Performance and Physicochemical Properties of α-Sulfo Fatty Acid Methyl Esters

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The detergency properties of α-sulfonated fatty acid methyl esters (α-SFMe) were evaluated and compared to those of conventional anionic surfactants by using a model heavy-duty detergent formulation. Several physicochemical properties of surfactants were measured to investigate the effective factors on detergency. α-SFMe showed good detergency performance under various washing conditions. These results were considered to correlate well with the good adsorption behavior on oils and dispersing capabilities for particles, as well as with the good solubilization capacity. Solubilization behavior of α-SFMe is discussed in relation to micelle properties. It is suggested that α-SFMe can form suitable micelles for solubilizing polar oils advantageously, due to its bulky hydrophilic group.

KEY WORDS: Aggregation number, detergency, dispersion, emulsification, micelle, solubilization, α-sulfo fatty acid methyl esters.

α-Sulfo fatty acid methyl esters (α-SFMe) are well known as surfactants derived from natural fats and oils. A number of studies on surface activities already have been reported (1–3). The addition of α-SFMe to major surfactants for heavy duty laundry detergents is already known to create high tolerance against calcium ion, as well as superior detergency for fabrics (4,5). Furthermore, α-SFMe has become of great interest due to its good biodegradability (6–8) and the emphasis on renewable natural resources.

However, manufacturing of good-quality α-SFMe on a commercial basis is quite difficult. The two main factors hampering industrial production are (9): i) The dark color of the sulfonated product, which occurs during the sulfonating process of the fatty acid methyl esters; and ii) the easy hydrolysis of the ester group. The hydrolyzed product is the disodium salt of the sulfonated fatty acid, which has poor surface activity at normal washing temperatures due to its high Krafft point. Moreover, the hydrolysis problem has become an obstacle to designing a detergent formulation with good stability because α-SFMe is easily hydrolyzed in concentrated aqueous solution and at the high pH values of detergent manufacturing processes.

Recent new manufacturing technology developed by the Lion Corp. (Tokyo, Japan) has provided a possible solution to the above-mentioned problems, which leads to the manufacture of good-quality α-SFMe, and which is applicable to laundry detergent manufacturing (9).

In this study, the detergency properties of α-SFMe were evaluated and compared to those of conventional anionic surfactants by using a model heavy-duty detergent formulation. Tolerance against water hardness, the influence of carbon number and various washing conditions on detergency were examined. Further, some physicochemical properties of surfactants used were measured in order to investigate the effective factors on detergency.

The authors found that α-SFMe showed good detergency performance under various washing conditions and these results correlated with the higher adsorption and dispersing capabilities for particles and oily soil, as well as the good solubilization ability. The solubilization ability is discussed in relation to micelle properties and molecular structure.

EXPERIMENTAL PROCEDURES

Materials. Sodium α-sulfo fatty acid methyl ester, linear alkyl benzene sulfonate (LAS) and sodium dodecyl sulfate (AS) were used as surfactants. These surfactants were purified by usual methods. The chemical structure and purity of these surfactants are shown in Table 1. Ion-exchanged water was used for adsorption and dispersion tests. In the light scattering experiments, the water used was of biochemical grade.

Detergency. A Terg-O-Tometer (U.S. Testing Co., Hoboken, NJ) was used as a washing machine. Detergent solution (900 mL) was poured into the washing tub and washing was carried out under the following conditions: Rotor speed, 120 rpm; washing time, 10 min; liquor ratio, 30:1; rinsing time, 10 min × 2 times.

After drying, reflectances of test swatches were measured with a reflectance meter (Nihon Denshoku Kogyo Co. Ltd., Tokyo, Japan). Detergency was calculated from the following Kubelka-Munk equation (10):

$$\text{Detergency (\%)} = \frac{(\mathrm{K/S})_{\mathrm{soiled}} - (\mathrm{K/S})_{\mathrm{washed}}}{(\mathrm{K/S})_{\mathrm{soiled}} - (\mathrm{K/S})_{\mathrm{initial}}} \times 100 \qquad [1]$$

$$\frac{\mathrm{K}}{\mathrm{S}} = \frac{\left(1 - \dfrac{\mathrm{K}}{100}\right)^2}{\dfrac{2\mathrm{R}}{100}} \qquad [2]$$

where R is reflectance, K is the extinction coefficient and S is the scattering coefficient.

