

Φ -Sulfo Fatty Methyl Ester Sulfonates (Φ -MES): A Novel Anionic Surfactant

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Φ -Sulfo Fatty Methyl Esters sulfonates (Φ -MES) are new anionic surfactants obtained via sulfoxidation of fatty acid methyl esters (FAME) with SO₂, O₂, and ultraviolet light of appropriate wavelength. The designation of Φ refers to the random positioning of SO₃ in the alkyl chain. In this work we summarize the most relevant results of our research started fifteen years ago, on the synthesis, separation, and analysis of Φ -sulfo fatty methyl ester sulfonates known as Φ -MES, and we update our last findings. This work describes the optimum batch conditions for the sulfoxidation of FAME and a reaction mechanism is proposed. The paper depicts an improved workup for the separation of reaction products from non reacted methyl ester and the GC-MS analysis of Φ -sulfo fatty methyl ester sulfonate is shown. Besides, an interpretation of conversion and selectivity of sulfoxidation reaction is given. Even if this paper doesn't describe performance, we can advance that the experimental results obtained indicate that Φ -MES can be regarded as a potential component of detergent formulations and most likely of body care products mainly due to a very low skin irritation as it is shown in this work.

1. Introduction

Fatty acid methyl esters are products derived from fats. The chain length is within 12 to 18 carbon atoms. The names of the detergent range are lauric (C12), myristic (C14), palmitic (C16) and stearic (C18).

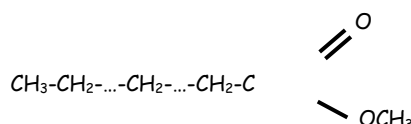


Figure 1: Fatty Acid Methyl Ester (FAME)

α -Sulfo fatty methyl esters sulfonates (α -MES) are well known surfactants derived from natural fats and oils, obtained via traditional sulfonation with SO₃.

During past years there have been a number of studies on their synthesis, surface properties, calcium tolerance, detergency and environmental behavior (Davidson et al 1985, Smith et al 1989). However, one of the distinct limitations in the use α -methyl ester sulfonates is their poor water solubility, which makes them less satisfactory products compared to alkylaryl sulfonates (LAS). α -MES exhibit a remarkable specificity in that sulfonate group is added almost exclusively to the α position of the long chain when conventional processes using SO_3 is employed, presumably being the reason for their low water solubility. To overcome this drawback sulfoxidation is proposed, that is the addition of sulphur dioxide and oxygen in the presence of UV light of appropriate wavelength to saturated fatty acid methyl esters. The sulfoxidation reaction proceeds through a radical mechanism unlike the α -MES traditional sulfonation, which proceeds through an electrophilic substitution. Due to the latter, a characteristic of sulfoxidized methyl esters is that the sulfonate group is randomly distributed over all, except the α and ω positions, of the alkyl chain, being this the reason why they are named Φ -MES. The main reaction product is monosulfonic acid:

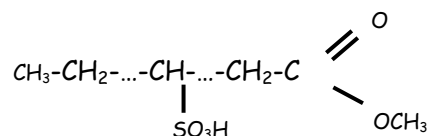


Figure 2: Φ -MES sulfonic acid.

In this investigation the batch reaction was conducted in an anhydrous medium, the optimal wavelength was determined and Φ -MES were synthesized, separated and analyzed. As a result of our investigation on Φ -MES started in 1993, several papers have been published by Cohen and Trujillo (1998, 1999a), and Cohen et al. (2001a, 2001b 2002, 2003, 2006a, 2008 and 2010). These studies have led to two patents accepted (Cohen and Trujillo, 1999b; Cohen et al, 2006b).

2. Experimental

Photochemical reactor and sulfoxidation procedure

All experiments were water free batch reactions. Experimental setup consisted of a Rayonnet photochemical reactor with 16 lamps (Southern New England Ultraviolet Company, Hamden, CT). Three sets of lamps with three different wavelengths (253.4, 300 and 350 nm) were assayed. Operating conditions were as follows:

Reaction temperature: 40°C, Volume of ME: 250 mL, Gas flow: SO₂ and O₂ (excess).

