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ORIGINAL CONTRIBUTION

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Light scattering study on the micellar systems solubilizing a fatty acid

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Abstract The effect of oleic acid on the aggregational behavior of the α-sulfonated fatty acid methyl ester sodium salt (α-SFMe) and sodium linear C_{12}/C_{14}-alkylbenzenesulfonate (LAS) has been studied using a light-scattering method. The solubilizing capacity of α-SFMe was larger than that of LAS, and depended both on the number of micelles in the surfactant solution and the solubilized amount per micelle.

When the micellar weights for the α-SFMe and LAS systems were determined at the various oleic acid/surfactant ratios, the micellar weights initially decreased by small amounts of solubilizate and then increased with the further increase in the solubilized amounts. It was found that the solubilization process is accompanied by a reconstitution of the micelles.

Key words Solubilization – micelle – aggregational state – light scattering – oleic acid – reconstitution

Introduction

Recently, α-sulfonated fatty acid methyl esters (α-SFMe) have been attracting much attention, not only due to their relatively quick availability from renewable vegetable materials, but also due to their good biodegradability [1–3]. Furthermore, the formulation of α-SFMe in laundry detergents is already known to create superior detergency for fabrics [4–6], as well as having a high tolerance against calcium ions [7]. Many of the physicochemical functions of surfactants such as adsorption, dispersion, emulsification and solubilization have been investigated in order to elucidate mutual relations with washing performance. The authors studied the solubilizing capacity of α-SFMe for unsaturated fatty acids as one of the important factors of its superior detergency performance. Many reports have so far been published with regard to solubilization [8–10], but only a few papers have attempted to describe solubilization from the viewpoint of the aggregational behavior of micelles [11–15]. Nakagawa et al. [11] have reported the aggregational behaviors of alkane and/or alkanol-solubilized nonionic surfactant micelles using a light-scattering method. Almgren et al. [12] and Malliaris [13] have reported the aggregational behaviors of alkane and/or alkanol solubilized-ionic surfactant micelles using the fluorescence quenching method. In these papers, it was reported that the aggregation number of micelles decreased with the addition of a polar solubilizate and increased with the addition of a hydrophobic solubilizate. However, the effect of a long-chain fatty acid on the aggregational behavior of an anionic surfactant with regard to the mechanism of detergency has not been studied. In this paper, the aggregational behavior of α-SFMe micelles solubilizing oleic acid was investigated using a light-scattering technique with comparison to that of LAS.

Experimental

Materials

The α-sulfonated C_{14}/C_{16}-fatty acid methyl ester sodium salt (α-SFMe) was synthesized from a mixture of myristic acid and palmitic acid (3/7 by weight) according to the method described in a previous paper [7], Sodium linear C_{12}/C_{14}-alkylbenzenesulfonate (LAS) was a commercial grade product of the Lion Corporation (Takyo, Japan). The purification of α-SFMe was carried out by repeated recrystallization from ethanol/water mixtures (3/2 by volume). LAS was utilized after desalting and removing any unreacted alkylbenzene. It was confirmed that no surface chemical impurity was contained in these surfactants based on the absence of a surface tension minimum around the CMC of their aqueous solutions.

Biochemical grade oleic acid was purchased from Wako Pure Chemical Industries Co., Ltd. (Tokyo, Japan) and utilized without further purification.

Determination of solubilization limit

Fifty mL of surfactant solutions containing various amounts of oleic acid with various concentrations of surfactant were placed in 100 mL screw-capped glass tubes.

The glass tubes were shaken in a thermostated water bath (30 ± 0.1 °C) for 20 h.

The scattered light intensity of these solutions due to coarse oil droplets was then determined. The solubilization limit for a surfactant solution is expressed by the threshold value of the oleic acid content, where the intensity of the scattered light steeply increases.

Determination of CMC

The CMC values of each oleic acid/surfactant system were determined using the usual conductivity method [7]. Specific conductance measurements were performed using an electronic conductivity meter (TOA Model CM-40S, Tokyo, Japan).

