High Pressure Liquid Chromatography of Alpha Olefin Sulfonates

R.O. JOHANNESSEN, W.J. DeWITT, R.S. SMITH and M.E. TUVELL, Ethyl Corporation, Baton Rouge, LA 70808

ABSTRACT

Alpha olefin sulfonates (AOS) are a complex mixture of the positional isomers of hydroxyalkane sulfonates, alkene sulfonates, and disulfonates. This paper describes a qualitative method for separating these various components by reverse-phase high pressure liquid chromatography. The column utilized was a DuPont Zorbax TMS (4.6 mm × 25 cm) with a water/methanol (25:75, v/v) mobile phase containing sodium nitrate at a concentration of 0.4M. The hydroxyalkane sulfonate and alkene sulfonate peaks were identified using laboratory prepared standards. The disulfonate peaks were located using controlled sulfonation conditions. More work needs to be done to separate an overlap of C_{16} 3-hydroxyalkane sulfonate and C_{14} 2-alkene sulfonate in 1416 AOS. However, if studies are based on single carbon number AOS samples, the overlap of these peaks can be avoided. This method can be utilized as a qualitative tool for the comparison of sulfonation runs, the identification of AOS within a detergent, or the identfication of the olefin type used for sulfonation.

INTRODUCTION

Alpha olefin sulfonates (AOS) are becoming increasingly popular as the major surfactant for personal care and detergent products. This gain in popularity is due to a combination of good properties, favorable economics, and ample supplies of the alpha olefin feedstocks. AOS made from $C_{14}-C_{16}$ alpha olefin mixtures are particularly useful in liquid formulations such as shampoos, liquid soaps, and dishwash liquids.

Sulfonation of olefins generally requires closer control of conditions than practiced for sulfonation of other feedstocks such as linear alkylbenzenes, alcohols, or alcohol ethoxylates. Both physical and functional properties of AOS depend, to a large extent, on variations in composition resulting from differences in sulfonation conditions. A need for a reliable, quick method for determining the composition of AOS is apparent.

Analyses of alpha olefin sulfonates by thin layer chromatography (1) and gas chromatography (GC) (2) have been reported. These methods can be time-consuming and susceptible to operator error. A recent paper (3) describes a high pressure liquid chromatographic (HPLC) procedure for the analysis of ionic surfactants; however, AOS was not included in that work.

Analysis by HPLC is rapid and does not require derivatization as is necessary when using a GC procedure. Operator error is thus minimized by the simplicity of this method. The improved technology, quality, and availability of reversed-phase columns currently on the market make HPLC a valuable tool for surfactant analysis.

We carried out reverse-phase HPLC studies on C_{14-16} AOS utilizing a water/methanol mobile phase containing 0.4M sodium nitrate. A Waters Associates μ Bondapak C18, a Whatman Partisil-5 ODS, and a Du Pont Zorbax TMS column were all investigated. The Du Pont Zorbax TMS gave superior resolution, especially of the vinylidene sulfonates. The sodium nitrate was used to control the capacity factors. To prevent precipitation, the system was flushed with methanol/water (50:50, v/v) after each use.

EXPERIMENTAL

Instrumentation and Operating Conditions

A Waters Associates HPLC system was used for this work. The apparatus consisted of a Model 6000A pump, an R401 differential refractometer, and U6K injector. The recording system was a Hewlett-Packard 3390A.

The column selected for this work, as mentioned previously, was a Du Pont Zorbax TMS (4.6 mm × 25 cm). The mobile phase consisted of methanol/water (75:25 v/v) containing sodium nitrate at a concentration of 0.4 molar. All solvents were HPLC grade. The solvent mix was vacuum filtered through a 0.45 μm millipore filter and the flow rate for the analysis was set at 0.7 mL/min, which resulted in an operating pressure of 1500 psi.

Sample and Standard Preparation

Samples were prepared as 3-5% solutions by weight in HPLC grade water. Sample size for injection varied from 5-10 μL. All sample solutions were filtered through 0.45 μm millipore filter paper.

The hydroxyalkane sulfonate and alkene sulfonate standards were synthesized using laboratory hydrolysis procedures as described in a previous paper (4). Controlled sulfonation conditions were used to prepare samples for the location of the disulfonate peaks. Less than theoretical amounts of SO_3 result in alpha olefin sulfonates having a lower disulfonate content. Vinylidene sulfonates were located by comparison of AOS prepared from olefins containing low and high concentrations of vinylidene olefins and confirmed by spiking AOS with C_{16} vinylidene sulfonate.

