Aqueous Properties of Mixed Anionic Gemini Surfactant and Conventional Anionic Surfactant

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Edited by A. Masuyama, Osaka Univ., and accepted October 16, 2001 (received for review September 7, 2001)

Abstract: In order to determine the characteristics of a mixed system of an anionic gemini surfactant with N,N-dialkylamido-urea and arginine and a conventional anionic surfactant, aqueous solutions of (CH₂)₂[NCO(C₁₇H₃₅)₂C₂H₄CO₂Na]₂ (2:1)/sodium dodecyl sulfate (soap) mixture were studied. The following parameters were measured: critical micelle concentration (cmc), micelle composition, surface tension, foaming power, degree of micelle ionization, and pH values. For the sake of comparison, mixtures of SDSa/soap (SDSa = sodium N-dodecyl-N,N-dimethylammonium acetate, the corresponding monomer of 2:1) were also investigated. The cmc values of the SDSa/soap mixture monotonously increase with increasing molar fraction of soap at 30°C. In contrast, the cmc values of the 2:1/soap mixture are intermediate between those for the pure surfactants over a broad region at 30°C. The composition of 2:1/soap mixture in micelles is kept at a 2:1 molar ratio in the plateau region. With increase in temperature of 2:1/soap mixture, cmc values reach a maximum at a soap molar fraction of 0.6. This is obvious at 50°C. The surface tension of 2:1/soap mixture is minimal at a soap molar fraction of 0.6 at 30°C, at which the surface tension is the lowest among those of the pure surfactants. The foaming power of the 2:1/soap mixture is maximal at the soap molar fraction of 0.6, at which the foaming power is the largest among those of the pure surfactants. Greater degree of micelle ionization for 2:1/soap mixture than for SDSa/soap mixture was observed over a broad region. The reason for this is the larger proton uptake by the arginine group of 2:1 than that of SDSa, which releases Na⁺ into the bulk phase in the micellization process. The evidence for this is the larger increase in pH in the mixed cmc solutions for 2:1/soap mixture than for SDSa/soap mixture. The unexpected synergistic interaction between 2:1 and soap molecules is due to stronger reduction of the mutual repulsion between the anionic head groups in the 2:1 molecule in the presence of a soap molecule.


Key words: gemini, anionic, surfactant, mixed system of two anionics

1 Introduction

Surfactants with two hydrophilic and two hydrophobic groups in the molecule, called "gemini" surfactants (1-19), have attracted attention since the beginning of the 1990's, because their various surface-active properties are superior to those of corresponding conventional surfactants with one hydrophilic and one hydrophobic groups. Thus, they have much lower cmc values and are more efficient in reducing the surface tension of water. Because of the two hydrophilic groups in a gemini molecule, solubility in water is increased greatly, permitting the gemini molecule to contain many more car-
bon atoms in an alkyl chain and still remain water-soluble, with a resulting great increase in surface activity (20).

In many practical applications, the properties of mixtures of surfactants are important and attractive (21). The presence of two charge-sites in an ionic Gemini surfactant suggests that it should interact more strongly with surfactants of neutral and opposite charge than do conventional surfactants (20). Studies involving anionic Gemini surfactants and polyethoxylated nonionic or amine oxide focused on the search for synergism in micellation and monolayer formation at the air/water interface (22-24). Synergism in dynamic surface tension or mixed micelle formation were observed (22, 23). Concerning the structural characteristics of Gemini surfactant, the Gemini structure was found to more prone than non-Gemini structures to exhibit synergism in surface tension, reduction efficiency, and effectiveness, and less prone to exhibit synergism in mixed micelle formation (24). A recent study involving anionic Gemini surfactant and polyethoxylated nonionic surfactant found that a mixture of an anionic Gemini surfactant with a hydrophilic spacer and a nonionic surfactant did not exhibit synergism in micellation, but that a mixture of an anionic Gemini surfactant with a hydrophobic spacer and a nonionic surfactant exhibits synergism (25). In addition, studies involving mixtures of anionic Gemini surfactants and cationic conventional surfactants focused on aggregation behavior as a clue to the micellar shape, or the existence of “cross-linked” micelles. (26). Another important mixed system is that including ionic Gemini surfactants and the conventional ionic surfactants with the same charge, since in most practical applications, i.e., in cosmetic products, mixing an ionic surfactant with another surfactant bearing the same charge is common. A study involving cationic Gemini surfactants and the corresponding monomeric surfactant focused on localization of the monomeric surfactant in the threadlike micelles in the mixed solutions at low molar fraction of monomeric surfactant (27). The two surfactants were found to mix intimately, with no evidence for preferential localization of the monomeric surfactant. A study involving an anionic Gemini surfactant, \((\text{CH}_3)_2\text{[NCO(C}_1\text{H}_{23})\text{C}_2\text{H}_4\text{CO}_2\text{Na}]_2}\), named 2/2, and a conventional anionic surfactant, sodium dodecyl sulfate (SDS), has recently been reported (28). It was found that 2/2/SDS mixtures forms 2:1 complexes during micellization and film formation.