Light-scattering measurement

Light-scattering measurements were carried out using a Model DLS-700 photon-counting laser light scattering photometer (Otsuka Denshi Co., Ltd., Tokyo, Japan) according to the method described in a previous paper [7]. Specific refractive indices were measured using a differential refractometer (Union Giken Co., Ltd., Model RM-102, Tokyo, Japan). Both measurements were performed at 30 ± 0.1 °C. The sample solutions were prepared by the dilution of approx. 30 mM-surfactant solutions previously solubilized with various amounts of oleic acid in distilled water followed by shaking at 30 ± 0.1 °C for 20 h. The pHs of these solutions were 5.2 ± 0.2. The micellar weight of the oleic acid-solubilized micelle was estimated from the Debye plot [7, 11, 16], since no significant angular dependence was observed in the intensity of the scattered light for any solutions. If the good linear correlations in the Debye plots are valid, the micellar weight of oleic acid-solubilized micelle (M_{mic}) can be obtained from the intercepts on the vertical axis while the second virial coefficients (A_2) are obtained from the slopes.

Results and discussion

Solubilizing capacity of α-SFMe and LAS

The solubilization limits for the α-SFMe and LAS solutions in the surfactant concentration range of 10–20 mM are listed in Table 1. The solubilization limit is represented as both the maximal concentrations of oleic acid (mM) in the solution and the [oleic acid]/[micellar surfactant] ratios (mole/mole). From Table 1, the solubilizing capacity of α-SFMe was approx. 1.8 times larger than that of LAS, and the [oleic acid]/[micellar surfactant] ratios at the solubilization limit in these surfactant concentration

Table 1 Solubilization limit for each surfactant solution

Surfactant	Surfactant concentration (mM)	Solubilization limit max. concentration of oleic acid (mM)	 [oleic acid]/[micellar surfactant] ratio (mole/mole)[a])
α-SFMe	10	2.80	0.31
	15	4.26	0.30
	20	5.32	0.28
LAS	10	1.60	0.19
	15	2.30	0.17
	20	2.84	0.15

[a]) [micellar surfactant] = [total surfactant] − [surfactant at CMC] [surfactant at CMC] is 0.86 mM for the α-SFMe system and 1.35 mM for the LAS system, respectively.

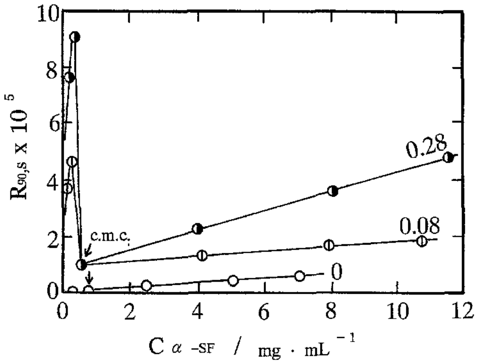


Fig. 1 Reduced scattering intensities of α-SFMe micellar solutions solubilizing oleic acid as a function of α-SFMe concentration. Numbers in figure indicate the [oleic acid]/[total α-SFMe] ratio. Arrows indicate the CMC

ranges slightly decreased with an increase in surfactant concentration for both systems.

Factors participating in the solubilization limit

In Fig. 1, the reduced scattering intensities of the α-SFMe solutions solubilizing various amounts of oleic acid at a 90° angle ($R_{90,s}$) were plotted versus the concentration of α-SFMe ($C_{\alpha\text{-SFMe}}$). The scattering intensities of solutions consisting of only α-SFMe were weak and increased only slightly with an increase in the α-SFMe concentration above its CMC. On the other hand, the scattering intensities of the solutions solubilizing oleic acid above their CMC were larger than that of the solutions not solubilizing oleic acid. In addition, a very strong scattering was observed in the region below their CMC. These results indicate that the scattering with the medium intensities above the CMC originated from the oleic acid-solubilized micelle and those with the strong intensities below the CMC were due to formation of oleic acid droplets. These phenomena were very similar to the results of the *n*-decane/nonionic surfactant system reported by Nakagawa et al. [11].

