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ORIGINAL PAPER

The Use of a Eutectic Mixture of Olive Pomace Oil Fatty Amides to Easily Prepare Sulfated Amides Applied as Lime Soap Dispersants

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Abstract Sulfated diethanolamides of fatty acids are known to be effective lime soap dispersing agents. However, their preparation from fatty acids via fatty amides requires the use of organic solvents due to the high viscosity of both fatty amides and sulfated fatty amides. This study shows that the preparation of sulfated fatty amides is relatively easy when using olive pomace oil as the raw material. The latter, is converted into sulfated fatty amides by performing the following steps: saponification, hydrolysis, esterification, amidation, and sulfation. In the final step, the mixture obtained has sufficient fluidity, due to its high linoleic acid amide content, to obviate the use of organic solvents, as usually suggested in the literature. Characterization of the product was carried out by chemical analyses, FTIR, ^{13}C NMR, GC, and HPLC. It was shown that the yield of the amidation reaction is about 80%, and that of the sulfation reaction can exceed 100% against the pure amide (more than one sulfate group could be linked to one amide molecule). On the other hand, the Borghetty test showed that the product is an effective dispersant with a lime soap dispersing power equal to five.

Keywords Olive pomace oil · Fatty amides · Sulfated fatty amides · Lime soap dispersing power

Introduction

The oldest, most widely known, and most important surface active agents are soaps. Fatty acid soaps in moderately hard water are known to provide excellent soil removal and very good suspension of oil in the wash cycle of laundering. Soaps, however, have the disadvantage of precipitating with heavy metal ions particularly those of calcium and magnesium found in hard water.

This shortcoming of soap has been alleviated with the aid of so-called lime soap dispersing agents (LSDA) which keep the lime soaps finely divided and suspended in hard water. Several types of LSDA have been proposed for use in soap-based detergents.

Lime soap dispersing agents, as cited in the literature, include sulfated ethoxylated fatty alcohols [1], *N*-alkyl-*N*,*N*-dimethylamine oxide [2], nonionics derived from tallow alcohols [3], fatty amides [4], α-sulfoalkanol amide [5], sulfated alkanol fatty amides [6], as well as polymers derived from maleic acid [7]. More recently, Shukla et al. [8] have reported that anionic gemini surfactants with two sulfate or sulfonate head groups have much better lime soap dispersing ability than that of single chain surfactants that have only one sulfate or sulfonate head group.

The mono and diethanolamides derived from long-chain fatty acids, such as oleic acid, are waxy materials, and are slightly soluble in water. It is stated in the literature [4] that they do not improve the lathering power or soil removal efficiency of detergents, but they are valuable dispersing agents for calcium soap.

It is possible, by preparing the acid esters of sulfuric acid of these alkanolamides to produce surfactants which are anionic in their behavior and thus more soluble in water than fatty amides. The sodium salts of the sulfated

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hydrogenated tallow amides of various alkanolamines such as mono and diethanolamine, monoisopropylamine, and diglycolamine [6], show a superior solubility in water, and also a greater ability to retain dirt particles in suspension and to disperse curd calcium soap than alkanolamides. However, the high melting points of the alkanolamides and their relative insolubility in organic solvents such as dichloroethane and chloroform make sulfation on an industrial scale difficult [6]. In particular, due to the high viscosity of the sulfated fatty alkanolamide such as sulfated tallow diethanolamide, it is extremely difficult to control the sulfation procedure to ensure that the finished product is free from undesirable by-products which impair efficiency. This explains why the sulfated alkanolamides are not one of the big volume surfactants or detergent admixtures and have never equaled the alkanolamides in popularity.

The present work shows that these difficulties may be overcome by the use of olive pomace oil as a specific raw material for producing fatty alkanolamides which are completely sulfated.

The aim of this first paper in a series is to describe a process of converting olive pomace oil to sulfated fatty amide, to characterize the reaction intermediates and final product and to evaluate the lime soap dispersing power of the sulfated amide thus obtained. The purpose of the next paper will be to describe an optimal method for the synthesis of sulfated fatty amides using experimental design methodology, and to study the robustness of the process using a supersaturated design.

Experimental Procedures

Materials

1. Raw material: refined olive pomace oil.

Crude olive pomace oil is the oil extracted from pomace, the ground flesh and pits obtained after pressing olives, with hexane. It is intended for soap making or for refining for use for human consumption. In this study, refined olive pomace oil (purchased from the SIOS-Zitex Company—Sfax Tunisia) was saponified according to the Marseille's process and then hydrolyzed to constitute a mixture of fatty acids.

Table 1 indicates the composition and some characteristics of refined olive pomace oil used in the present work.