The aim of this paper is to elucidate aqueous and surface properties of mixtures of \((\text{CH}_3)_2[\text{NCO(C}_1\text{H}_{23})\text{C}_2\text{H}_4\text{CO}_2\text{Na}]_2\) and sodium dodecanoate (soap) in order to determine synergism in micellization in bulk phase and/or film formation at the air/water interface. The chemical structures of the anionic Gemini surfactant, 2/2, the corresponding monomer, sodium N-dodecanoylsarcosinate, SDGs, and soap are shown in Fig. 1. The structural characteristic of 2/2 is the simultaneous presence of \(N, N\)-dialkylamide and carboxylate groups in one molecule.

2 Experimental Materials

2·1 Materials

The details of the preparation of Gemini surfactant (2/2) have been described elsewhere (29). Sodium N-dodecanoylsarcosinate SDGs, (Tokyo Kasei Co., LTD, Japan) was used after recrystallization (5 times) from mixed solvent of tetrahydrofuran and water. Sodium dodecanoate (soap) was purchased from Wako Chemical Industries, Ltd and used after recrystallization (5 times) from ethyl alcohol.

\[
\begin{align*}
\text{C}_{11}\text{H}_{23}\text{CONCH}_2\text{CH}_2\text{CO}_2\text{Na} \quad \text{C}_{11}\text{H}_{23}\text{CONCH}_2\text{CO}_2\text{Na} \\
(\text{CH}_2)_2 \quad \text{CH}_3 \\
\text{C}_{11}\text{H}_{23}\text{CONCH}_2\text{CH}_2\text{CO}_2\text{Na} \quad \text{SDGs} \\
\text{soap}
\end{align*}
\]

Fig. 1 The Chemical Structures of 2/2, SDGs, and Soap.
2.2 Measurements

Measurements for surface tension of the aqueous solutions of each surfactant and mixed surfactant solutions were made by the Wilhelmy plate technique (surface tensionmeter CBVP-A3; Kyowa Kaimen Kagaku Co., LTD, Japan) with a platinum plate in nitrogen atmosphere. Measurements were taken until constant surface tension values indicated that equilibrium had been reached. For determining the cmc of mixed surfactant solutions ('mixed cmc' in the text), the specific conductivity data were collected with a conductometer (CM-30V, TOA Electronics Ltd, Japan) using a platinum electrode with a cell constant of 105.7 m⁻¹. Each concentration series was made up by progressive dilution in the cell. The cmc was determined as the concentration at the intersection of the lines from the plots of conductance-total molar concentration. Foaming power was observed for the mixed surfactants solutions, of which concentrations were adjusted to the mixed cmc values. Foaming experimental was done by the following.

![Graphs showing conductivity data for 212/soap mixtures](image)

**Fig. 2** Typical Conductance-total Concentration Plots for 212/soap Mixture.
method: 20 mL of mixed surfactants solutions were placed in 50 mL Epton tubes, which is set in water bath at 40°C, the tube were then shaken up and down 100 times per min by hand. The foaming heights were recorded immediately after the shaking and after 10 min.

3 Results and Discussion

Bulk behavior

Typical conductance-total concentration plots of 2/1/2 soap and SDSa/soap mixtures at 30°C are shown in Fig. 2a and 3, respectively. Note that these plots were obtained without pH adjustment. Figure 2a shows that the cmc of 2/1/2 is very low, 0.04 mM, which corresponds to the break point in the plot. This concentration closely corresponds to the value of 0.03 mM, obtained by the surface tension method at pH 10.5 and at 30°C (30). For soap, the plot in Fig. 2c yields a cmc value of 28.2 mM (the value in the literature is 26 mM at 25°C as determined by the dye method). For the 2/1/2/soap mixture with a soap molar fraction of 0.5, the conductivity plot shown in Fig. 2b yields the mixed cmc value of 17.5 mM. For SDSa, the conductivity plot (Fig. 3a) yields a cmc value of 12.4 mM at 30°C (the value in the literature is 13 mM at 40°C as determined by the dye method (31)). Note that slopes below and above a break point in the conductance-total concentration plot for the

2/1/2/soap mixture (Fig. 2b) are close to each other, in compared with those for the pure surfactants (Fig. 2a and 2c) and those for the SDSa/soap mixtures with soap molar fraction of 0.5 (Fig. 3b).