The Debye plots for the α-SFMe and LAS systems in the surfactant concentration range of approx. 5–30 mM (C_s–C_{cmc}; approx. 1–10 mg·mL^{-1}, C_s is the total solute concentration) are shown in Figs. 2(a) and (b). The M_{mic} and the A_2 obtained from Fig. 2 are summarized in Table 2 together with the CMC values (C_{cmc}). The CMC values for both systems decreased with solubilization of a small amount of oleic acid and slightly increased during a further increase in the [oleic acid]/[total surfactant] ratio. These behaviors of the CMC changes were similar to the results of the hydrophobic solubilizate/surfactant systems reported by Nakagawa et al. [11] and Marangoni et al. [15]. Debye's formula is derived assuming that the micellar constitution is not altered by a concentration change in the micellar solution, but its applicability may be suspect in the solubilizate/surfactant system. However, it can be presumed that the constitutions of oleic acid-solubilized micelles do not change within these concentration ranges, since our curves in Fig. 2 derived according to Debye's treatment formed good linear correlations. The M_{mic} of both systems reached a minimum at the [oleic acid]/[total surfactant] ratio of 0.08, and increased again with the further addition of oleic acid up to each solubilization limit. Here, the M_{mic} can be represented by Eq. (1) with respect to 1 l of the surfactant solution solubilizing oleic acid.

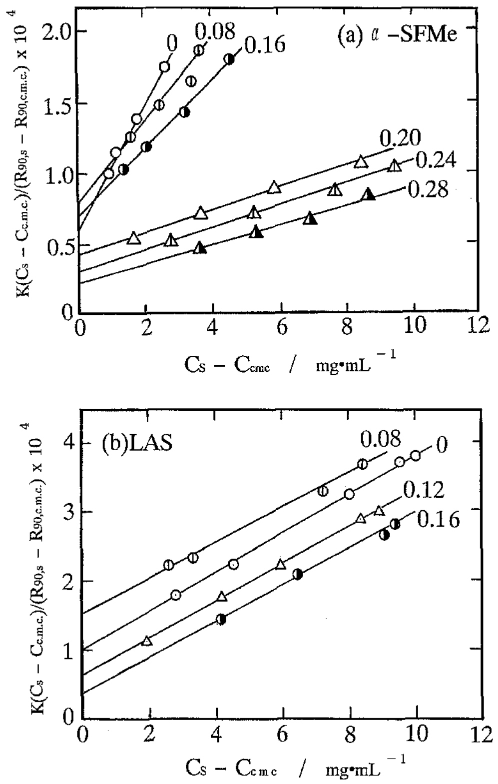


Fig. 2 Debye plots of each oleic acid/surfactant system. a) oleic acid/α-SFMe system, b) oleic acid/LAS system, Numbers in figure indicate the [oleic acid]/[total surfactant] ratio

$$M_{mic} = N_{O/mic} \times M_O + N_{S/mic} \times M_S \ , \qquad (1)$$

where $N_{O/mic}$, $N_{S/mic}$, M_O and M_S are the number of oleic acids in a micelle, the number of surfactant molecules in a micelle, the molecular weight of oleic acid, and the molecular weight of the surfactant, respectively. The total number of oleic acid molecules ($N_{O/total}$) and that of surfactant molecules in a solution ($N_{S/total}$) can be represented by

Table 2 Effect of added oleic acid on aggregational state of micelles

Surfactant	Surfactant concentration (mM)	[oleic acid]/[total surfactant] ratio (mole/mole)	C_{cmc} (mM)	M_{mic}	A_2 (10^{-2} mole · mL/g)	$N_{\mathrm{S/mic}}$ (molecules/micelle)	$N_{\mathrm{O/mic}}$ (molecules/micelle)	Z_{mic}[a]) (10^{20} micelles/1L-solution)	P (charge/micelle)
α-SFMe	4.1–8.3	0	1.80	16,400	2.02	44.8	0	1.1	4.4
	4.6–9.3	0.08	0.87	11,500	1.50	29.5	2.6	1.9	1.9
	3.9–11.4	0.16	0.94	13,200	0.81	31.8	5.5	1.7	1.5
	4.6–20.4	0.21	1.04	27,000	0.62	62.8	14.3	0.88	2.8
	7.1–22.1	0.25	1.16	38,300	0.69	86.6	23.5	0.63	4.3
	8.9–20.1	0.28[b])	1.10	41,500	0.51	91.7	28.1	0.60	3.8
LAS	10.5–31.6	0	2.10	9,370	1.29	27.1	0	1.8	2.2
	9.7–24.4	0.08	1.51	8,070	1.15	21.7	2.9	2.4	1.5
	6.6–24.9	0.12	1.48	21,500	1.32	55.9	7.7	0.93	4.0
	12.1–25.8	0.16[b])	1.57	27,800	1.04	70.1	12.6	0.74	4.6