Table 1 Composition and characteristics of refined olive pomace oil

Characteristics	Values
Composition (% fatty acids)	$C_{16:0}$: 23–25; $C_{16:1}$: 2–3; $C_{18:0}$: 2–3; $C_{18:1}$: 56–59; $C_{18:2}$: 13–15
Peroxide value	6 milliequivalents of active oxygen/kg oil
Appearance at 20 °C	Limpid
Saponification value	187 mg KOH/g oil
Iodine value (Wijs)	91
Free fatty acids (expressed as oleic acid)	0.3 g/100 g oil

1. Solvents: methanol, *n*-hexane, chloroform, and ethanol were all of high performance liquid chromatography quality and were purchased from Fluka-Germany;
2. Reagents: Oleum (15% SO_3) was supplied by a local fertilizer industry (SIAPE—Sfax-Tunisia);

The other reagents of analytical-reagent grade: diethanolamine (98% pure), chlorosulfonic acid (97% pure), Hyamine 1622 (98% pure) were purchased from Fluka Germany.

1. Standards: methyl esters (99% pure) of lauric, myristic, palmitic, oleic, and stearic are reference substances for GC and starting materials for preparation of fatty acid amide standards. They were purchased from Fluka Germany.

Method of Preparation

The preparation of sulfated amide of fatty acids derived from olive pomace oil was carried out according to the flow-sheet represented in Fig. 1.

Analyses

1. Chemical analyses: the course of esterification reaction was followed by pH-metric titration of residual fatty acids. Sulfated amide active matter was determined by volumetric titration in a water-chloroform medium using a hyamine solution as titrating agent [9], and a mixture of patent blue V and dimidium bromide as indicator.

Free sodium sulfate was determined by volumetric titration in a water-ketone medium using a lead solution as titrating agent and dithizone as indicator.

Free diethanolamine present in the fatty amide was determined by volumetric titration in isopropanol using a 0.5 N HCl in isopropanol as titrating agent and bromophenol blue as indicator.

% H_2O was determined in fatty esters and fatty amides by the Karl Fisher method.

1. IR spectroscopy: infrared spectra of samples of lyophilized fatty amides and sulfated fatty amides in KBr pellets were recorded from 400 to 4,000 cm^{-1} using a Nicolet impact 410 FTIR spectrometer.

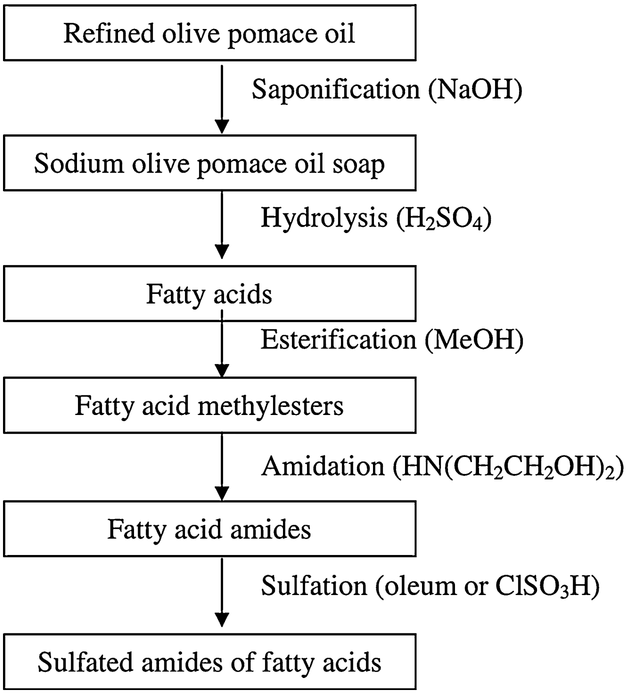


Fig. 1 Flow sheet of the preparation procedure of the sulfated amide of fatty acids derived from olive pomace oil

2. ^{13}C NMR: fatty amides and sulfated fatty amides were characterized by high resolution solid state NMR using a Bruker ASX 300 spectrometer. NMR spectra of fatty amide and sulfated fatty amide samples were recorded at a ^{13}C frequency of 75.5 MHz (field of 7.04 T). All ^{13}C resonances were referenced to TMS.
3. GC: analysis of olive pomace oil after methyl esterification was carried out by GC (Shimadzu GC 2004) using a J&W GC capillary DB-5 (30 m × 0.250 mm), FID detector, temperature program: linear increase from 150 to 200 °C for a period of 5 min followed by isothermal at 200 °C for 25 min.

The content of methyl ester fatty acids was calculated from the corresponding peak area on the base of direct absolute calibration. For this purpose 0.5–1% solution of each standard in hexane was used.