Figure 4a and 4b show the variation of mixed cmc values with mixture composition for the two mixtures 2/1/2/soap and SDSa/soap at 30°C. For the 2/1/2/soap mixtures, the mixed cmc values are nearly constant and intermediate between the cmc values of the two components over a broad range of mixture composition. On the other hand, for the SDSa/soap mixtures, mixed cmc values monotonously increased with increase in molar fraction of soap.

The compositions of mixed micelles, which consist of two components, may be determined by thermodynamic analysis (32). For the present mixed solutions, we have used the following equation at constant temperature and pressure:

\[ X_2^n = X_2^* - X_2^* X_1^* \left( \frac{\partial \ln \text{cmc}}{\partial X_1^*} \right) \]  \[ \text{(1)} \]

where \( X_2^n \) denotes the molar fraction of component 2 in the mixed micelles, and \( X_1^* \) and \( X_2^* \) are the molar fractions in the solution of components 1 and 2, respectively. The equation was applied to the two mixtures of 2/1/2/soap and SDSa/soap. The results are shown in Fig. 5a and 5b, respectively. For both of the two mixtures, the two components mix homogeneously with each
other in the micelles. For the SDSa/soap mixture, the two components mix intimately with each other and exhibit almost ideal mixing over the entire range of testing. For the 212/soap mixture, the composition of soap in the mixed micelles, $X_{\text{soap}}$, is constant, ca. 0.3, over a broad range of solution composition, $X_{\text{soap}}$. Consequently, even in the region of higher composition of soap in solution, $X_{\text{soap}}$, i.e., when $X_{\text{soap}}$ is 0.75, the micellar composition appears to be rich in 212 to produce a constant composition of mixed micelles. Thus, it was found that the mixture forms a molecular complex with a 2:1 molar ratio of 212/soap during micellization (28). The molecular complex in the 212/soap mixture can be formed by only 20 mol% addition of 212 to soap. In view of this, the properties of 212/soap mixture are similar to those of the 212/SDS mixture. Thus, again, the highly surface active gemini molecules form a main continuous arrangement in mixed micelles of an anionic gemini and a conventional anionic surfactant, independent of any interaction between the ionic head groups (28).

For the 212/soap mixture, measurements for mixed cmc at higher temperatures were also carried out. Figure 6 shows the variation of mixed cmc values with
mixture composition at 40°C and 50°C together with that at 30°C. It is interesting to note that a maximum may exist at a soap molar fraction of 0.6 at 50°C. Different behavior below and above a soap molar fraction of 0.6 in the 2/2/soap mixture has also been observed for Orange OT in solubilizing behavior (30).

**Surface behaviors**

**Figure 7** shows the variation of surface tension at the mixed cmc for the 2/2/soap mixture with the mixture composition at 30°C, which includes a minimum at about soap molar fraction of 0.6, at which the surface tension is lower than those of the pure surfactants. **Figure 8** shows the variation of foaming power at the mixed cmc for the 2/2/soap mixture composition at 40°C, which includes a maximum at about a soap molar fraction of 0.6, at which the foaming power of the mixture is the highest among those of the pure surfactants. The foam at about a soap molar ratio of 0.6 is finer and has better stability than those obtained below and above that molar fraction. These synergistic effects imply that the tightly packed mixed adsorption film is formed at a soap molar fraction of 0.6 in the solution. The minimum in surface tension and the maximum in foaming power suggest that two kinds of mixed adsorption film may exist below and above 0.6. It can be seen in **Fig. 7** and **8** that the synergistic effect is most pronounced for compositions rich in soap. Thus, the addition of 2/2 to soap will mainly have the effect of reducing the chemical potential of the mixed film (33). These synergistic behaviors of the 2/2/soap mixture at air/water interface were not observed for the 2/2/sodium dodecyl sulfate mixture (28). The synergism at about a soap molar frac-

![Fig. 7](image)

**Fig. 7** Surface Tension at Mixed cmc for 2/2/soap Mixture with Mixture Composition.

![Fig. 6](image)

**Fig. 6** Mixed cmc for 2/2/soap Mixture at Different Temperatures.

![Fig. 8](image)

**Fig. 8** Foaming Power at Mixed cmc for 2/2/soap Mixture with Mixture Composition.
tion of 0.6 in the 212/soap mixture may be attributed to the subtle balance of steric factor in the ionic group of soap.

