Sulfoxylated Methyl Esters as Potential Components of Liquid Formulations

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ABSTRACT: Sulfoxylated methyl esters (Φ-MES) are obtained *via* sulfoxidation of fatty acid methyl esters with SO_2, O_2, and ultraviolet light of appropriate wavelength. These products may be used as co-surfactants with linear alkylbenzene sulfonate and alkyl ether sulfate, either in heavy-duty or in hand dishwashing liquids. Standard hand dishwashing formulations based on Φ-$MESC_{16}$ are presented and discussed with regard to solubility, viscosity, performance, and skin compatibility. The experimental results obtained indicate that the above-mentioned products can be regarded as potential components for liquid formulations.

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KEY WORDS: Φ-MES, LAS, AES, hand dishwashing liquids.

In previous papers (1,2), the synthesis, characterization, and performance of sulfoxylated methyl esters (Φ-MES) were described. According to these results (2), Φ-MES showed: good solubility, very low viscosity of water solutions even at high concentration, and low sensitivity to water hardness. Furthermore, these are natural products and are then expected to have (i) excellent biodegradability and (ii) good skin compatibility. As a result, these products can be viewed as new anionic surfactants with potential application in formulations for hand dishwashing liquids or for heavy-duty liquids.

The aim of the present work is to study their behavior in hand dishwashing formulations, where Φ-MES has been combined with the leading types of surfactants used in the world today: linear alkylbenzene sulfonate (LAS), alkyl ether sulfate (AES), and alcohol ethoxylate (AE).

DISHWASHING LIQUID FORMULATIONS

A competitive dishwashing liquid has to meet certain basic requirements, such as: good water solubility, low viscosity even at high concentrations, mildness to skin, effective fat and oil dissolution, and high and stable foam. Almost all European dishwashing liquid formulations are a mixture of LAS, AES, and other minor components and solvents (most frequently water). In order to study how the former formulations would behave if one or both of the major components (LAS or AES) were replaced partially by Φ-MES, the following ternary formulations (Table 1) were tested with regard to solubility, viscosity, stability to water hardness, skin compatibility, foaming, and hand dishwashing performance.

TABLE 1
Formulation Composition (wt%)[a]

Φ-MES	LAS	AES	AE
20	2.5	2.5	0
15	5	5	0
12.5	5	7.5	0
12.5	7.5	5	0
10	5	10	0
10	10	5	0
7.5	7.5	10	0
7.5	10	7.5	0
20	5	0	4
18.75	6.25	0	4
16.66	8.3	0	4
15	10	0	4
12.5	12.5	0	4
10	15	0	4
7.5	17.5	0	4

[a]Active ingredient: 25%; balance: water. Φ-MES, sulfoxylated methyl esters; LAS, linear alkylbenzene sulfonate; AES, alkyl ether sulfate; AE, alcohol ethoxylate.

MATERIALS

Φ-$MESC_{16}$ sodium salt (where C_{16} = carbon chain length). This product was obtained in our laboratory according to a modification of the methodology described (1). Basically, the modification consists of the use of hot water instead of a mixture of water and ethanol for the separation of the acid phase at the reactor outlet. In addition, the sodium sulfonate has been extracted with *n*-butanol. The detailed analytical procedure has been published previously (3). The selection of the methyl ester carbon range was done according to the performance previously obtained (2).

LAS sodium salt. A commercial sodium sulfonate mixture derived from a linear alkylbenzene (LAB) with the following wt% composition: <phenyl C_{10}, 1.3; phenyl C_{10}, 17.0; phenyl C_{11}, 54.6; phenyl C_{12}, 25.3; phenyl C_{13}, 1.3; phenyl C_{14}, 0.3; 2-phenyl alkane, 16.9. Molecular weight: 233.3.

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AES sodium salt. A commercial sodium laurylethersulfate derived from a C_{12}–C_{14} alcohol blend with 2 EO (moles of ethylene oxide).

AE. A commercial ethoxylated alcohol derived from a C_{12}–C_{14} alcohol blend with 7 EO.

RESULTS AND DISCUSSION

Solubility. Krafft points, defined as the temperature at which an aqueous solution of surfactant becomes turbid on cooling, were measured for the different formulations, as seen in Figures 1 and 2. In Figure 1, most of the formulations are between –7 to –10°C interval. As can be observed in Figure 2, all Krafft points of MES/LAS/AE mixtures are between –5 and –11°C. It must be pointed out that in these cases the total active ingredient is nearly 30%. As far as solubility is concerned, a synergism seems to exist between the surfactants that results in a significant improvement as compared to each surfactant alone.