1. HPLC analyses: reversed phase HPLC was used for separations and quantitative analyses of diethanolamide and sulfated diethanolamide of olive pomace oil fatty acids. Crude reaction products were analyzed without treatment or preliminary separations. Measurement conditions such as eluent composition, flow rate, and temperature were empirically determined for each type of reaction product.

Reversed phase type RP-18 steel column (250 × 4.6 mm) packed with Eurospher-100 C18, 5 μm (origin: Knauer—Germany) was used.

Standard curves relating peak areas to amide concentrations were obtained using purified fatty amide references (1–6 g/l) prepared by amidation of methyl ester standards. Purification of fatty amide standards was carried out firstly by the addition of phosphoric acid and then by a separation, as indicated in the literature [10].

Evaluation of Lime Soap Dispersing Properties

A lime soap dispersant is a material that prevents the precipitation of sodium fatty acids by calcium or magnesium ions. A numerical measure of the effectiveness of a lime soap dispersant is given by the lime soap dispersing power (LSDP) which is determined using the Borghetty test [11, 12].

In the Borghetty lime soap dispersion test, 5 ml of a 0.5% by weight solution of sodium oleate is added to a test tube, followed by 10 ml of a hard water solution containing 600 ppm Ca^{2+} and 400 ppm Mg^{2+} which will cause formation of a lime soap deposit. An initial small amount of the dispersing agent is then added to the test tube and the total volume is adjusted to 30 ml. The test tube is stoppered, inverted 20 times and allowed to stand 30 s. The test tube is then visually inspected to check if the lime soap deposit is still intact or whether it has been dispersed into the solution. The test procedure is repeated under the same conditions but using increasing amounts of dispersing agent solution until the minimum amount of the dispersant causing dispersion of the lime soap deposit is obtained. The lime soap dispersing power (LSDP) is calculated as follows:

$$\mathrm{LSDP}(\%) = \frac{\text{minimum weight required of the dispersing agent}}{\text{weight of sodium oleate}} \times 100$$

Thus, in accord with this test method, a dispersant with a low LSDP is more effective than one with a high LSDP.

Results and Discussion

Preparation and Characterization

Sulfated amides of fatty acids derived from olive pomace oil were prepared according to the flow-sheet represented in Fig. 1.

Saponification

Refined olive pomace oil was saponified according to the Marseille's process (full fire heating process) which includes: saponification, separation, rinsing, molding, and drying. This process leads to a sodium soap containing 70% fatty matter.

Saponification was included in this process in order to consider its extension to the use of crude olive pomace oil, instead of the refined olive pomace oil, as the raw material. Indeed, saponification will be required for the elimination of colored impurities present in the crude oil.

Esterification

The esterification step was included in the process in order to prepare sulfated diethanolamide via methyl esters instead of fatty acids of olive pomace oil. This allowed us to use milder conditions during synthesis and to obtain finished products of a higher purity (with very low amounts of esteramine, esteramides, piperazine…). A 100-g sample of fatty acids was esterified with 60 g methanol in the presence of 0.25 g H_2SO_4 (98%) as catalyst. Esterification proceeds rapidly at inert (N_2) atmospheric pressure and at a temperature of the oil bath close to 120 °C. Greater than 98% of a theoretical maximum product was formed within 4 h. Excess unreacted methanol was recovered by distillation.

The amount of water in the methyl ester fatty acids obtained was below 0.5%, estimated by the Karl Fisher method.

Gas chromatography: Fig. 2 represents a typical chromatogram of the mixture of fatty acid methyl ester derived from olive pomace oil. Quantitative analysis allowed us to determine the composition of such a mixture (Table 1).

An examination of the relative abundance of the different fatty acids derived from olive pomace oil cannot permit one to predict that such a composition will create a mixture of fatty diethanolamides having sufficient fluidity to be sulfated at low temperature without adding organic solvents. This unexpected behavior will be explained in the following section, on the basis of HPLC results, by the presence of a relatively high level of unsaturated fatty acids (oleic and linoleic) and by the possible formation of particular eutectic mixtures of fatty amides with a low melting point.

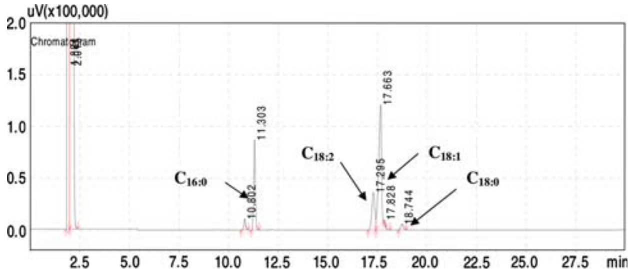


Fig. 2 Chromatogram of fatty acid methyl esters derived from olive pomace oil

Amidation

Alkanolamides were prepared as described in the literature [4, 13, 14].