Results and Discussion

The effect of the concentration of sodium nitrate in the mobile phase on the capacity factor is shown in Figure 1. Capacity factors are related to retention time. However, retention times vary with flow rate, whereas capacity factors do not. The capacity factor is defined as the ratio of the total moles of solute in the stationary phase to the total moles of solute in the mobile phase. Relating this definition to retention time, the formula for capacity factor is as follows:

$$k' = \frac{t_R - t_0}{t_0}$$

where k' = capacity factor of component, t_R = retention time of component, and t_0 = unretained component time

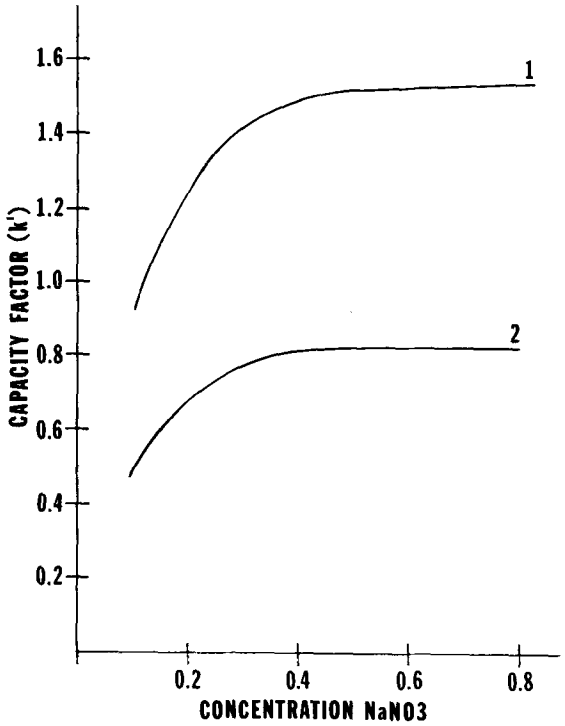

FIG. 1. Concentration sodium nitrate vs capacity factor (k'). (1) C_{14} 2-alkene sulfonate; (2) C_{14} 3-hydroxyalkane sulfonate.

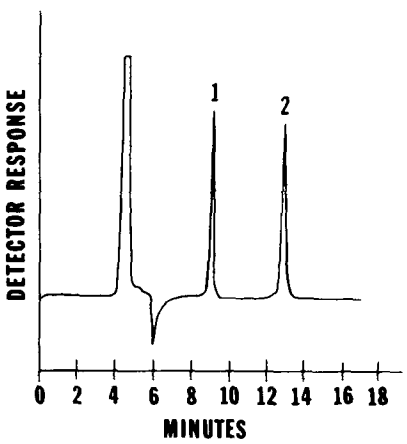

FIG. 2. Separation of hydroxyalkane sulfonates. (1) C_{14} 3-hydroxyalkane sulfonate; (2) C_{16} 3-hydroxalkane sulfonate.

(solvent front).

Using C_{14} 2-alkene sulfonate and C_{16} 3-hydroxyalkane sulfonate components as standards, a reduction in salt concentration below 0.4 molar resulted in a decrease in the capacity factor. With a sodium nitrate concentration of 0.1 molar, it was found that the alkene isomers were no longer separated. The capacity factors were constant above 0.4 molar $NaNO_3$.

Chromatograms of the C_{14} and C_{16} 3-hydroxyalkene sulfonate, C_{14} and C_{16} mixed alkene sulfonates, and C_{14} 2-alkene sulfonate standards are shown in Figures 2, 3 and 4. As can be seen, separation by double bond position is also being achieved. A potassium permanganate catalyzed periodate oxidation (5) of a C_{14} mixed alkene sulfonate standard followed by HPLC analysis of the resulting fatty acids verified that these peaks are double bond positional

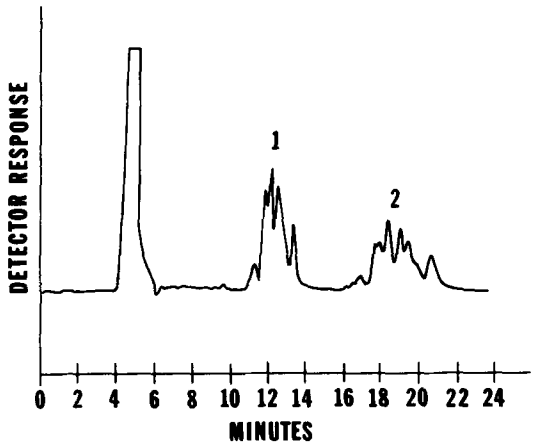

FIG. 3. Separation of alkene sulfonates. (1) C_{14} alkene sulfonates; (2) C_{16} alkene sulfonates.