[a]) at 10 mM-surfactant concentration
[b]) solubilization limit

Eqs. (2) and (3), respectively.

$$N_{\mathrm{O/total}} = N_{\mathrm{O/bulk}} + N_{\mathrm{O/mic}} \times Z_{\mathrm{mic}} \tag{2}$$

$$N_{\mathrm{S/total}} = N_{\mathrm{S/bulk}} + N_{\mathrm{S/mic}} \times Z_{\mathrm{mic}} \ , \tag{3}$$

where $N_{\mathrm{O/bulk}}$, $N_{\mathrm{S/bulk}}$ and Z_{mic} are the number of oleic acid molecules in the bulk water of the solution, the number of surfactant molecules in the bulk water of the solution, and the number of micelles in the solution, respectively. Since the solubility of oleic acid in water is negligibly small compared to the amount of the solubilized one, Eq. (2) is reduced to Eq. (4).

$$N_{\mathrm{O/total}} = N_{\mathrm{O/mic}} \times Z_{\mathrm{mic}} \tag{4}$$

$N_{\mathrm{O/mic}}$ is regarded as the solubilizing capacity per micelle. Since $N_{\mathrm{S/bulk}}$ equals the number of surfactant molecules at the CMC ($N_{\mathrm{S/bulk}} = C_{\mathrm{cmc}} \times N_{\mathrm{A}}$, where N_{A} is Avogadro's constant.), Eq. (5) is obtained from Eqs. (3) and (4).

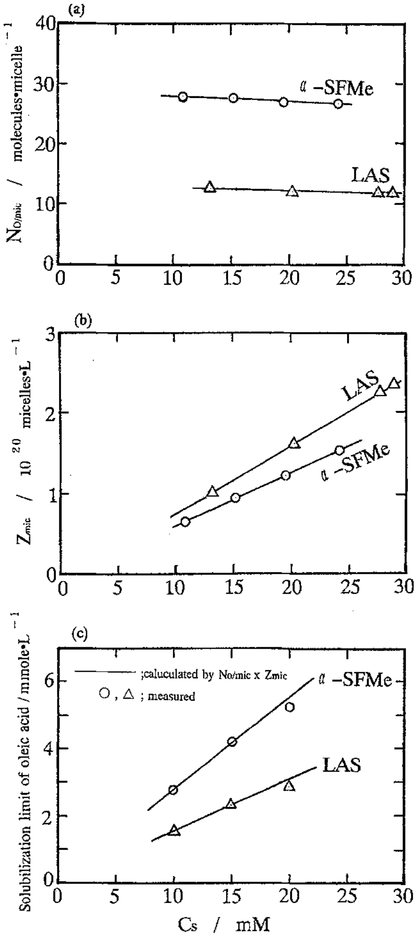
$$N_{\mathrm{S/mic}} = N_{\mathrm{O/mic}}(N_{\mathrm{S/total}} - C_{\mathrm{cmc}} \times N_{\mathrm{A}})/N_{\mathrm{O/total}} \tag{5}$$

Equation (6) can then be derived from Eqs. (1), (4) and (5).

$$Z_{\mathrm{mic}} = (1/M_{\mathrm{mic}})\,\{M_{\mathrm{O}} \times N_{\mathrm{O/total}} + M_{\mathrm{S}}(N_{\mathrm{S/total}} - C_{\mathrm{cmc}} \times N_{\mathrm{A}})\} \tag{6}$$