Viscosity. Determination of this property was done in a CSR-10 rheometer from Bohling (Bohling Instrument, Cirencester, United Kingdom). Experimental results are plotted in Figures 3 and 4. As seen in Figure 3, all the formulations exhibit viscosities below 30 centipoises. As with solubility, a synergism seems to exist between the surfactants which results in a significant reduction in viscosity as compared to each surfactant alone (see Table 2). These formulations can be considered as water-like solutions. Due to the presence of AE, viscosity is somewhat higher, and, as expected, the higher the LAS content the higher the viscosity.

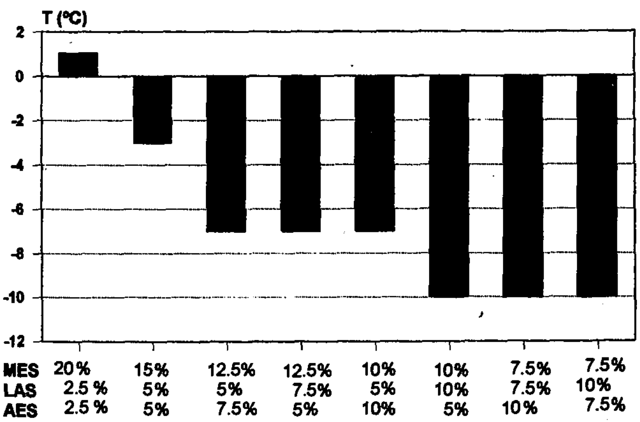

FIG. 1. Krafft points of sulfoxylated methyl esters (MES)/linear alkylbenzene sulfonate (LAS)/alkyl ether sulfate (AES) mixtures. Active ingredient: 25%.

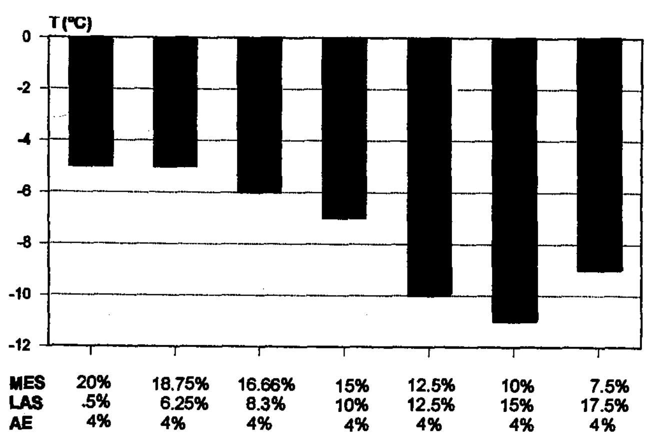

FIG. 2. Krafft points of MES/LAS/ethoxylated alcohol (AE) mixtures. Active ingredient: 29%. See Figure 1 for other abbreviations.

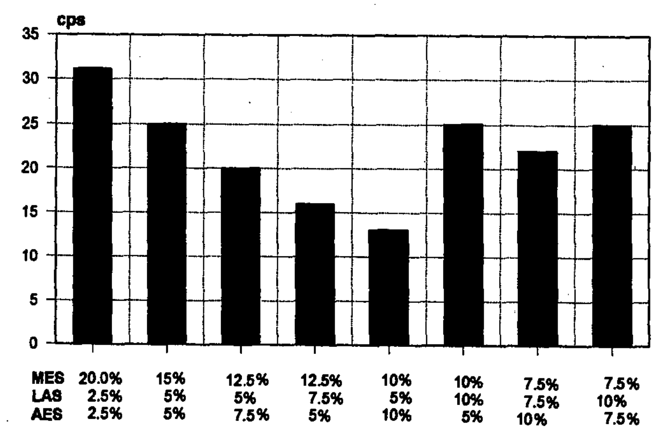

FIG. 3. Viscosity of aqueous solutions. Temperature: 20°C. Active ingredient: 25%. See Figure 1 for abbreviations.