A 50-g sample of olive pomace oil fatty acid methyl esters were added to a reaction mixture of 21.3 g diethanolamine (the molar ratio amine to ester was 1.2) and 0.25 g sodium methoxide heated to 120 °C. This heating was continued for 5–6 h with constant stirring under atmospheric pressure until methanol stops being collected.

The weight of the amide obtained was 66.6 g. The amount of water in the diethanolamide of olive pomace fatty acids was below 0.5%. The yield of amidation was 82% against fatty methyl esters as determined by HPLC analysis using chromatographic conditions similar to those indicated in the literature [15]. The amount of residual diethanolamine in fatty amides was 9.7%.

Characteristic peaks present in the IR spectra of diethanolamide of olive pomace oil fatty acids (Fig. 3a) can be assigned as reported in the literature [16] without ambiguity (Table 2). It can be noted that the progress of the amidation reaction can be followed by the examination of the intensity of characteristic bands: the band located at about 1,620 cm^{-1} corresponding to the C=O stretching vibration of the amide group and that located at 1,730 cm^{-1} corresponding to the C=O stretching vibration of the residual methyl ester.

A ^{13}C-NMR spectrum of fatty diethanolamide is shown in Fig. 4. ^{13}C-chemical shifts of the fatty diethanolamides are close to those reported in the literature [17]. Assignments are indicated on the fatty amide structure represented in Fig. 4.

Figure 5a represents the HPLC analysis of the fatty amide. As expected from a reversed phase chromatography applied to the separation of homologous amides of fatty acids, the retention time increases with alkyl chain length and decreases with the insaturation number. The capacity factors increase and the resolution is improved with increasing water content in the mobile phase. Quantitative analysis leads to the following composition of the fatty amide mixture: 2% $C_{16:1}$, 14% $C_{16:0}$, 24% $C_{18:2}$, 53% $C_{18:1}$ and 3% $C_{18:0}$ fatty amides. Small peaks representing less than 5% of by-products appear in some of the chromatograms (Fig. 5a) but are ignored for the purpose of this report (mono and di-esteramines, esteramides…).

It is noteworthy that an examination of the composition of the fatty amides obtained shows that the amidation reaction yield of linoleic acid ($C_{18:2}$) methyl ester (mp: −35 °C) was greater than that of palmitic acid ($C_{16:0}$) methyl ester (mp: 33 °C). Indeed, the amounts of $C_{16:0}$ and