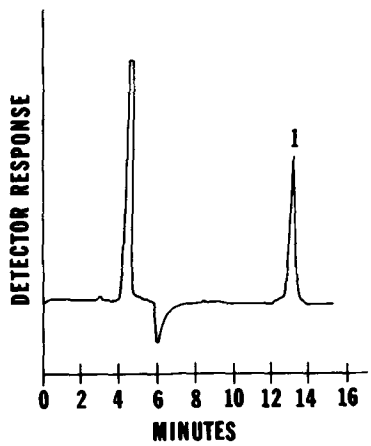

FIG. 4. Chromatogram of C_{14} 2-alkene sulfonate.

isomers. The overlap of C_{16} 3-hydroxyalkane sulfonate and C_{14} 2-alkene sulfonate was confirmed by spiking AOS with these components.

Figure 5 shows a chromatogram of a C_{14} alpha olefin sulfonate. The locations of the 3-hydroxyalkane sulfonate and the 2-alkene sulfonate components were identified using laboratory standards. The 4-hydroxyalkane sulfonate peak elutes just prior to the 3-hydroxyalkane sulfonate. This was verified using a 4-hydroxyalkane sulfonate standard. This standard also contained some alkene sulfonate. An HPLC chromatograph of 4-hydroxalkane sulfonate is shown in Figure 6. Spiking with 3-hydroxyalkane sulfonate reveals that the resolution of the hydroxalkane isomers is excellent (Fig. 7). A 1416 AOS with enriched 4-hydroxy is shown in Figure 8. Typically, 1416 AOS has the 3-hydroxy as the predominant hydroxyalkane isomer (Fig. 9).

Since disulfonates are the most polar components in AOS, they will elute early in this reverse-phase system. The disulfonate content can be controlled by the extent of sulfonation. Concentrations of SO_3 below theoretical would yield AOS with a low disulfonate content, and larger concentrations of SO_3 will give correspondingly higher amounts of disulfonate. Our studies have found that the peaks nearer the solvent front (prior to the 4-hydroxyalkane sulfonate) are larger and more numerous at the

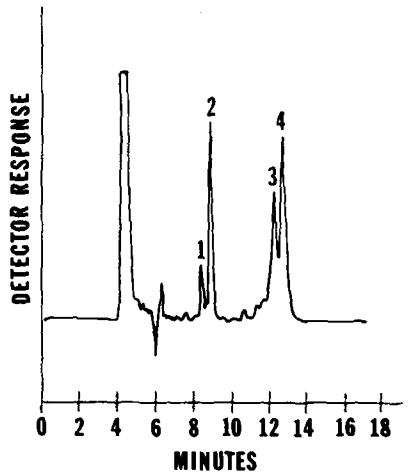

FIG. 5. Separation of C_{14} alpha olefin sulfonate. (1) C_{14} 4-hydroxyalkane sulfonate; (2) C_{14} 3-hydroxyalkane sulfonate; (3) C_{14} 3-alkene sulfonate; (4) C_{14} 2-alkene sulfonate.

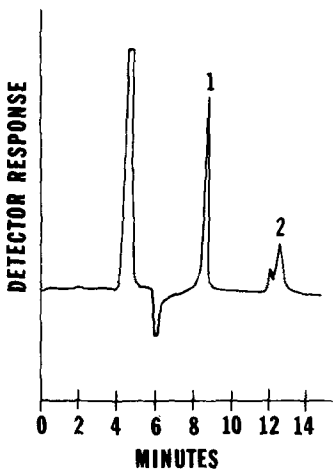

FIG. 6. Chromatogram of C_{14} 4-hydroxylalkene sulfonate with C_{14} alkene sulfonate. (1) C_{14} 4-hydroxyalkane sulfonate; (2) C_{14} alkene sulfonates.

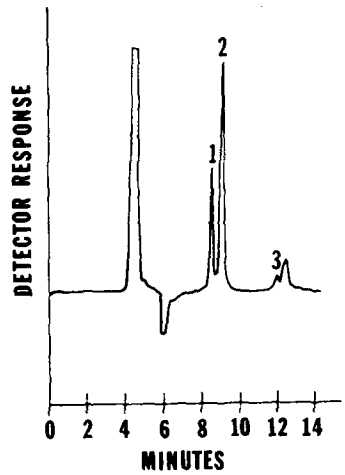

FIG. 7. Separation of hydroxyalkane sulfonates. (1) C_{14} 4-hydroxyalkane sulfonate; (2) C_{14} 3-hydroxyalkane sulfonate; (3) C_{14} alkene sulfonates.