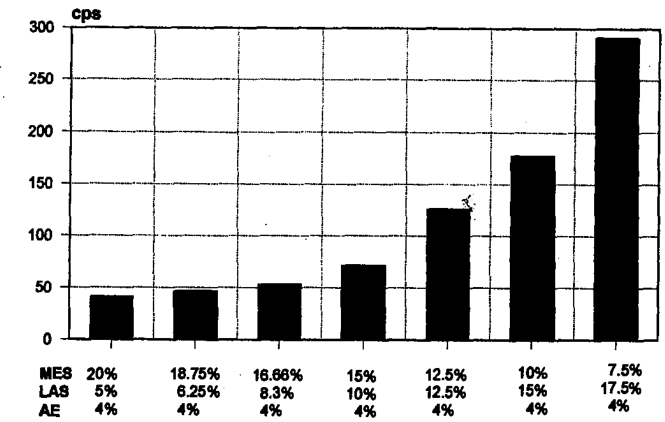

FIG. 4. Viscosity of aqueous solutions. Temperature: 20°C. Active ingredient: 29%. See Figures 1 and 2 for abbreviations.

In conclusion, the ternary formulations with Φ-$MESC_{16}$ at up to 30% active ingredient are very low viscous solutions, eliminating the use of hydrotropes and making the manufacture of liquid products easier due to the reduction in pumping facilities and costs.

Foaming. (i) Foam height. The Ross-Miles test was conducted. The concentration used refers to formulation, so that the actual surfactant concentration is 1 g/L. Experimental results are represented in Figure 5. All the results are between 60 and 80 mm regardless of the water hardness that was used. No significant differences appear between

TABLE 2
Viscosity of Aqueous Solutions at 25%(w/w) Active Ingredient[a]

	Viscosity (centipoises)
Φ-MES	52
LAS	2900
AES	1000

[a]See Table 1 for abbreviations.

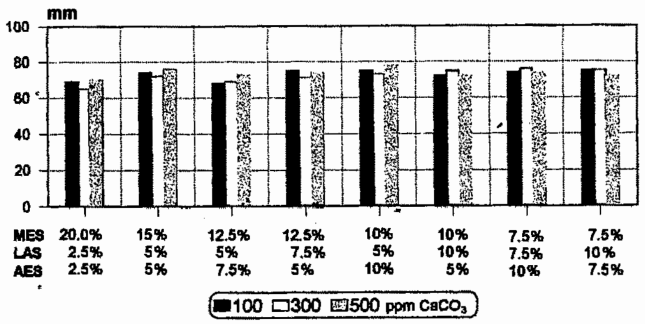

FIG. 5. Foam height (t = 0). Concentration: 4 g/L. Temperature: 49°C. See Figure 1 for abbreviations.

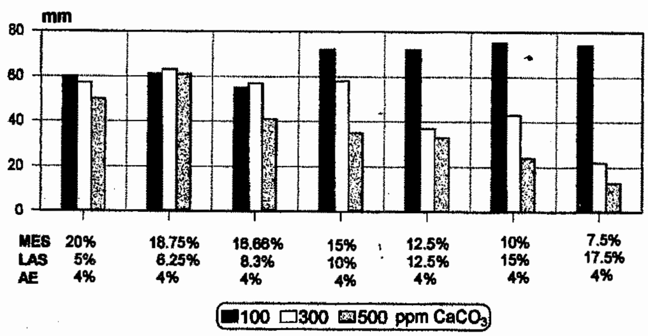

FIG. 6. Foam height (t = 0). Concentration: 4 g/L. Temperature: 49°C. See Figures 1 and 2 for abbreviations.

the different formulations tested. As shown in Figure 6, at 100 ppm hardness the best results correspond to formulations with high LAS content, while for higher hardness, the best formulation is the one with 18.75% of Φ-MESC$_{16}$.

(ii) Foam stability. According to the Ross-Miles test, foam stability is given by the foam height variation after 5 min. The results given in Figures 7 and 8 for 500 ppm $CaCO_3$ show a high foam stability level.

Stability to water hardness. The determination of the stability to water hardness ions was carried out through the precipitation boundary diagram. This widely used diagram (Fig. 9) is a log-log plot of the surfactant and calcium/magnesium ions concentration. It reflects the water hardness stability of the surfactant in a more precise form than does the more widely used stability test (DIN 53905). Only one selected formulation is presented to illustrate behavior in water containing calcium and magnesium ions.

