Surfactant Analysis by High Performance Liquid Chromatography: I. A Rapid Analysis for Mixtures of Amphoteric Surfactants and Soap

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ABSTRACT

A method has been developed for the rapid and direct analysis of amphoteric surfactants (sulfobetaines) in combination with mixtures of coconut and tallow soaps, with the aid of reverse phase high performance liquid chromatography (HPLC). The mobile phase consisted of methanol-water (85:15, v/v) with 0.2% by volume acetic acid (pH ≐ 4). At this pH, tallow and coconut soap mixtures are analyzed as the fatty acids and are conveniently separated from the sulfobetaine. A typical HPLC analysis of such mixtures requires 25 min.

INTRODUCTION

Sulfobetaine surfactants have been found to be excellent lime soap dispersing agents when used in combination with soaps (1-4); however, up to the present no reliable method has existed for the determination of the amount of surfactant present in such mixtures. Recently, a method developed in this laboratory for the separation and analysis of a homologous series of fatty sulfobetaines was reported (5). Originally, the separation and analysis of homologous series of long chain fatty acids by high performance liquid chromatography (HPLC) was carried out by first preparing UV-absorbing derivatives of the fatty acids in order to achieve the necessary sensitivity (6-9). Later Scholfield (10) and Warthen (11) separated the methyl esters of a homologous series of fatty acids by reverse phase HPLC with a differential refractometer detector, which eliminated the need for the preparation of derivatives.

The objective of the present study was to develop methodology for the separation and direct analysis of soap and of mixtures of soap and sulfobetaine type surfactants with the aid of reverse phase HPLC.

EXPERIMENTAL PROCEDURES

Materials

The (2-hydroxy-3-sulfopropyl)dimethyl(3-lauramidopropyl)ammonium inner salt was prepared by a previously published procedure (4). Commercial samples of the coconut fatty acid derived analogous sulfobetaine, $RCONHC_3H_6N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$, were obtained through the courtesy of the Ashland Chemical Company, Columbus, OH. Lauric and stearic acids obtained from chemical supply houses were distilled, and their purity was determined to be >99% by gas liquid chromatography. Coconut and tallow fatty acids were obtained through the courtesy of Acme-Hardesty Company, Inc., Philadelphia, PA. Potassium coconut and potassium tallow soaps were prepared by neutralizing the above fatty acids (previously dissolved in aqueous ethanol) with potassium hydroxide to a phenolphthalein end-point and removing the solvent by evaporation. Potassium soaps were used rather than sodium soaps because of their more desirable solution properties.

HPLC Apparatus

The apparatus consisted of a mini pump (Milton Roy, Riviera Beach, FL) with an injection port (Rheodyne, Berkeley, CA) fitted with a 200-μl loop. The analytical column was a μ-Bondapak-C_{18} (Waters Assoc., Milford, MA) and was preceded by a guard column containing Co:Pell ODS (Whatman) of sufficiently low capacity so as not to significantly affect the number of theoretical plates of the analytical column. The detector used was a differential refractometer (Waters Assoc. Model R-401).

Sample Preparation

Stock solutions of 1 M, 1 M, and 4 M for the sulfobetaine, coconut, and tallow soaps, respectively, were prepared by dissolving them in methanol-water (85:15, v/v) containing 0.2% by volume acetic acid. Various mixtures of known composition were prepared by blending the above stock solutions. The mixtures comprised the following composition ranges: 1-10% sulfobetaine, 10-20% coconut soap, and 75-85% tallow soap. The composition of these mixtures and the corresponding HPLC analytical data are given in Table I.

HPLC Operating Conditions

The mobile phase consisted of methanol-water (85:15, v/v) containing 0.2% by volume acetic acid, and the flow rate was maintained at 1 ml/min. All solvents were filtered through a millipore filter before use. Samples, 200 μl, containing ca. 0.5 mg of test material were injected for each analysis. About 25 min were required for each HPLC analysis. Table II shows the composition of the tallow and coconut soaps as determined by HPLC. Standard curves

TABLE I

Analysis of Known Soap-Sulfobetaine Mixtures by HPLC

	Sulfobetaine				Coconut soap				Tallow soap			
Sample	Theory (%)	Found (%)	Relative error	Maximum relative deviation	Theory (%)	Found (%)	Relative error	Maximum relative deviation	Theory (%)	Found (%)	Relative error	Maximum relative deviation
1	2	2	0	.10	12	15	.25	.06	86	83	.03	.07
2	3	4	.33	.03	13	14	.08	.03	84	82	.02	.04
3	5	6	.20	.02	14	16	.14	0	81	78	.03	.08
4	7	8	.14	.02	15	17	.13	.03	78	75	.02	.05
5	9	10	.11	0	15	17	.13	.07	76	73	.03	.05