Artificially and naturally soiled swatches were used for the detergency test. Artificially soiled swatches were prepared by dipping the cloth into an aqueous dispersion containing soil, protein, carbon black and clay (red-yellow diluvium), then drying at 105°C for 30 min. The components of artificial soil are shown in Table 2. Naturally soiled swatches were prepared by rubbing the test swatches ($\phi = 6$ cm) on human faces. It was confirmed that the hydrolysis of α-SFMe, which was mentioned in the introduction, does not occur during the washing conditions at low temperature and low surfactant concentrations.

Adsorption onto clay. Surfactant solutions were contacted with clay in 500-mL beakers for 3 h with stirring. The concentration of clay was 0.4 wt%. The amount of

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TABLE 1

Chemical Structure and Purity of Surfactants

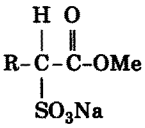
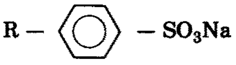
Surfactant	Chemical structure	Purity
Sodium α-sulfo fatty acid methyl ester (α-SFMe)	 $R-\overset{H}{\underset{SO_3Na}{C}}-\overset{O}{\overset{\|}{C}}-OMe$ $R = C_{12\sim14}$	>98%
Sodium linear alkyl benzene sulfonate (LAS)	 $R = C_{10\sim14}$	>98%
Sodium dodecyl sulfate (AS)	$ROSO_3Na$ $R = C_{12}$	>98%

TABLE 2

Components of Artificial Soil[a]

Oleic acid	28.3%
Triolein	15.6%
Cholesterol oleate	12.2%
Liquid paraffin	2.5%
Squalene	2.5%
Cholesterol	1.6%
Protein	7.0%
Carbon black	0.5%
Clay	29.8%

[a] Reference 11.

surfactant adsorbed on the clay was determined by measuring the difference of surfactant concentration before and after testing.

Zeta potential of oil. The zeta potential of oil droplets was measured with a micro-electrophoretic analyzer (Laser Zee model 501, Pen Kem Inc., Bedford Hills, NY). Artificial soil for detergency testing was used as an oil component. The measurement was carried out with an applied potential gradient of 10 V/cm at 25°C. For zeta potential measurements the emulsions containing 0.04 wt% of oil were prepared with hand shaking and were allowed to stand for 3 h. The emulsions were dispersed again before use.

Dispersion of clay. Into a 100-mL test tube, 90 mL of surfactant solution was placed, 0.5 g of clay (described above) was added and the mixture was shaken 20 times. The height of the dispersed phase was measured after standing for 18 h.

Emulsification of oily soil. The surfactant solution was poured into a 1000-mL beaker; 2 g of artificial oily soil was added into 1000 mL of surfactant solution and emulsified by homogenizer for 5 min. After standing for 3 h, the particle distribution was measured with an automatic particle analyzer (Capa-500, Horiba, Kyoto, Japan). The emulsifying ability was obtained as a percentage of particles below 10 μm.

Solubilization of oily soil. Fifty mL of surfactant solutions were placed into 100-mL glass-stoppered Erlenmeyer flasks, varying amounts of oily material (oleic acid, reagent grade) were added. The flasks were shaken in a constant-temperature bath (30°C) for 24 h, followed by standing for 12 h until equilibrium was established. The turbidities of the solutions were observed visually.

Average size and aggregation number of micelles. Average size of the micelles was measued by the dynamic light scattering method (Submicron Particle Analyzer System 4700, Marvern Co., Tokyo, Japan). The intensity of light scattering at a 90° angle was determined. The micelle size was calculated as a hydrodynamic particle size from the transitional diffusion coefficient, which was obtained by the autocorrelation function. Aggregation number was measured by the static light scattering method (DLS-700, Otsuka Electric Co., Osaka, Japan). The intensity of light scattering at a 90° angle was determined. The aggregation number was calculated by a Debye plot (12).