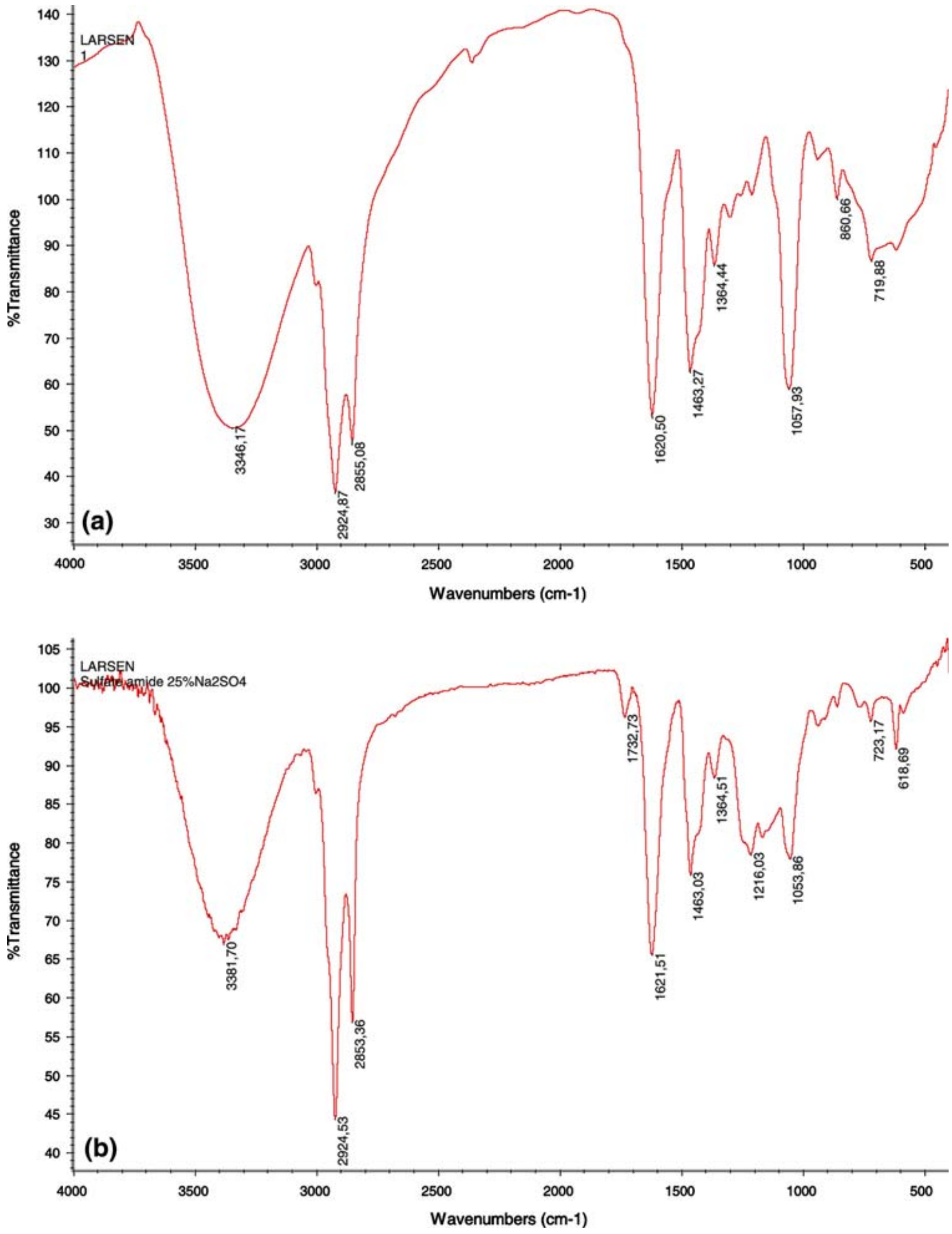


Fig. 3 **a** IR spectra of diethanolamide, and **b** sulfated diethanolamide, of fatty acids derived from olive pomace oil

$C_{18:2}$ chains which are 24 and 14% respectively in the mixture of fatty acid methyl esters, appear in the reverse order in the mixture of fatty amides. The presence of a relatively high percentage of linoleic acid amide at the expense of palmitic acid amide may explain the relatively low viscosity of the product and its aptitude for being sulfated in the absence of organic solvent.

Sulfation Reaction

The final step of the process is the sulfation of the obtained fatty acid diethanolamides. Several sulfation methods of fatty amide using different organic solvents have been described in the literature. The sulfation reaction was carried out in benzene, carbon tetrachloride, 2-butanol, 1,1,1-trichloroethane, chloroform, methylene chloride and pyridine. Bistline [6, 18] suggested the addition of 5–15% of a low molecular weight alcohol (isopropanol) to the fatty alkanolamide and co-sulfating the two reagents.

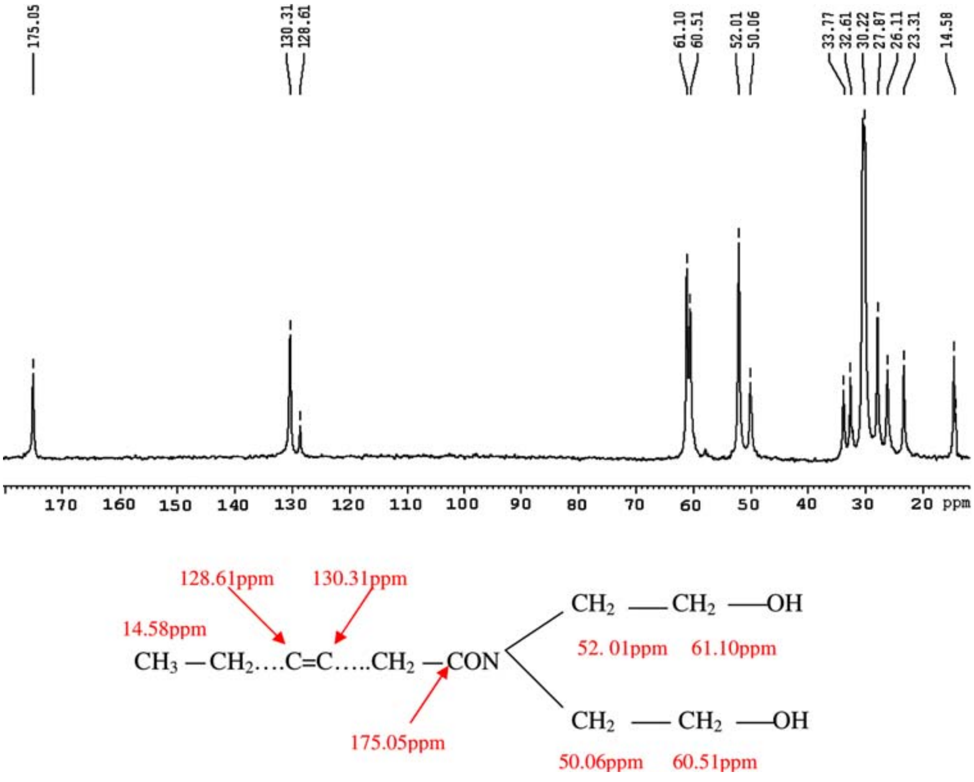
In this work, the sulfation step was conducted as described in the literature [6, 18] apart from the fact that the reaction was carried out without solvent. Two ways were explored:

