Studying on the properties of Mixed Surfactant Systems

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Abstract. The Anionic-nonionic Gemini Surfactant oxalamide polyoxyethylene lauryl ether (7) succinate sodium sulfonate (OPLES-7) was synthesized. It was mixed with the dodecyl glucoside in different ratios to enhance application performance. The mixed critical micelle concentration (CMC) of the binary surfactant systems was determined by surface tension measurement. Critical micelle concentration of mixed system is 0.141mmol L⁻¹ when the molar fraction of OPLES-7 to dodecyl glucoside 1:1. The influence of NaCl on surface properties of the mixed system was also studied. The surface activity was enhanced with the increase of NaCl concentration.

1. Introduction
Many surfactants are used in mixtures. The surfactant mixtures can achieve the excellent properties [1-7].

(1) The performance of surfactant is improved greatly. The surfactant produces synergistic effect by compounding, which makes the mixed system has superior performance than that of the single surfactant.

(2) The cost of surfactant use is reduced. On the one hand, the synergistic effect of the mixed surfactant is enhanced and application amount of mixed surfactant is also reduced. On the other hand, the actual use price of surfactant is also reduced by compounding technology.

(3) The environmental pollution of mixed surfactant is reduced. The total use amount of surfactant is decreased and the ecological environment pollution is also decreased by compounding technology.

The mixed system properties of OPLES-7 and dodecyl glucoside were studied in this paper. The aim is to provide a theoretical basis for the practical application and reduce the amount of surfactant used.

2. Experiments
2.1 Materials and Apparatus
Materials: The anionic-nonionic Gemini surfactant—OPLES-7 is laboratory synthesized surfactant and is analyzed by FT-IR, mass spectrometry, elementary analysis. Dodecyl glucoside (reagent grade, Tianjing Reagent Factory), the water of the experiment is ultrapure water (lab-synthesized water).

Apparatus: K100 Surface tensiometer (KRUSS, Germany), BP2MKII Dynamic surface Tensiometer (KRUSS, Germany), Ultrapure water machine (Sichuan youpu super pure technology co. LTD), etc.
2.2 Determining mixed proportion
The anionic-nonionic Gemini surfactant OPLES-7 was selected for compounding with dodecyl glucoside. Mixed proportion of OPLES-7 and dodecyl glucoside was selected. The effects of different content of sodium chloride(0-0.2%) on the properties of compound system were also investigated.

2.3 Physicochemical Characterization
Equilibrium surface tension($\gamma$) of mixed systems of OPLES-7/dodecyl glucoside was measured by K100 automatic surface tensiometer under 25℃. 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$$_{cmc}$ was obtained from the breakpoint of the curve of surface tension versus the logarithm of molar concentration.

Emulsification power is determined to the literature [8].

3. Results and Discussion

3.1 Mixed systems properties of OPLES-7/dodecyl glucoside
Surface tension($\gamma$) of mixed systems of OPLES-7/dodecyl glucoside was measured. Table 1 shows the measurement results. Measurement results show that the surface tension of the mixed system of OPLES-7 and dodecyl glucoside is lower than that of OPLES-7. It shows that the mixed system surface activity is better than that of single surfactant.

Table 1 Surface chemical parameters for different mole fraction of the dodecyl glucoside (dg for short in table1) in mixture surfactants

| αd   | CMC mmol$\cdot$L$^{-1}$ | CMC$_{ideal}$ mmol$\cdot$L$^{-1}$ | $\gamma$$_{cmc}$ mN$\cdot$m$^{-1}$ | C$_{20}$ mmol$\cdot$L$^{-1}$ | $\Gamma$$_{max}$ μmol$\cdot$m$^{-2}$ | A$_{min}$ nm$^{2}$ | A$_{ideal}$ nm$^{2}$ |
|------|-------------------------|-----------------------------------|---------------------------------|----------------------------|-----------------------------------|-------------------|-------------------|
| 1.00 | 1.781                   | 1.781                             | 33.71                           | 0.044                      | 0.89                              | 1.49              | 1.49              |
| 0.90 | 0.892                   | 1.784                             | 28.57                           | 0.027                      | 0.38                              | 0.63              | 1.94              |
| 0.70 | 0.461                   | 0.547                             | 27.39                           | 0.032                      | 0.47                              | 0.71              | 2.04              |
| 0.50 | 0.141                   | 0.314                             | 26.80                           | 0.035                      | 0.74                              | 1.25              | 2.17              |
| 0.30 | 0.269                   | 0.445                             | 22.69                           | 0.045                      | 1.22                              | 2.03              | 2.32              |
| 0.10 | 0.552                   | 0.769                             | 22.12                           | 0.076                      | 1.41                              | 2.34              | 2.58              |
| 0.00 | 0.324                   | 0.324                             | 23.29                           | 0.178                      | 2.02                              | 3.36              | 3.36              |

The surface maximum absorption capacity $\Gamma$$_{max}$ and the smallest area A$_{min}$ per molecule occupied were calculated by gibbs adsorption isotherm (1) and (2) respectively.

$$\Gamma_{max} = \frac{1}{2.303RT} \left( \frac{\gamma}{\log C} \right)$$

$$A_{min} = 10^\frac{\alpha_1}{N_A \Gamma_{max}}$$

T—absolute temperature, R—8.314 J/(mol·K), N$_A$—Avogadro constant, $\alpha$—constant, which is the ionic number changing with the change of surfactant concentration. Unit of $\Gamma_{max}$, A$_{min}$ is μmol/m$^2$, Å$^2$ respectively.