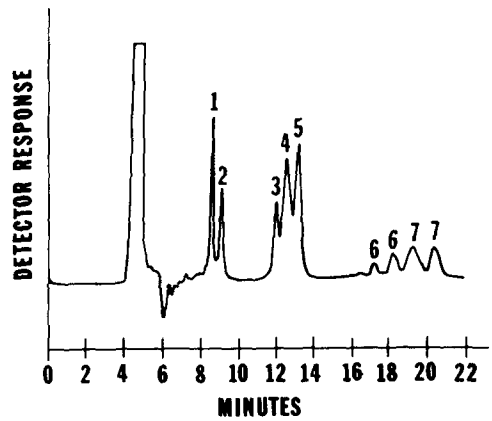

FIG. 8. Separation of Ethyl olefin based $C_{14\ 16}$ AOS enriched with 4-hydroxyalkane sulfonate. (1) C_{14} 4-hydroxyalkane sulfonate; (2) C_{14} 3-hydroxyalkane sulfonate; (3) C_{16} 4-hydroxyalkane sulfonate; (3) C_{16} 4-hydroxyalkane sulfonate; (4) C_{14} 3-alkene sulfonate; (5) C_{14} 2-alkene sulfonate + C_{16} 3-hydroxyalkane sulfonate; (6) C_{16} vinylidene sulfonates; (7) C_{16} alkene sulfonates.

more severe sulfonation conditions. More work still needs to be done on specifically identifying these peaks.

Vinylidene sulfonates, a branched component characteristic of Ethyl's olefin based AOS, but present to a lesser degree in all AOS, were located by comparing chromatograms of Shell's and Ethyl's olefin based AOS (Figs. 10 and 11). The C_{16} vinylidene sulfonates elute just prior to the C_{16} alkene isomers in the Ethyl's olefin based chromatogram. The C_{14} vinylidene sulfonates are more difficult to locate, even on comparison with C_{14} AOS chromatograms.

The difficulty in preparation of pure standard components plus the number of isomers present in AOS make quantitative analysis difficult. This method is currently being used as a qualitative tool. To quantitate 1416 AOS, the overlap of the C_{16} 3-hydroxyalkane sulfonate and C_{14} 2-alkene sulfonate peaks must be resolved either chemically or chromatographically.

Differential refractometer response factors have been calculated for C_{14} 3-hydroxyalkane sulfonate, C_{14} 2-alkene sulfonate, and C_{16} 3-hydroxyalkane sulfonate. Three concentrations of each were run and the areas plotted. The

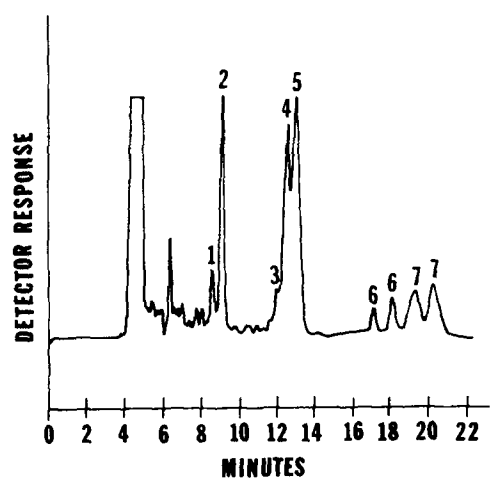

FIG. 9. Separation of a typical Ethyl olefin based $C_{14\ 16}$ AOS. (1) C_{14} 4-hydroxyalkane sulfonate; (2) C_{14} 3-hydroxyalkane sulfonate; (3) C_{16} 4-hydroxyalkane sulfonate; (4) C_{14} 3-alkene sulfonate; (5) C_{14} 2-alkene sulfonate + C_{16} 3-hydroxyalkane sulfonate; (6) C_{16} vinylidene sulfonates; (7) C_{16} alkene sulfonates.