RESULTS AND DISCUSSION

Detergency performance under various washing conditions. The performance of α-SFMe was compared to that of LAS and AS, which have long been utilized as the main components of heavy duty detergents. Previous studies have shown good calcium tolerance of α-SFMe, but there are other features to be considered in the washing performance. So, the washing performance of three kinds of surfactants were determined under various washing conditions. To clarify the evaluation results, a simple model detergent solution containing 270-ppm of two typical alkaline builders, but without sequestering builders, was used.

First of all, the effect of carbon chainlength of α-SFMe on detergency was evaluated under both typical Japanese washing conditions (low water hardness and low temperature) and European or U.S. conditions (high water hardness and medium temperature). As shown in Figure 1, among the various carbon numbers of α-SFMe, the best detergency was obtained with C16, the second with C18,

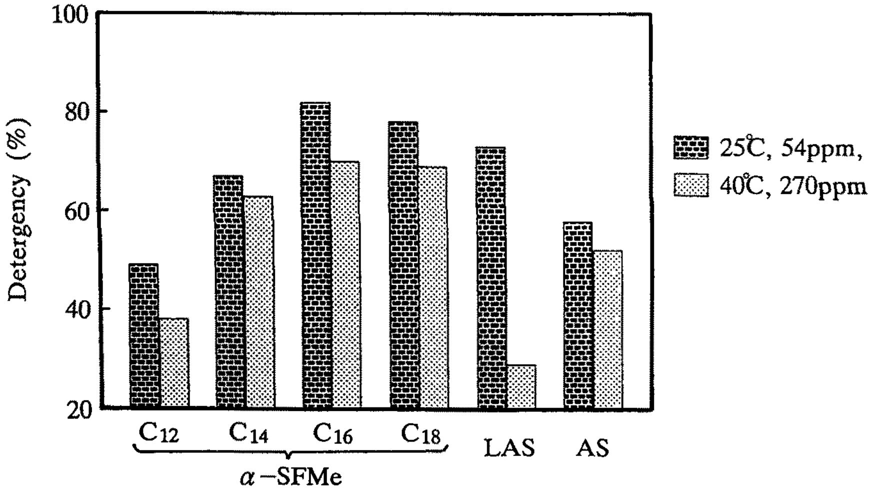


FIG. 1. Effect of carbon chainlength of α-SFMe on detergency. Terg-O-Tometer, artificial soil (cotton), liquor ratio, 30; water hardness, 54 or 270 ppm ($CaCO_3$); surfactant, 200 ppm; Na_2CO_3, 135 ppm; and silicate, 135 ppm.

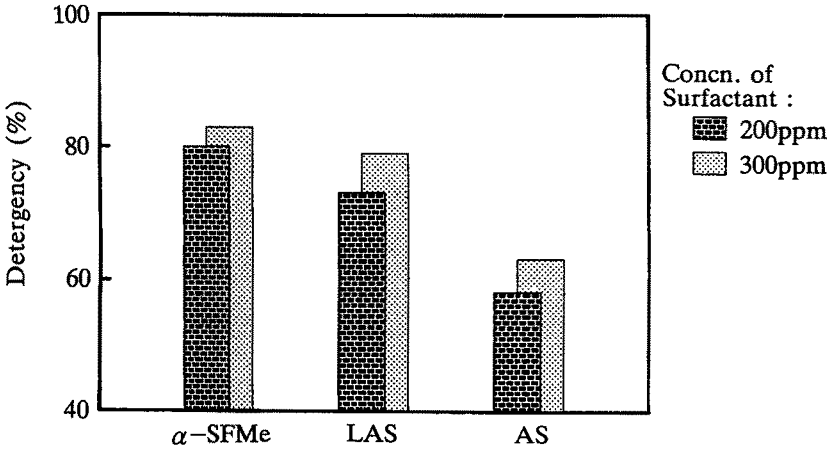


FIG. 2. Detergency for artificial soil (cotton). As in Figure 1, except for water hardness, 54 ppm ($CaCO_3$).