- by using oleum as sulfating agent: in this case, oleum (3.6 g) was added slowly to the crude fatty amide (10 g) (molar ratio SO_3/amide = 1.75) with vigorous

Table 2 Assignments of IR wave numbers of diethanolamide and sulfated diethanolamide of fatty acids derived from olive pomace oil

Bands	Origins	Vibration band characteristics	Wave numbers (cm^{-1})
O–H	Water	Strong, broad (stretching)	3,380–3,300
C–H	Carbon chain	Strong, sharp (stretching)	2,960–2,850
C=O	Ester of residual reagent	Weak, sharp (stretching)	1,728
C=O	Amide	Strong, sharp (stretching)	1,619
C–H	Carbon chain	Medium, broad (bending)	1,460
C–H	CH3	Weak, sharp (bending)	1,364
C–O	Alcohol of diethanolamine	Medium, broad (stretching)	1,207
C–N	Amine	Strong, broad (stretching)	1,063
S–O	Linked sulfate	Medium, sharp (stretching)	1,221
S–O	Free sulfate	Medium, sharp (stretching)	1,130
S–O	Free and linked sulfate	Weak, sharp (bending)	618–600

Fig. 4 ^{13}C-NMR spectrum and developed structure of diethanolamide of fatty acids derived from olive pomace oil



mixing while maintaining the temperature at 10 °C for 2 h. The reaction mixture was then diluted with an equal weight of ice and neutralized with NaOH (5 mol l^{-1}). The pH of the product was adjusted to 8–9. The yield of sulfation was about 90% against the pure fatty amides. The amount of free sulfate in the dry sulfated fatty amide without purification was in the range of 11%.

- by using chlorosulfonic acid: 4.6 g of $ClSO_3H$ was added to 10 g fatty amide (molar ratio SO_3/amide = 1.75) dropwise with rapid stirring while the temperature was maintained at 10 °C. Stirring was maintained until hydrogen chloride gas ceases to be produced. The reaction mixture was then neutralized as above. The yield of sulfation was about 105% against the pure fatty amides. This indicates that more than one mole of sulfate can be linked to one mole of amide (by sulfation of the second OH group of diethanolamine or the double bond of ethylenic carbon). This result was confirmed by the ^{13}C-NMR and HPLC analyses as detailed below. Similar results have been reported by Bistline et al. [6]. The amount of free sulfate in the dry sulfated fatty amide without purification was in the range of 9%.

