Comparison of High-Temperature Gas Chromatography and CO_2 Supercritical Fluid Chromatography for the Analysis of Alcohol Ethoxylates[1]

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This work compares capillary supercritical fluid chromatography (SFC) and capillary high-temperature gas chromatography (HTGC) for the quantitative characterization of nonionic alcohol ethoxylate surfactants. Supercritical fluid chromatographic separations of the alcohol ethoxylates were obtained with a density-programmed carbon dioxide mobile phase and a fused silica capillary column. High-temperature gas chromatographic separations were obtained with a high-temperature polyimide-coated fused silica capillary column. In addition, a procedure was developed for the quantitation of the capillary chromatographic data using flame ionization molar response factors based on the effective carbon theory. The alcohol and ethoxylate distributions, mean molecular weights and average moles of the ethylene oxide are rapidly calculated from the chromatographic data. Advantages and limitations of SFC and HTGC procedures are illustrated and discussed. Based on this work, the following conclusions can be drawn: i) For routine quality control analyses of known alcohol ethoxylates, SFC and HTGC appear to be equally applicable. ii) SFC has the advantage of time because derivatization is not required, although derivatization does improve resolution. iii) HTGC has the advantage of resolving C_{12} through C_{18} alcohol ethoxylate oligomers, avoiding ambiguous identification of components. iv)SFC and HTGC both have disadvantages. SFC has a resolution limitation and HTGC discriminates against high molecular-weight components.

KEY WORDS: **Alcohol ethoxylates, FID response factors, high-temperature gas chromatography, nonionic surfactants, supercritical fluid chromatography.**

Characterization of commercial alcohol ethoxylates is important for quality control in both surfactant manufacturing and in the development of new detergent formulations. These surfactants play a significant role in the effectiveness of formulated products. Therefore, the quantitative characterization of these surfactants, through determination of alcohol and ethylene oxide distributions, is necessary for comparison of surfactant type and efficiency in the detergent formulations.

Alcohol ethoxylates have been characterized as their acetate derivatives by packed-column gas chromatography (1) and, in this laboratory, as their silylated derivatives using a fused silica capillary column (Fig. 1). Conventional gas chromatography, however, has a major limitation. Only the free alcohols and short-chain ethoxylate homologues, up to approximately 13 ethylene oxide (EO) oligomers, are eluted from the chromatographic column. Therefore, the gas chromatographic data obtained are essentially a partial fingerprint. They do not represent the entire sample, only the lower molecular weight components, and identification of the sample could be ambiguous.

High-performance liquid chromatography (HPLC) has been used for the separation of alcohol ethoxylate oligomers (2–4). Because these compounds have no significant ultraviolet (UV) absorption, they must be derivatized prior to HPLC analysis with a UV detector (2,3). Flame ionization detectors (FID) with HPLC have been used to analyze alcohol ethoxylates as the acetate derivatives (4). However, HPLC lacks the resolution to separate the alcohol ethoxylates adequately to provide both alcohol and ethylene oxide distributions.

Supercritical fluid chromatography (SFC) was proposed as an alternative analytical procedure for the analysis of compounds that are thermally unstable or have low volatility, and are not amenable to gas chromatographic analysis (5). The feasibility of using SFC for the qualitative characterization of nonionic surfactants has been adequately demonstrated in the literature (6–11). Geissler (12) has proposed a novel approach to the quantitative characterization of alcohol ethoxylates, in which the molar responses for the individual components are calculated based on their oxygen-to-carbon ratios.

High-temperature gas chromatography (HTGC) using aluminum-clad fused-silica capillary columns for the separation of crude oils and polywaxes (polyethylenes averaging 500 and 655 molecular weight) has been described (13). Lipsky and Duffy (13) believed that the majority of analyses of high-molecular weight compounds performed by SFC with fused-silica capillary columns could be more simply, rapidly, economically and efficiently accomplished by means of high-temperature capillary gas chromatography. Capillary HTGC also has been demonstrated as a viable method for the qualitative characterization of alcohol ethoxylates (11, 14,15).