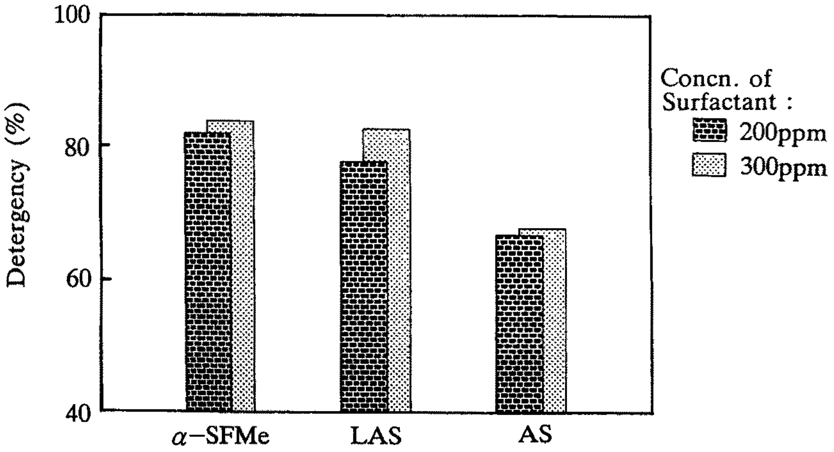


FIG. 3. Terg-O-Tometer, artificial soil (PE/cotton), 25°C, liquor ratio, 30; water hardness, 54 ppm ($CaCO_3$); Na_2CO_3, 135 ppm; and silicate, 135 ppm.

and the third one with C14 for both laundry conditions. The detergency of LAS showed a big decrease in high water hardness, and AS had poor detergency as compared to α-SFMe. From these results, C14-16 α-SFMe was chosen as an optimum carbon number in this study. C18 α-SFMe gave good detergency, but it was regarded as unsuitable for low-temperature washing because of the high Krafft point of the surfactant.

The detergency of α-SFMe was then compared to that of LAS and AS under Japanese standard washing conditions with cotton and cotton/polyester swatches (Figs. 2 and 3). α-SFMe showed the best detergency among the three kinds of surfactants on both cotton and polyester/cotton swatches. α-SFMe also gave good results because a decrease in concentration led to only a small decrease in detergency.

The detergency properties at varying washing liquor ratios were tested. As shown in Figure 4, α-SFMe exhibited a low decrease in detergency as the liquor ratio decreased, which means that α-SFMe had good washing efficacy under low mechanical power.

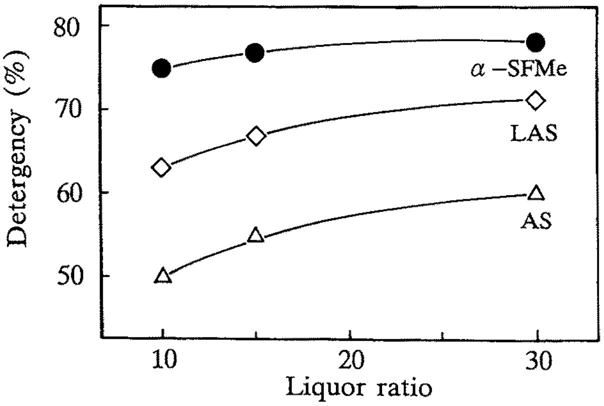


FIG. 4. Effect of liquor ratio on detergency. Terg-O-Tometer, artificial soil, 25°C, water hardness, 54 ppm ($CaCO_3$); surfactant, 270 ppm; Na_2CO_3, 135 ppm; and silicate, 135 ppm.

Confirmation of the above-mentioned performances was attempted with naturally soiled swatches. The evaluation results with facial soil are shown in Figure 5. Even at a concentration of 200 ppm, α-SFMe has better detergency than LAS at 300 ppm, and is almost equal to that of AS at 300 ppm.

Physicochemical properties. The mechanism of the washing process correlates well with the physicochemical properties of surfactants, such as penetration, adsorption, swelling, dispersion, emulsification and foaming. In this study, α-SFMe was compared to LAS and to AS in the test of adsorption onto oily soil, dispersion of particle soil and solubilization. All of them are considered to be factors directly affecting dirt during laundry operations.

First, the adsorption of surfactants onto clay soil was evaluated (Fig. 6). The adsorption amount of α-SFMe was higher than that for LAS and AS. These results point to a good effect on the stability of an aqueous dispersion system. As shown in Figure 7, the α-SFMe system had the best dispersion stability among the three surfactants, especially at low concentrations.