Different reaction times were used ranging from 0.5 to 6 hours. At the end of the reaction time, SO₂ and O₂ injections were stopped and N₂ was then used for 1 h to remove residual SO₂.

2.1 Separation procedure

The main components were monosulfonic acid, polysulfonic acids and a very small amount of fatty acids coming from the hydrolysis of methyl esters. Two procedures for the separation of the reaction products from the non reacted methyl esters, are depicted by Cohen et al (2001a), namely the water and the hexane extraction. According to the

water procedure mentioned, after the separation of the non-reacted methyl ester, a small amount of dissolved methyl ester and some fatty acid remained in the aqueous phase that had to be removed in order to improve the final product quality. An updated procedure, is herein depicted. The reactor outlet was mixed with an equivalent amount of water and the two phases let to separate at 60 °C in the oven. After separation of both phases, the unreacted methyl ester could be used for a new run and the water solution followed further treatment consisting in adding a volume of methanol equal to that of water. The mixture was then extracted with a non polar solvent such as n-hexane. In the hexane phase all the dissolved fatty acid and methyl ester were recovered, while the water-methanol solution was distilled under a slightly reduced pressure and all the methanol recovered. The remaining water solution was then neutralized with sodium hydroxide and concentrated as desired. As mentioned above, basically, the modification consisted of the use of a mixture of methanol-water 50/50 v/v and hexane, to perform the extraction of *dissolved impurities*. Besides this, an improvement herein depicted, is that the upper layer formed by the non reacted methyl ester can be reesterified with methanol in order to convert the whole free fatty acid present. The improved detailed procedure is depicted by Cohen et al. (2008).

3. Results and Discussion

Proposed reaction mechanism,(Cohen et al, 1998).

We have summarized in Figure 3 the ways in which the hydrocarbon sulfoxidation reaction proceeds in the *absence of water*. The reaction seems to proceed by two mechanisms: an irradiated reaction, where the persulfonic acid molecule disappears through its action as an electron donor, and a dark reaction, where the persulfonic molecule disappears by thermal decomposition. A more detailed explanation of the reaction mechanism is depicted by Cohen et al (2010).

Effect of wavelength, (Cohen et al, 1998).

The optimal conversion- selectivity ratio was obtained at 253.4 nm. Therefore, all the experiments were conducted at this wavelength.

Effect of reaction time

As a general trend, *conversion* increases with reaction time and *selectivity*, expressed as monosulfonate to disulfonate ratio, decreases. Data are shown for Φ -MES C16 in the Table 1. The selected time for the batch process was 6 h, in order to obtain enough sample.

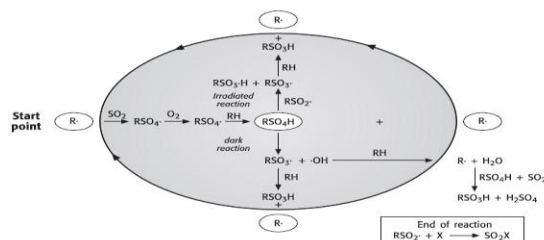


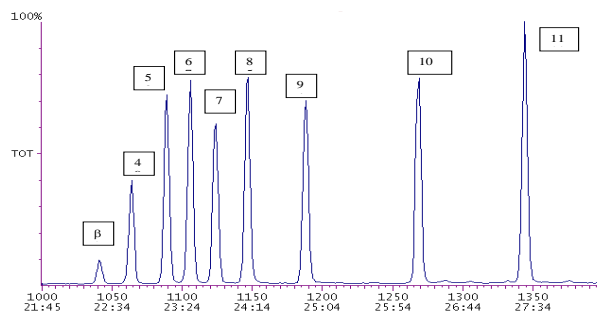
Figure 3: Proposed reaction mechanism

Table 1 Conversion-selectivity vs reaction time

Reaction Time (h)	Conversion wt/wt %	Mono/di ratio
0.5	4	7.5
1	8	6.2
2	14	4.7
5	33	3.3
6	43	2.3

Effect of chain length, (Cohen et al, 2006a).