The $N_{\mathrm{O/mic}}$ and Z_{mic} were calculated using Eqs. (4) and (6) at the various [oleic acid]/[total surfactant] ratios for both systems, and are summarized in Table 2. Using the data for the maximal [oleic acid]/[total surfactant] ratios in Table 2, the $N_{\mathrm{O/mic}}$ and the Z_{mic} values as a function of the surfactant concentration are plotted in Figs. 3(a) and (b). It was found that the $N_{\mathrm{O/mic}}$ of the α-SFMe system was fairly higher than that of the LAS system and that the Z_{mic} of the LAS system was slightly larger than that of the

Fig. 3 $N_{\mathrm{O/mic}}$, Z_{mic} and $N_{\mathrm{O/mic}} \times Z_{\mathrm{mic}}$ as a function of surfactant concentration for each oleic acid/surfactant system. a) number of solubilized oleic acid molecules per micelle ($N_{\mathrm{O/mic}}$); b) number of micelles in solution (Z_{mic}); c) solubilization limit calculated ($N_{\mathrm{O/mic}} \times Z_{\mathrm{mic}}$, represented as solid lines) and measured (represented as symbols)



α-SFMe system. The $N_{O/mic} \times Z_{mic}$ values (solid lines) corresponding to the solubilization limit are shown in Fig. 3(c) together with the plots of the experimentally obtained data in Table 1. Since the $N_{O/mic} \times Z_{mic}$ calculated values agreed with the experimentally obtained data, the solubilizing capacity per micelle ($N_{O/mic}$) and the number of micelles in the solutions (Z_{mic}) were considered to contribute to the solubilization limit of oleic acid using these surfactant solutions. From the previously mentioned results, the larger solubilized amount of oleic acid for the α-SFMe solution was concluded to be due to the larger solubilizing capacity per α-SFMe micelle.

Changes in aggregation state with an increase in the oleic acid/surfactant ratio

The authors discussed the changes in the aggregation state of the oleic acid-solubilized micelles with an increase in the [oleic acid]/[total surfactant] ratio, utilizing the data in Table 2, which are the number of oleic acids in a micelle ($N_{O/mic}$), the number of surfactant molecules in a micelle ($N_{S/mic}$), the number of micelles in the solutions (Z_{mic}) and the surface charges of a micelle (P). The surface charges of a micelle (P) were obtained from Eq. (7) [17].

$$P = M_{mic}(2A_2 \times C_{cmc} \times 10^{-6})^{1/2} \tag{7}$$

For the α-SFMe system, the Z_{mic} increased while the $N_{S/mic}$ decreased when the [oleic acid]/[total surfactant] ratio increased from zero to 0.16. In these ratio regions, the solubilization is considered to proceed with a reconstitution of micelles by incorporation of oleic acid. It seems to be the reverse of the general rule of micellar aggregation that the $N_{S/mic}$ in these ratio regions was small in spite of their smaller micelle surface charge and their smaller CMC values. However, the aggregation number is not always large just because the surface charge and the CMC value are small as shown in the study about the decyltrimethylammonium alkyl carboxylate micellar systems reported by Anacker et al. [18]. It was presumed that the steric factors due to the incorporation of the bulky oleic acid molecules play a role in the decrease of the aggregation number rather than the surface charge. In the ratio range of 0.16–0.28, the Z_{mic} decreased while the $N_{S/mic}$ increased with an increase in the ratio. This indicates that the increase in the solubilized amounts accompanies the coalescence of micelles and the conformational change of oleic acid in the micelles. It is favorable for the coalescence of micelles that the mutual repulsion between charged micelles is weak. This was supported by the fact that the P value is minimum at the ratio of 0.16, above which the Z_{mic} decreased and the $N_{S/mic}$ increased. Similar changes in the aggregation states were observed in the LAS system. However, the coalescence of the oleic acid/LAS micelles began at a lower ratio (0.08) than that (0.16) of the α-SFMe system. For the LAS system, the $N_{O/mic}$ as the solubilizing capacity per micelle was smaller than that of the α-SFMe system and the coalescence terminated at a lower ratio.

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