixed system reaches the minimum 0.146 mmol\textpercontent{L}\textsuperscript{-1} when the molar fraction of OPLES-9 to SDS is 1:1. The performance of reducing the surface tension of OPLES-9/SDS mixed system exhibits the decreasing effect as molar fraction of OPLES-9 to SDS changes from 0.3 to 0.5. Performance of reducing the surface tension of OPLES-9/SDS mixed system exhibits increasing effect as molar fraction of OPLES-9 to SDS changes from 0.7 to 0.9.

Critical micelle concentration of OPLES-9/AEO\textsubscript{9} mixed system reaches the minimum 0.259 mmol\textpercontent{L}\textsuperscript{-1} when the molar fraction of OPLES-9 to AEO\textsubscript{9} is 0.9:1. The micellation of either OPLES-9/SDS or OPLES-9/AEO\textsubscript{9} mixed system is a spontaneous process. The synergistic effect of the OPLES-9/SDS and OPLES-9/AEO\textsubscript{9} mixed system can make their performance better, so there is a very wide application prospect.

Acknowledgements
Thanks for supporting by Foundation of Liaoning Province Educational Commission of China (Project L2014592) and Yingkou Institute of Technology.

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