The measurement of surfactant adsorption on oil is difficult because the surface area of the oil droplet changes as emulsification proceeds. Thus, the adsorption of surfactants was evaluated in this study by measuring the zeta potential of an oil droplet dispersed in aqueous surfactant solution (Fig. 8). The zeta potential has a negative value, and as the surfactant concentration increases, the negative charge of the droplet surface increases. The values leveled off above 40 ppm of surfactant concentration. Figure 8 shows that α-SFMe gave the highest negative charge among the three surfactants. These results indicate that α-SFMe has a better adsorptive behavior on oily dirt than does LAS or AS.

Furthermore, this result must certainly have a positive effect on the stability of an emulsion. Figure 9 shows the stability test results for the emulsion prepared by emulsifying the oil component of artificial soil used for detergency evaluations into various surfactant solutions. The α-SFMe system showed better stability compared to the other two surfactants, thus the results showed good agreement between adsorption properties and emulsion stability.

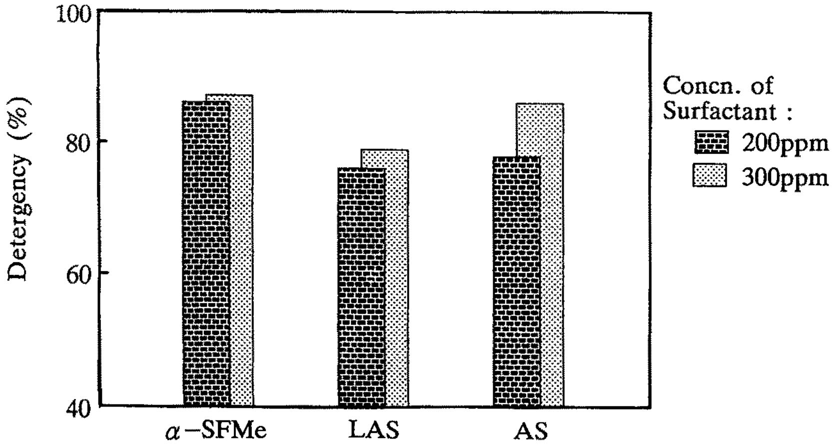


FIG. 5. Detergency for natural soil (cotton). As in Figure 3, except for natural soil (cotton).

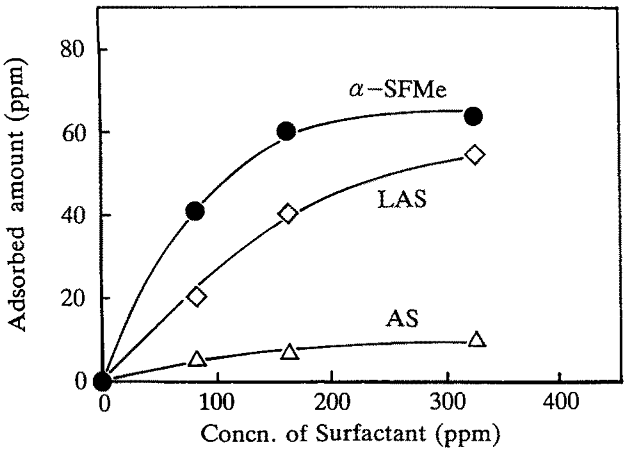


FIG. 6. Adsorption of surfactants onto particle soil. 25°C, Clay, 0.4%; and Na_2CO_3, 170 ppm.

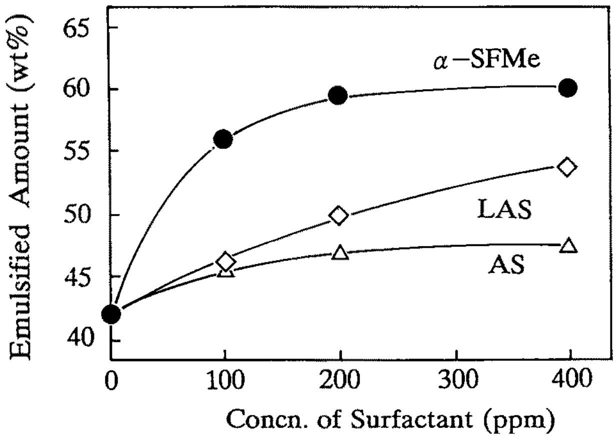


FIG. 9. Emulsification of oily soil by surfactants. Artificially oily soil, 0.2%, 25°C, and Na_2SO_4, 170 ppm.