If there is no interaction between the two components (OPLES-7 and dodecyl glucoside), the CMC$_{ideal}$ and the ideal cross-sectional area A$_{ideal}$ of each molecule occupying of the mixed system can be calculated by formula (3) and (4). The X$_i^o$ and X$_i^m$ were calculated by equation (5) and (7), and $\beta^o$ and $\beta^m$ were calculated by plugging X$_i^o$ and X$_i^m$ into equation (6) and (8). Their synergistic effects were determined by using the judgment criteria.

$$\frac{1}{CMC_{ideal}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2}$$

$$A_{ideal} = \alpha_1 A_{min,1} + \alpha_2 A_{min,2}$$

$\alpha_1$ and $\alpha_2$ are the molar fraction of component 1(OPLES-7) and component 2(dodecyl glucoside) in the mixed system; Amin,1 and Amin,2 are each molecule of mixed system occupying equal area on the surface.
X₁—the mole fraction of component 1 (OPLES-7) on the surface phase;

C₁₂—total concentration of mixed surfactant under a given surface tension;

C₁0 and C₂₀ are the single surfactant concentration of component 1 (OPLES-7) and component 2 (dodecyl glucoside) under the same surface tension.

α₁—the mole fraction of component 1 (OPLES-7) in the mixed system; β⁺—the interaction parameters between two components on the surface phase.

X₁ᵐ—the mole fraction of component 1 (OPLES-7) in the micelle;

C₁₂ᵐ—critical micelle concentration of mixed surfactant;

C₁m and C₂m are the critical micelle concentration of component 1 (OPLES-7) and component 2 (dodecyl glucoside), respectively.

α₁—the mole fraction of component 1 (OPLES-7) in the mixed system; β⁻—The interaction parameters between the two components of mixed micelle.

The interaction parameters β (β⁺ and β⁻) 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:

\[
β^+ < 0 \quad \beta^+ - \beta^0 \geq \ln \left( \frac{C^m}{C_2^m} \right)
\]

(2) Judgment criteria of efficiency of reducing surface tension:

\[
β^- \geq \ln \left( \frac{C^m}{C_2^m} \right)
\]

(3) Judgment criteria of forming micellar power:

\[
β^- \geq \ln \left( \frac{C^m}{C_2^m} \right)
\]

The calculated data is shown in table 2.

**Table 2 Composition and interaction parameters of the OPLES-7/dodecyl glucoside (dg) mixed system at 298K**

| α₀dg | X₁ᵐ | β⁺ | X₁⁺ | β⁻ | β⁺⁻β⁻ |
|------|-----|----|-----|----|-------|
| 0.1  | 0.178 | -4.537 | 0.228 | -4.859 | -0.308 |
| 0.3  | 0.269 | -4.182 | 0.287 | -3.448 | 0.729 |
| 0.5  | 0.335 | -4.071 | 0.354 | -3.287 | 0.773 |
| 0.7  | 0.367 | -2.274 | 0.432 | -2.962 | -0.678 |
| 0.9  | 0.525 | -1.332 | 0.572 | -2.492 | -1.156 |

α₀ expresses β₁₂ ave

Calculation result shows that both β⁺ and β⁻ value are negative, and β⁺⁻β⁻ is in the OPLES-7/dodecyl glucoside system, which indicates that OPLES-7/dodecyl glucoside system meet the conditions of reducing surface tension efficiency and synergistic effect. α₀ is 0.3-0.5, β⁺⁻β⁻> 0
and in OPLES-7/ dodecyl glucoside system, which indicates that synergistic effect shows decreasing effect when the surface tension decreases to a maximum.

Table 3 shows that 0.1% aqueous mixed surfactant solution (40 ml) does not separate from mineral oil for 70min, which reveals the strong emulsifying behavior of OPLES-7/ dodecyl glucoside.

Table 3 Surface activity of mixed surfactant

| surfactant                  | Emulsification Power |
|-----------------------------|----------------------|
| OPLES-7/ dodecyl glucoside. | 70 min               |
| sodium dodecyl sulfate      | 35 min               |

It may be conjectured that OPLES-7/ dodecyl glucoside is an effective emulsifier.

It can be seen from the above calculation and test results that OPLES-7/ dodecyl glucoside system show good synergistic effect and can be widely used in washing field, emulsification, and other fields.

3.2 Effect of NaCl on the surface activity of mixed systems

Different concentrations of sodium chloride were added and the effect of sodium chloride content on mixed system surface activity was investigated when the molar fraction of OPLES-7 to dodecyl glucoside is 1:1. Experimental results showed that sodium chloride not only reduced the surface concentration of the same solution and also reduced the CMC of the mixed system.

The concentration of the counterion of the surfactant was increased and double layer between the surfactant surface and the surrounding micelles was compressed when NaCl was added to the complex system as a counterion. The electric repulsion between the adsorption layer and the surfactant ions in the micelles was weakened to make them more closely arranged, and CMC and $\gamma_{CMC}$ were reduced.

4. Conclusion

Critical micelle concentration of OPLES-7/dodecyl glucoside mixed system is 0.141 mmol L$^{-1}$ when the fraction of OPLES-7 to dodecyl glucoside is 1:1 (mole:mole).

Calculation results show the micellization of OPLES-7/dodecyl glucoside mixed system is a spontaneous process. The surface activity of the mixed system is better than that of the single system. There is broad application prospects for OPLES-7/dodecyl glucoside mixed system.

The surface activity of the mixed systems was increased when the sodium chloride solution was within a certain concentration range.

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