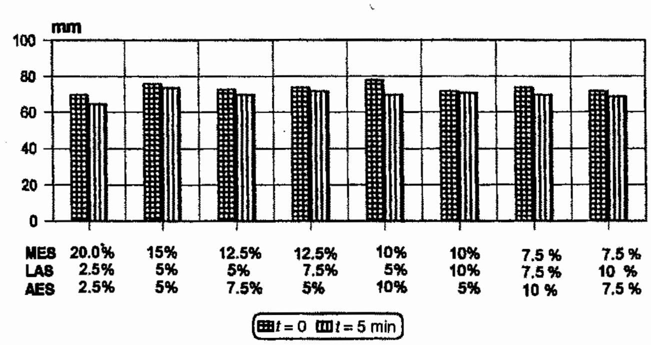

FIG. 7. Foam height (t = 5 min). Concentration: 4 g/L. Temperature:

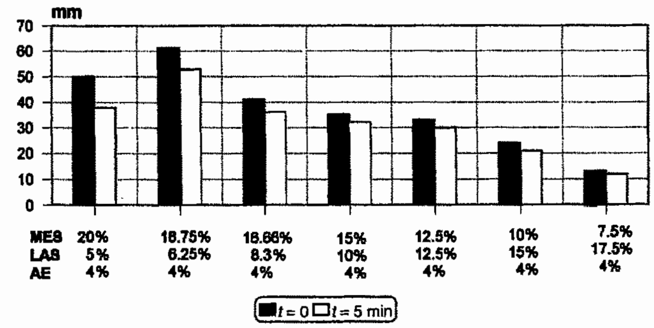

FIG. 8. Foam height (t = 5 min). Concentration: 4 g/L. Temperature: 49°C. 500 ppm $CaCO_3$. See Figures 1 and 2 for abbreviations.

Dishwashing. The method used gives a stability index for foam generated using a certain type of soil at a definite surfactant concentration (4). A correlation exists between the stability index and a hypothetical number of dishes washed according to the typical dishwashing manual test. The concentration used refers to formulation so that the corresponding surfactant concentration is 0.25 g/L. A choice has been made so that the value 50 is an indication when the number of dishes washed is above 50. The results plotted in Figures 10 and 11 show that an optimal performance is reached with this type of formulation regardless of the range in water hardness.

Skin compatibility: Zein test. The Zein test, a widespread screening *in vitro* test for the evaluation of skin irritancy of surfactants, was used. The test is based on the solubilization of the water-insoluble zein protein by surfactants. Solubilization of zein is measured through the determination of nitrogen content of the solubilized protein, giving the so-called Zein number. According to Kaestner and Frosch (5), the ability of a surfactant to dissolve the water-insoluble zein protein correlates very well with *in vitro* test data. Irritation of human skin is due to the formation of a complex between protein present in skin and surfactant. According to Seibert and Bolsterdorf (6) the extent to which a combination of anionic surfactant and protein takes place depends on many factors. Only surfactant monomers or submicellar species penetrate membranes, whereas micelles would presumably be too large to penetrate. A reduction of critical micelle concentration (CMC) results in lower levels of free

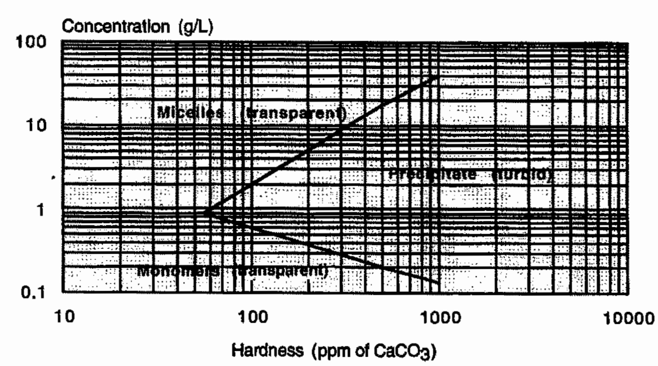

FIG. 9. Precipitation boundary diagram. Formulation: MES 12.5%; LAS 12.5%; AE 4%; temperature 20°C. See Figures 1 and 2 for abbre-

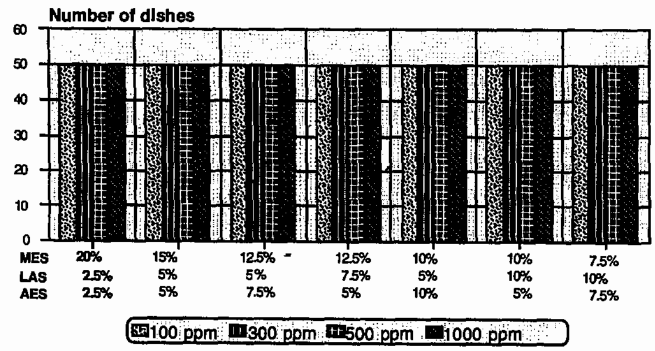

FIG. 10. Concentration: 1 g/L. Temperature: 49°C. Soil: 75% pig fat, 25% olive oil. See Figure 1 for abbreviations.