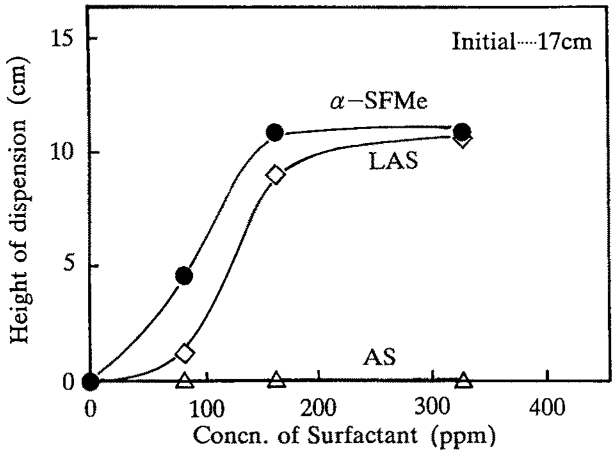


FIG. 7. Dispersion of particle soil by surfactants. 25°C, Clay, 0.5 g/mL, 18 h; and Na_2CO_3, 170 ppm.

Evaluation of the solubilization capacity is an advantageous way to study the interaction of a surfactant with oil. The solubilization amount of α-SFMe was determined as a function of concentration and compared to that of LAS and AS with oleic acid as the solubilizate (Fig. 10). The solubilization capacity increased remarkably as the surfactant concentration was increased, and when comparing the three kinds of surfactants at a concentration of 20 mM, α-SFMe was able to solubilize twice the amount of oil as LAS and AS.

To obtain more detailed information on aqueous α-SFMe solution, the diameter and the aggregation number of micelles were determined for three kinds of surfactants. The diameter was measured by dynamic light scattering and the aggregation number by static light scattering (Table 3).

The results suggested that LAS and α-SFMe had similar micelle diameters that were twice as big as those of AS. The aggregation number of α-SFMe was about 50, which is higher than that of LAS (27) and smaller than

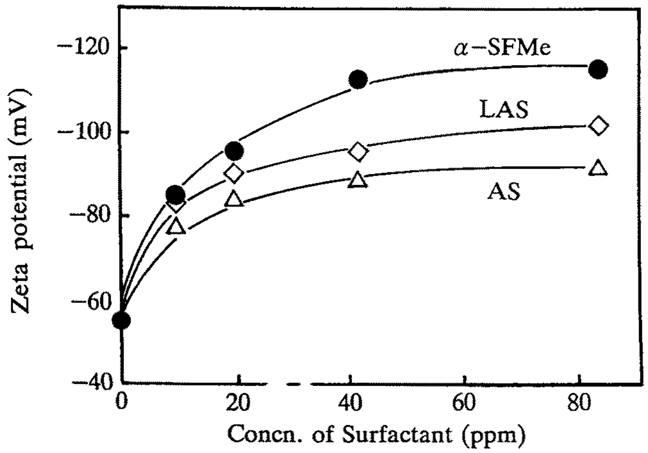


FIG. 8. Effect of surfactants on the zeta potentials of oily soil. Artificially oily soil, 0.04 wt %, 25°C, applied potential gradient, 10 V/cm.

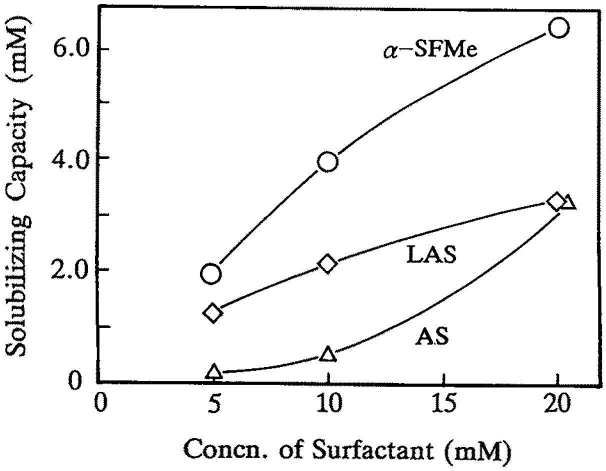


FIG. 10. Solubilizing capacity of surfactants for oleic acid.