TABLE II

Composition of Potassium Soaps (%) by HPLC

C	Tallow	Coconut
8		3
10		4
12		38
14	2	24
16	24	14
16:1	2	
18	22	4
18:1	46	11
18:2	4	2

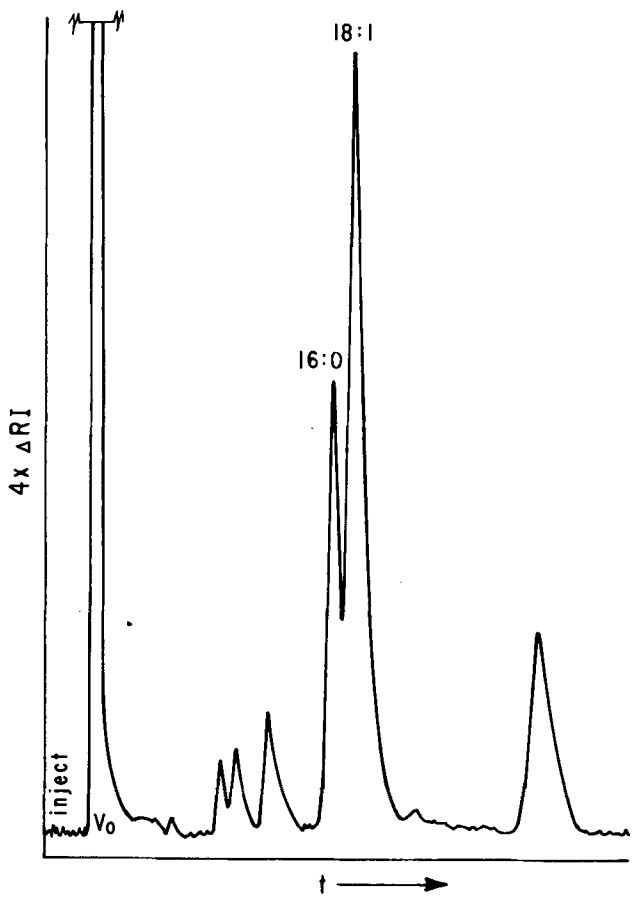

FIG. 1. Chromatogram of tallow-derived potassium soap.

relating peak height to concentration were prepared for the pure lauric acid derived sulfobetaine, lauric acid, and stearic acid. Peak height was used instead of peak area because peak height is less interfered with by neighboring, overlapping peaks (12) and slight changes in flow. Fatty Acids, rather than their potassium soaps, were used to prepare the standard curves because of the greater purity of the former; however, concentrations were calculated as the potassium soap. The amount of coconut soap present in a given mixture was determined from the intensity of its lauric acid peak. The lauric acid concentration was read off the standard curve, and the amount of coconut soap could be calculated from the composition data of Table II. Similarly tallow soap in a mixture was determined from the standard stearic acid curve, and the amount of tallow soap could be calculated on the basis of the tallow soap composition given in Table II. No correction was made for variations in detector response for the different homologs listed in Table II, since this error has been shown to be small (5).