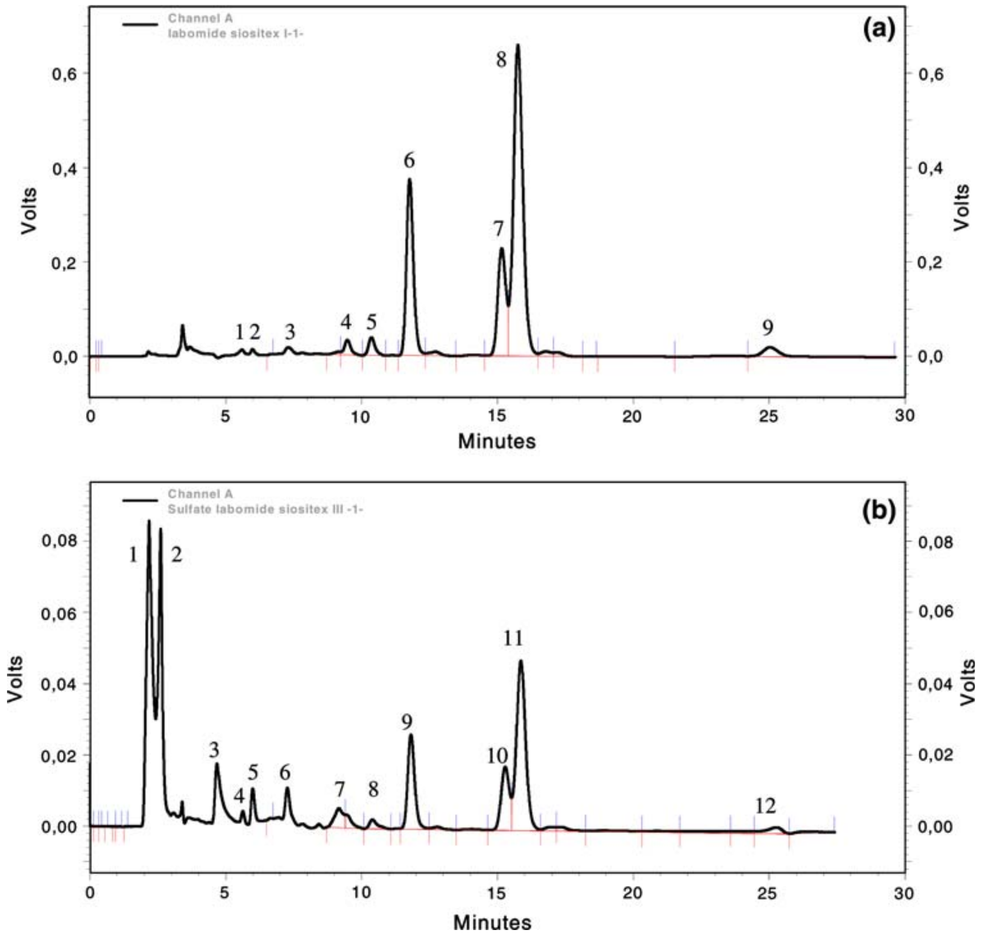


Fig. 5 **a** HPLC Chromatogram of diethanolamide of fatty acids derived from olive pomace oil *1–4* impurities (mono and di-esteramine, mono and di-esteramide), *5* $C_{16:1}$ amide, *6* $C_{18:2}$ amide, *7* $C_{16:0}$ amide, *8* $C_{18:1}$ amide, *9* $C_{18:0}$ amide. **b** HPLC Chromatogram of sulfated diethanolamide of fatty acids derived from olive pomace oil. *1,2* sulfated amides, *3* unidentified, *4–7* impurities (mono and di-esteramine, mono and di-esteramide), *8* $C_{16:1}$ amide, *9* $C_{18:2}$ amide, *10* $C_{16:0}$ amide, *11* $C_{18:1}$ amide, *12* $C_{18:0}$ amide. Column, Knauer packed with Eurospher-100 C18 5 μm; $L = 250$ mm; ID 4.6 mm; Temperature, 40 °C; Mobile phase, methanol/water 90:10, by vol; Flow rate, 0.8 mL/min; Detection, UV; $\lambda = 205$ nm; injection of 20 μL

The infrared spectrum of sulfated diethanolamide of olive pomace oil fatty acids (Fig. 3b) differs from that of fatty acid diethanolamide only in the region corresponding to the stretching and bending vibrations of sulfate groups (1,200–1,000 cm^{-1} and 720–500 cm^{-1}, respectively). The assignation of the observed wave number is indicated in Table 2.

The ^{13}C-NMR spectrum of sulfated diethanolamide of olive pomace fatty acids (Fig. 6) is similar to that of fatty amide except for the carbon atoms of diethanolamine linked to the sulfate groups which show more signals (8 vs. 4 for the fatty amide). The number of signals indicates that more than one of the OH groups can be substituted by sulfate. On the other hand, the signals related to the carbon atoms of the double bond are not disrupted. This indicates that no sulfate groups are linked to these carbon atoms. Chemical shifts of the ^{13}C atoms relative to TMS are indicated on the sulfated fatty amide structure represented in Fig. 6.