**Hydrogen-bonded ring formation in 212 molecule in the presence of soap molecule**

The conventional anionic surfactants containing both N-acylamide and carboxylate groups in the same molecule, sodium N-dodecanoyl-N-methyl-β-alanine (SDMA) and sodium N-dodecanoylsarcosinate (SDSa), were found to accept a proton, releasing Na⁺ during the micellization process with formation of a hydrogen bond between the protonated carboxylate group and the N-acylamide group (34). The evidence for this is increasing pH in the vicinity of the cmc values for these compounds in comparison with those for sodium N-dodecanoyl-N-methyltaurinate (SDMT) with a sulfonate group instead of a carboxylate group, and sodium decylxoyacetate (SDOA) with an ether oxygen instead of an amide group. The driving force for these processes for SDSa and SDMA is reduction in mutual repulsion between the anionic head groups as a result of the protonation. The cmc values determined by the conductance method for SDSa and SDMA are higher than those determined by the surface tension method, as a result of hydrogen-bonded ring formation between the amide group and the protonated carboxylate group, which releases Na⁺ during micellization. On the other hand, the anionic gemini surfactants with N,N-dialkylamide and carboxylate groups in their molecules exhibit little or no break point in conductance-concentration plots at pH 10.5 and an increase in pH in the vicinity of their cmc (30). This is attributed to accelerated Na⁺ release during micellization, protonation of the carboxylate group, and hydrogen bonded interaction with the amide group. Na⁺ release is easier in the gemini molecule than in the corresponding monomer, SDSa and SDMA. The pKa value of the gemini is larger than those of SDSa and SDMA. Additionally, pKa value is affected by the pH of surfactant solution. Here, also, in fact, it was confirmed that higher pH in aqueous solution results in larger pKa. This is the reason why the cmc value for 212 can be observed (see Fig. 2a) by the conductance method without pH adjustment. The pH value of 212 solution of the cmc was ca. 9, whereas, at pH 10.5, 212 has a smaller break point in the conductance plot than any of the monomers do, so small that there appears to be no break point in the plot (30).

Therefore, for the 212/soap mixture, it should also be possible that the gemini molecule, 212, accepts a proton and releases Na⁺ during micellization to reduce the relatively strong mutual repulsion in the presence of soap molecules, compared with pure 212. To test this hypothesis, the degree of micelle ionization calculated from slopes below and above the cmc obtained from the conductance data for the 212/soap mixture is shown in **Fig. 9**. The degree of micelle ionization of the 212/soap mixture is larger than those of the pure surfactants and those of SDSa/soap mixture over a broad range, suggesting that proton uptake by the carboxylate group of 212 molecule, which releases Na⁺ into bulk phase, is more promoted in the mixed micellization process than the proton uptake for the pure surfactants and the SDSa/soap mixture. This may be because of the stronger repulsive interaction of 212 molecule in the presence of soap molecule than that of SDSa molecule in the presence of soap, reflecting the difference between the pKa values of 212 and SDSa. In order to confirm the release of Na⁺ in the micellization process of the 212/soap mixture, we examined the pH variation at the mixed cmc for the two mixtures of 212/soap and SDSa/soap with the mixture composition at 30°C (Fig. 10). The pH values of

![Fig. 9](image-url)  
**Fig. 9** Degree of Micelle Ionization for 212/soap Mixture with Mixture Composition.
2/12 soap mixture increased with increase in soap molar fraction in the range of 0-0.4. With increase in the soap molar fraction in the range of 0.4-0.9, pH values were almost constant, with pH values larger over the entire region. The pH values of the 2/12 soap mixture are larger than those of the SDSa/soap mixture. Thus, for the 2/12 soap mixture, the gemini molecule, 2/12, releases Na⁺ and accepts a proton during micellization, which increases reduction in the mutual repulsion between the anionic head groups in the 2/12 molecule in the presence of soap molecule, compared with SDSa molecule.

This is the first paper showing synergism in a mixture of an anionic gemini surfactant and a conventional anionic surfactant. The synergism is probably due to the structural characteristic of simultaneous presence of N, N-diaryllylamine and carboxylate groups in the gemini molecule in a mixture with soap.

4 Summary and Conclusions

We studied a mixed system of an anionic gemini surfactant, with N, N-diaryllylamine and carboxylate groups, and sodium dodecanoate (soap) by measuring the mixed cmc, surface tension, foaming power, degree of micelle ionization, and pH as a function of composition. The conclusions obtained are as follows:

1. The mixture of the anionic gemini surfactant, 2/12, and soap forms 2:1 complexes over a broad region of composition during micellization.
2. Synergism in adsorption at the air/water interface (presence of a minimum in surface tension vs. composition plot and a maximum in foaming property vs. composition plot) was observed.
3. The combination of the values of the degree of micelle ionization and pH at the mixed cmc indicates protonation of the carboxylate group of the 2/12 molecule, which releases Na⁺ into the bulk phase. The tendency of forward protonation in the mixed micellization process is larger than for pure 2/12 and SDSa/soap mixture. The protonated carboxylate groups in 2/12 molecules in 2/12 soap mixture may be responsible for the synergy observed in interfacial properties, since the electrostatic repulsive interactions between head groups are markedly decrease by introduction of 2/12 into soap micelles.

References

30. Tsubone, K., unpublished data.