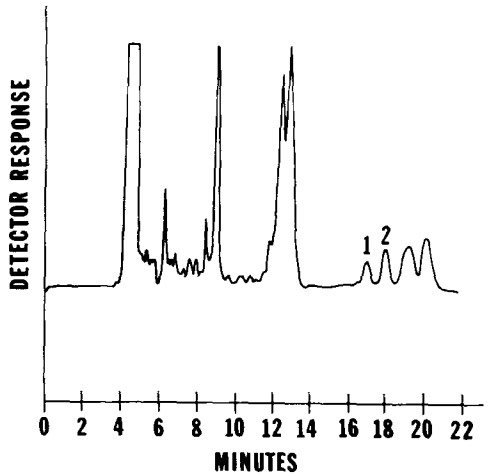

FIG. 10. Separation of Ethyl olefin based $C_{14\ 16}$ AOS showing location of C_{16} vinylidene sulfonates (1), (2).

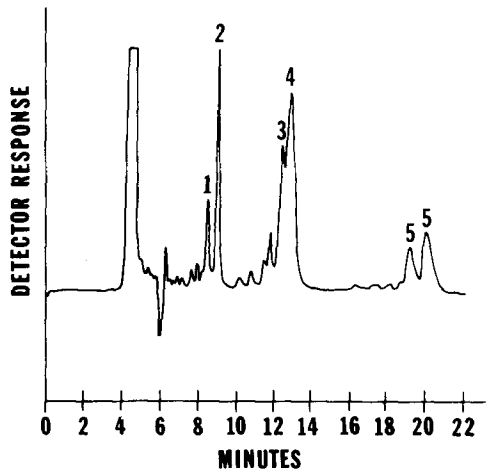

FIG. 11. Separation of a low vinylidene $C_{14\ 16}$ AOS. (1) C_{14} 4-hydroxyalkane sulfonate; (2) C_{14} 3-hydroxyalkane sulfonate; (3) C_{14} 3-alkene sulfonate; (4) C_{14} 2-alkene sulfonate + C_{16} 3-hydroxyalkane sulfonate; (5) C_{16} alkene sulfonates.

slope of the line through the points was taken as the response. The C_{16} 3-hydroxyalkane sulfonate and C_{14} 2-alkene sulfonate each had a refractometer area response ca. 70 % of that shown by the C_{14} 3-hydroxy. Setting C_{14} 3-hydroxy to 1.0, the response factors were calculated (Table I).

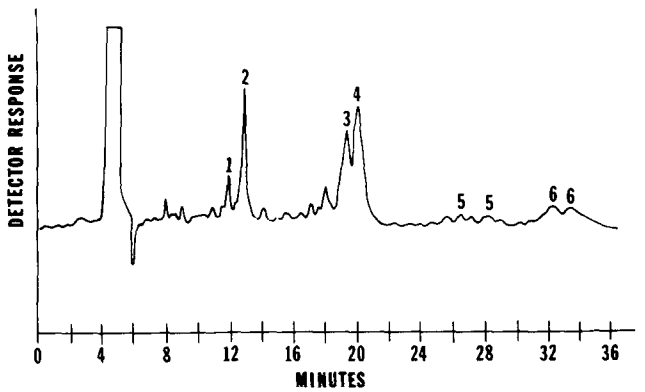

FIG. 12. Separation of an Ethyl olefin based $C_{16\ 18}$ AOS. (1) C_{16} 4-hydroxyalkane sulfonate; (2) C_{16} 3-hydroxyalkane sulfonate; (3) C_{16} 3-alkene sulfonate; (4) C_{16} 2-alkene sulfonate + C_{18} 3-hydroxyalkane sulfonate; (5) C_{18} vinylidene sulfonates; (6) C_{18} alkene sulfonates.

TABLE I

Response Factors for Different Components

Component	Slope (area vs conc)	Response factor
C_{14} 3-HA sulfonate	509000	1.00
C_{16} 3-HA sulfonate	370000	1.38
C_{14} 2-A⁻ sulfonate	356000	1.43

This method has also been used to identify 1618 AOS. The characteristics are basically the same, but the higher carbon number components start to show band spreading. A typical 1618 AOS chromatogram is shown in Figure 12.

REFERENCES

1. Allen, M.C., and T.T. Martin, JAOCS 48:790(1971).
2. Nagai, T., S. Hashimoto, I. Yamane, and A. Mori, JAOCS 47:505(1970).
3. Nakamura, K., Y. Morikawa, and I. Matsumoto, JAOCS 58: 72(1981).
4. Tuvell, M.E., G.O. Kuehnhanss, G.D. Heidebrecht, P.C. Hu, and A.D. Zielinski, JAOCS 55:70(1978).
5. Rudloff, E. von, JAOCS 33:126(1956).

[Received October 4, 1982]