Different fatty acid methyl esters ranging from C₁₂ up to C₁₈, were sulfoxidized and the reaction conversion obtained for the batch process at 6 hours reaction time. In order to calculate conversion, it was necessary first to separate the nonreacted methyl ester from the reaction products. The *conversion* was calculated as the recovered non reacted methyl ester divided by the starting amount. The results obtained showed that the conversion increases as the chainlength increases, going from 30 % for C₁₂ up to 50 % for C₁₈ (16). To confirm the relative sulfonatability of the different homologs during batch sulfoxidation reaction, a commercial 50/50 weight % mixture of C₁₆- C₁₈ was sulfoxidized. A GC analysis was carried out to the methyl ester mixture, both before and after the reaction. The results indicate that the relative content of C₁₆ methyl ester increases in the recovered unreacted material, while the corresponding C₁₈ relative content decreases, meaning that a higher amount of C₁₈ has been sulfonated as compared to C₁₆. In the sulfoxidation reaction, the main step is radical production. According to the radical mechanism, radical formation becomes easier the farther away the CH₂ group is from C(O)-OCH₃, as a result of the inductive effect of the latter. At least, part of the explanation, is that C₁₈ has 15 secondary active carbons to form radicals as compared to the C₁₆ methyl ester that has 13 sites (because the primary(ω), the carboxylic and α carbons do not react). Thus, the probability of reaction with (SO₂ + O₂) will be higher for the former. The use of instrumentation techniques such as GC-MS, LC-MS, or IR, in order to characterize and to identify Φ -MES components, allowed to establish for the first time, the composition of reaction products and to demonstrate the existence of random isomers that were identified (Cohen et al, 2002, 2003).

Figure 4: Φ -MESC12 Monosulfonate isomers distribution

Skin compatibility: Zein test. In the present work, we present the results of a standard experimental test, that have allowed us to compare skin irritancy of the most common commercial anionic surfactants such as LAS (Linear Alkylbenzene Sulfonate), SAS (Secondary Alkane Sulfonate) and α -MES (α -sulfo fatty Methyl Ester Sulfonate) to Φ -MES C16. 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.

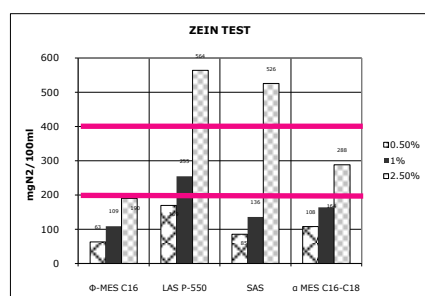


Figure 5: Zein test results at 0.5 %; 1 % and 2.5 % surfactant concentrations

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 show that Φ -MES C16 sodium salt is nonirritant up to 2.5 wt.% surfactant concentration and can be compared favorably to LAS, SAS and α -MES and gives similar results than Alcohol Ether Sulfate, Cohen et al 1998.

4. Conclusions

The optimum batch conditions for the sulfoxidation of FAME has been depicted and a reaction mechanism proposed. An improved workup for the separation of reaction products from non reacted methyl ester and the GC-MS analysis of Φ -sulfo fatty methyl ester sulfonate were shown. Besides, an interpretation of conversion and selectivity of the sulfoxidation reaction is given. Finally, we can state that Φ -MES performance (Cohen et al., 2008) indicate that Φ -MES can be regarded as a novel anionic surfactant and most likely as a component of body care products, mainly due to its very low skin irritation as it is shown in this work.

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