TABLE 3

Average Size and Aggregation Number of Micelles

Surfactant[a]	Diameter (nm)[b]	Aggregation number[c]
α-SFMe	12.8	50
LAS	12.5	27
AS	7.5	70

[a] Surfactant concentration, 10 mM.
[b] Dynamic light scattering.
[c] Static light scattering.

that of AS (70). This means that AS has densely packed small micelles, whereas LAS has roughly packed micelles. The micelles of α-SFMe were found to be intermediate among the three surfactants.

Furthermore, the micelle size in an oil-solubilized system was determined. Figure 11 shows the change in micelle diameter as a function of the amount of solubilized oleic acid. As shown in the Figure, the diameter of the micelles grew with increasing solubilizate amount. For α-SFMe the amount leveled off above 3 mM of surfactant concentration and then reached the limit of solubilization. In the case of AS, a small amount of oil was enough to reach the solubilization limit. LAS also showed a relatively small capacity. These results provide some hints about the micelle structure; it appears that AS forms small rigid micelles, whereas LAS forms roughly packed micelles.

A further solubilization study was carried out with non-polar n-octane as a solubilizate instead of oleic acid (Fig. 12). Solubilizing capacities are quite similar in the non-polar oil-solubilization system, that is, α-SFMe has a close interaction with a polar oil like oleic acid, but it has poor interaction with non-polar substances.

This solubilizing behavior is thought to depend on the molecular structure of surfactants used and is related to the surrounding of the hydrophilic group at the packed state of the molecule. Polar substances, such as oleic acid, are considered to be solubilized at the palisade layer. α-SFMe can form big micelles, which work to solubilize polar oils advantageously due to its bulky hydrophilic group. In addition, the micelle structure also may play a strong role in the adsorption of surfactant on oil.

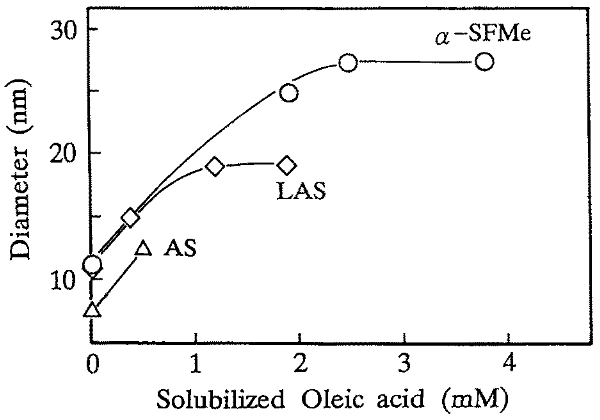


FIG. 11. Relation between diameter of solubilized micelle and concentration of oleic acid.

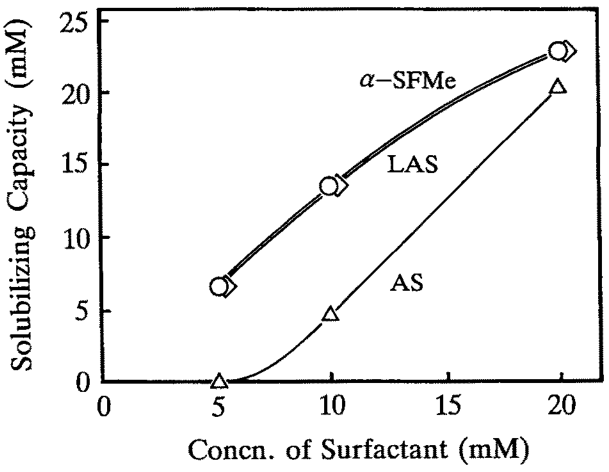


FIG. 12. Solubilizing capacity of surfactants for n-octane.

Typical surfactant properties have been discussed, such as dispersing ability, emulsification of oil and solubilization, which are considered important contributing factors to washing performance. Although the direct relationship between these physicochemical properties and detergency is somewhat difficult to assess, α-SFMe can be considered to be highly potent as the main surfactant of a detergent formulation based on total surface activity and detergency testing. α-SFMe will be utilized to a larger extent as the main surfactant of heavy duty detergents in the near future because of its good biodegradability, superior calcium tolerance and high washing performance.

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