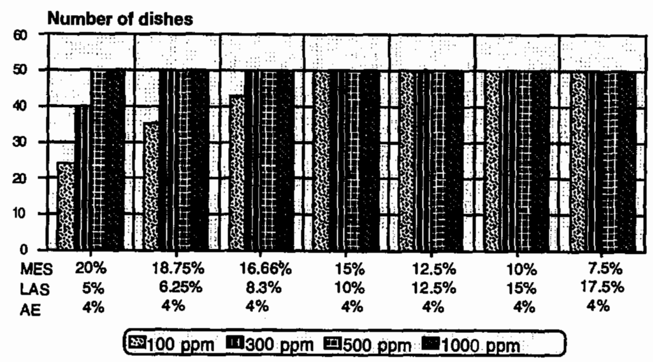

FIG. 11. Concentration: 1 g/L. Temperature: 49°C. Soil: 75% pig fat, 25% olive oil. See Figures 1 and 2 for abbreviations.

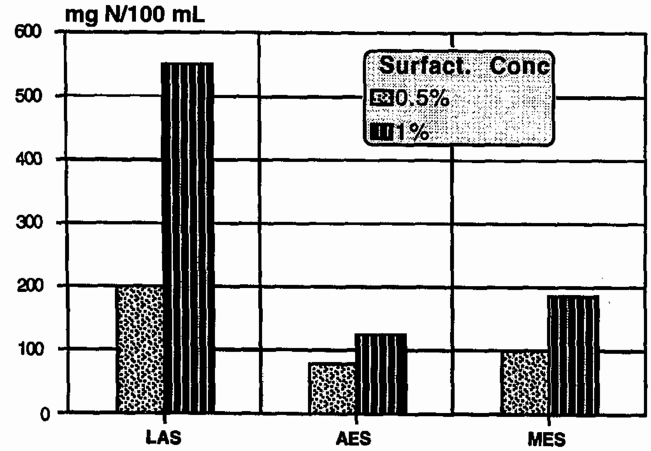

FIG. 12. Zein test. Zein protein concentration: 50 g/L. See Figure 1 for abbreviations.

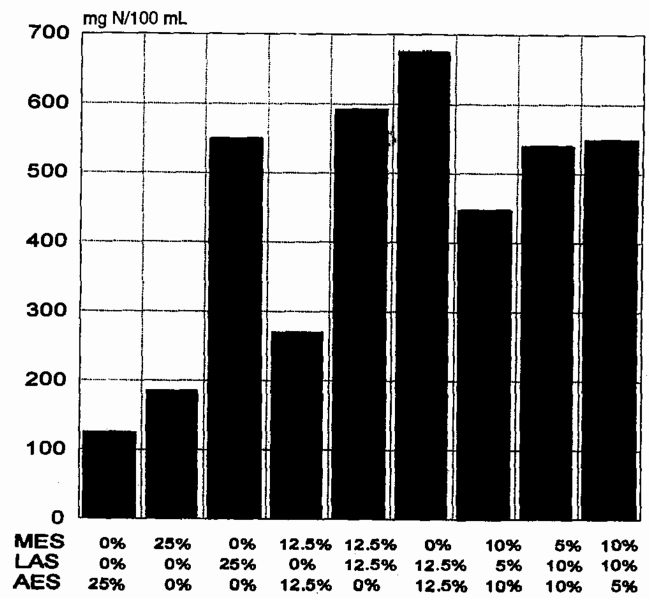

FIG. 13. Zein test. Zein concentration: 2 g/40 mL. Formulation concentration 4%. Temperature: 35°C. See Figure 1 for abbreviations.

monomers; therefore, surfactants with high CMC penetrate faster. It must be remembered (1) that Φ-MESC$_{16}$ has a CMC of 19 ppm whereas LAS has a CMC of 110 ppm. The nitrogen content of the solubilized protein gives the so-called Zein number which classifies anionic surfactants into: <200 mg N/100 mL: nonirritant; 200–400 mg N/100 mL: moderate irritant; >400 mg N/100 mL: strong irritant. The results plotted in Figure 12 agree with the CMC values, showing that Φ-MESC$_{16}$ sodium salt is nonirritant up to 1% and can be compared favorably to AES. In Figure 13, the results plotted correspond to binary and ternary formulations that have been tested as well. Here too, high Φ-MES or AES content lowers the amount of dissolved protein while the presence of LAS increases predicted irritation.

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