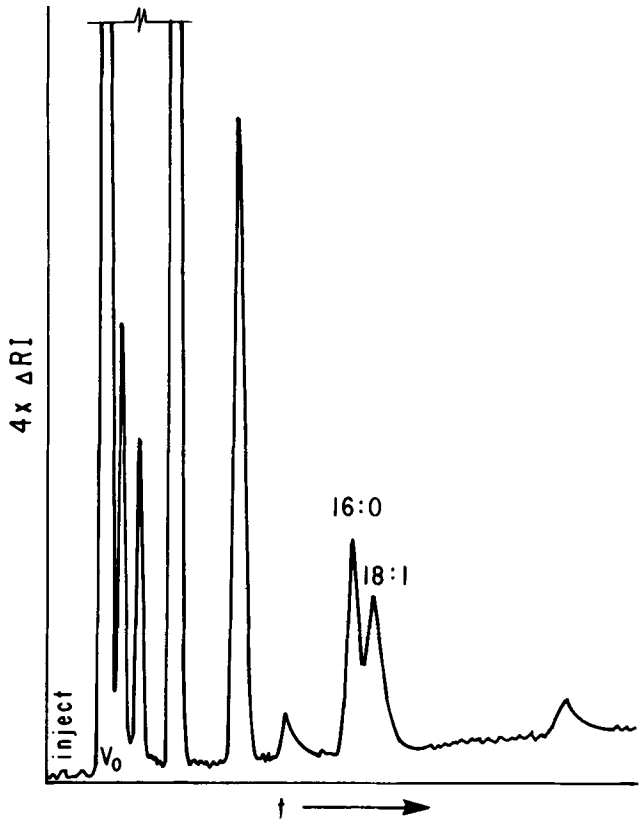

FIG. 2. Chromatogram of coconut oil-derived potassium soap.

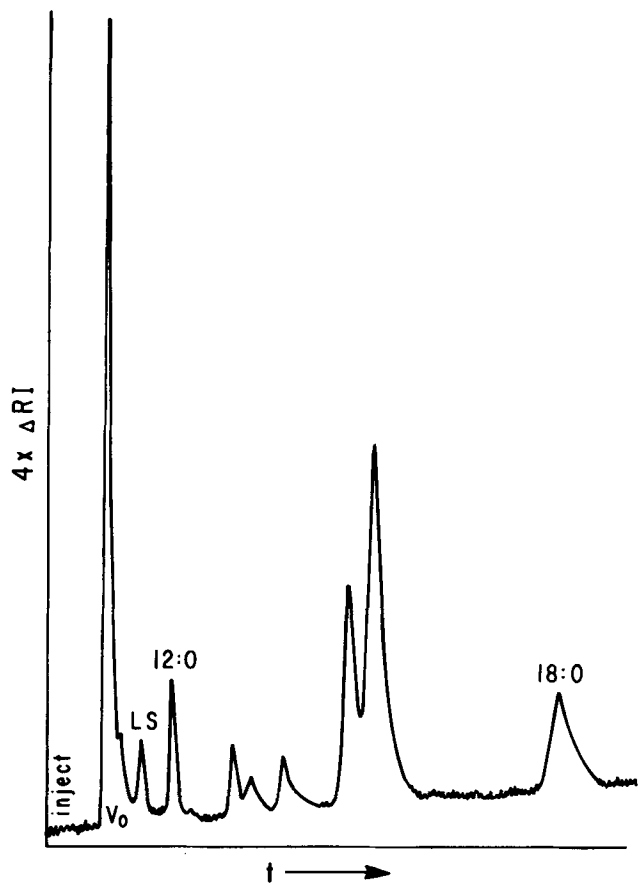

FIG. 3. Chromatogram of soap-sulfobetaine mixture: 2% lauroylamido sulfobetaine (LS), 14% coconut soap, 84% tallow soap.

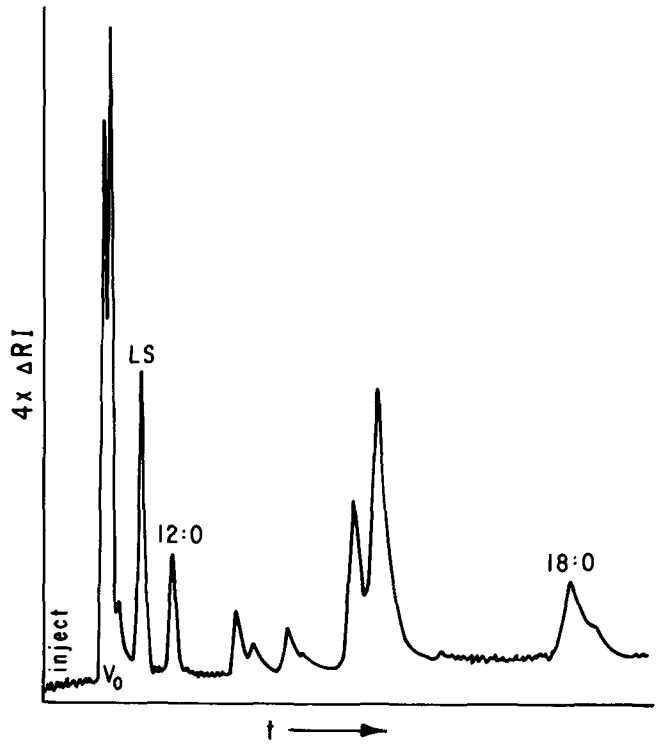

FIG. 4. Chromatogram of soap-sulfobetaine mixture: 9% lauroyl-amido sulfobetaine (LS), 15% coconut soap, 76% tallow soap.