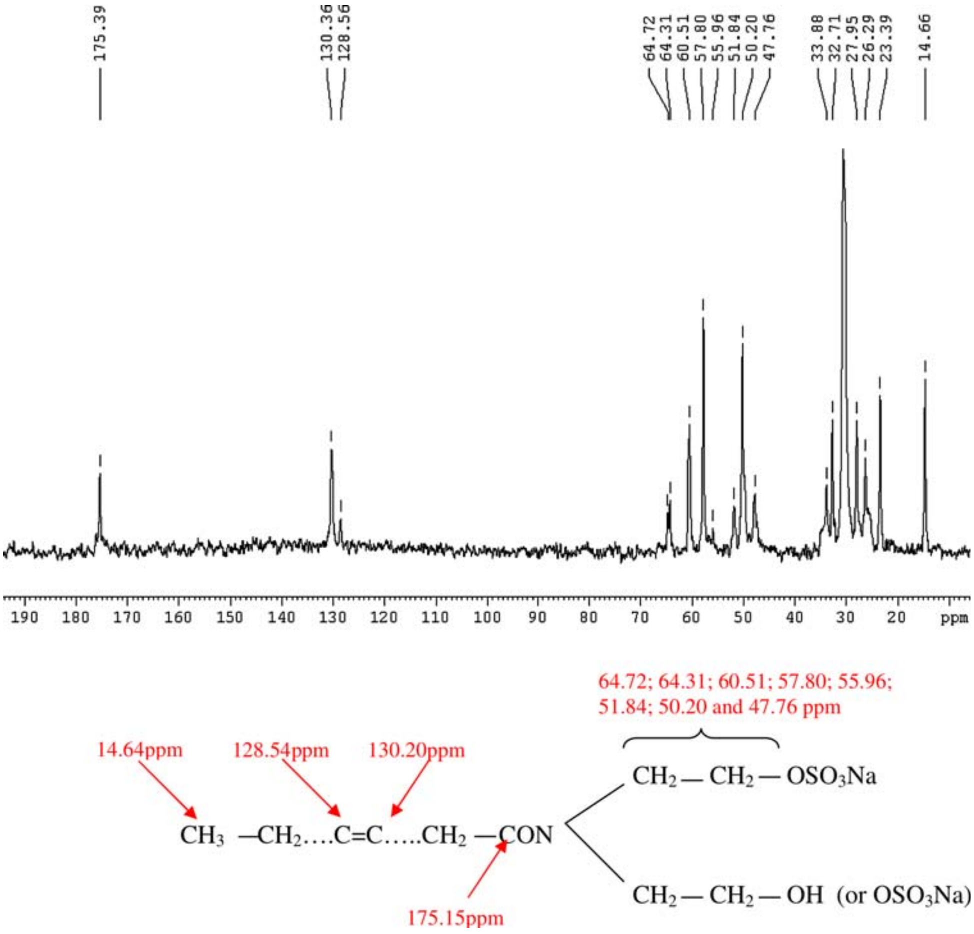
HPLC: Fig. 5b shows a reversed phase HPLC chromatogram of sulfated fatty amides. The same chromatographic conditions used for the separation of homologous amides were applied to the separation of sulfated fatty amides from residual fatty amides. As expected, sulfated fatty amides were eluted rapidly due to their higher polarity than the corresponding fatty amides. Consequently the peaks of the homologous sulfated fatty amides were superimposed to such an extent that it was impossible to determine with accuracy the content of each one. In addition, all the chromatograms show that residual fatty amides were present in the obtained products even those which were highly sulfated. This result confirms that more than one sulfate group can be linked to one molecule of amide.

General Remarks

The implementation of the whole process leads us to make the following remarks:

1. The most important result is that the mixture of fatty acids derived from olive pomace oil can be easily converted into amide and then into sulfated amide without using organic solvents in the sulfation step, owing to the low melting point of the obtained fatty amides. The use of such eutectic mixtures should facilitate sulfation on an industrial scale.

Fig. 6 A ^{13}C-NMR spectrum and developed structure of sulfated diethanolamide of fatty acids derived from olive pomace oil



2. The use of oleum leads to a product less sulfated and slightly darker in color than that obtained with chlorosulfonic acid.
3. The solubility of both amides and sulfated amides in water is quite high. The amides are quite stable to alkaline (pH >9.5) hydrolysis, while sulfated amides are more susceptible to hydrolysis.
4. Better results could be obtained for the reaction yield and the dispersing power by further reducing the amount of residual diethanolamine and free sulfates by selecting the optimal preparation conditions. This work is in progress. We have already identified 31 factors in the whole process and selected 11 of these to determine those which really influence the reaction yield by performing a Plackett-Burman screening design. This step will be followed by the use of a supersaturated design including all 31 factors to test the robustness of the whole process. The corresponding results will be described in the next paper of this series.

Lime Soap Dispersing Properties

The Borghetty-Bergman test was carried out, on the obtained sulfated fatty amide, as indicated above. The same procedure was applied to two other surfactants known to be good dispersing agents: a lauryl amine oxide and a sodium lauryl ethoxylated sulfate.

Remember that effective LSDA have a LSDP of no more than 8 [19] such as: C_{12}–C_{18} alkylethoxysulfates with a degree of ethoxylation of about 3 (LSDP = 4), the C_{13}–C_{15} alkylethoxylated alcohol with an average degree of ethoxylation of about 12 (LSDP = 6) [19] and sulfated *N*-methyl-*N*-(2-hydroxyethyl) stearamide (LSDP = 6) [20]. Although the anionic gemini surfactants are known to have a much better lime soap dispersing ability, the LSDP of the sulfated gemini with two decyl groups is about 6 [8].

The LSDP mean values obtained in this work were: 5 for sulfated amide of the olive pomace fatty acids (without purification), 3 for C_{12}–C_{18} alkylethoxysulfates and 2 for C_{12}–C_{18} alkyldimethyl amine oxide.

Results obtained in this work clearly show that the obtained sulfated fatty amide is a good dispersing agent for lime soap and thus may readily be combined with soap into effective soap-based detergent formulations.

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