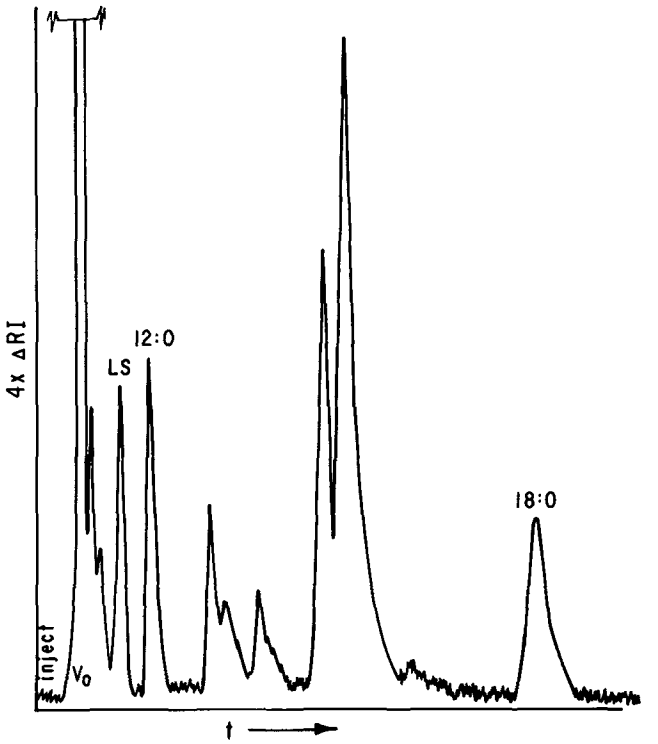

FIG. 5. Chromatogram of soap-sulfobetaine mixture: 9% coco-amido sulfobetaine (containing 38% LS), 14% coconut soap, 77% tallow soap.

RESULTS AND DISCUSSION

The analytical methodology for sulfobetaines by reverse phase HPLC, as reported elsewhere (5), was also found to be applicable to the separation of tallow and coconut soaps. It was necessary, however, to acidify the mobile phase in order to bring the pH within operating range of the analytical column and to facilitate separation of soap from sulfobetaines, as discussed below. Accordingly, a mobile phase consisting of methanol-water (85:15, v/v) to which 0.2% by volume of glacial acetic acid had been added was used. Figures 1 and 2 show the HPLC chromatograms for tallow soap and coconut soap, respectively. The incomplete separation of the peaks for the 16:0 and 18:1 acids did not affect the quantitative determinations of this study.

When mixtures of the two soaps and the lauric aicd derived sulfobetaine were subjected to HPLC separation, it was found that the chromatograms of the soaps and sulfobetaine were superimposed to such an extent that it was impossible to determine the content of either. When the mobile phase was acidified with acetic acid, the elution time for the fatty acids was increased and the sulfobetaine was unaffected so that it was then possible to resolve the sulfobetaine completely as shown in the chromatogram for a blend containing 2% sulfobetaine (Fig. 3) and that for a blend containing 9% sulfobetaine (Fig. 4). HPLC separation of these mixtures with a mobile phase containing no acetic acid caused the soap to elute first and not be resolved from the sulfobetaine.

A variety of mixtures of soaps and sulfobetaines was similarly chromatographed with the aid of the acidified mobile phase. The relative amounts of sulfobetaine, coconut, and tallow soaps were calculated as described above, and the result for the analyses of these known mixutres are given in Table I in terms of percent composition. It is clearly shown that the accuracy of this method, as indicated by the relative error, was best for the tallow soap, which comprises the major portion of the mixture. Precision, expressed as maximum relative deviation, was the greatest deviation from the average peak height for three consecutive injections and was 0.10 or less for all components of the mixture. No attempt was made to correct for the stearic acid contribution from the coconut fatty acid.

Another mixture was analyzed in which the sulfobetaine was a commercial coconut fatty acid derivative. The chromatogram of this mixture is shown in Figure 5 where the amount of surfactant present was calculated based on the lauroylamido sulfobetaine content. This sample contained inorganic salts and low molecular weight organic impurities which eluted with the void volume and did not interfere with the analysis. Detector response was such that less than 0.5 mg of the mixture was required for good resolution.

This method has proven to be rapid and reliable for the analysis of sulfobetaine and soap mixtures. However, it can readily be expanded to the analysis of other surfactant mixtures by adjusting various chromatographic parameters of the system.

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