This paper describes the comparison of capillary SFC and capillary HTGC for the quantitative characterization of commercial alcohol ethoxylate samples. Although the technique described by Geissler (12) is an interesting approach to quantitation, molar response factors based on effective carbon numbers (16) are used in the present study because of versatility and ease of application. With this approach, FID molar response factors can be calculated for various derivatives without obtaining pure standards. According to Sternberg *et al.* (16), the molar response of different chemical compounds can be expressed conveniently in terms of the effective carbon number (ECN). The ECN is the number of aliphatic carbon atoms to which the FID response of a sample molecule is equivalent. With this theory, each component's equivalent weight can be readily calculated from its FID area response. Aliphatic carbons have an ECN of 1.0, carbonyl carbons have an ECN of 0.0, ether oxygens have a −1.0 effective carbon (EC) effect, primary alcohols have a −0.6 EC effect, and secondary alcohols have a −0.75 EC effect. Later work by Ackman (17,18) predicted that primary alcohol carbons exhibit an ECN of 0.5–0.55, and secondary

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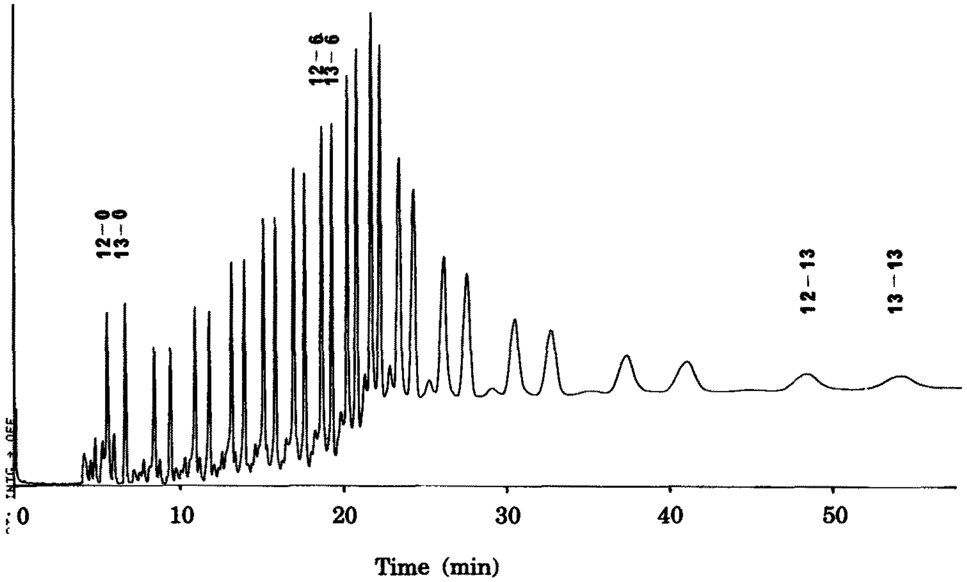

FIG. 1. Conventional capillary GC of a silylated C_{12}/C_{13} alcohol ethoxylate with an average of 6.6 moles of ethylene oxide (supplier's analysis). Column 5 m by 0.53 mm i.d., methyl silicone, 100°C for 2 min, programmed 10°/min to 300°C.

alcohol carbons have an ECN of 0.35. Scanlon and Willis (19) extended the effective carbon number concept to include the contribution of acetate groups (CH_2-O-CO-CH_3) to be 1.5 ECs, and the contribution of trimethylsilyl groups (CH_2-O-TMS) to be 3.69 ECs.

EXPERIMENTAL PROCEDURES

Supercritical fluid chromatography was conducted with a Lee Scientific Series 600 SFC system (Salt Lake City, UT). The chromatographic column was a 5 m by 50 μm i.d. fused-silica capillary coated with a 30% biphenyl/70% methyl polysiloxane bonded and crosslinked phase (Lee Scientific, SB-Biphenyl-30). Sample injection was achieved with a Rheodyne model 7526 HPLC injection valve, helium actuated, with a 0.5-μL internal volume. Injection time was 1 s and samples were split approximately 15:1 with a splitter. The system was equipped with a flame ionization detector, which was maintained at 375°C for these analyses. Carbon dioxide (SFC-grade) was used as the supercritical mobile phase, isothermally at 125°C and density programmed. The initial density, 0.200 g/mL, was held for 5 min to ensure separation of early eluting components from the solvent peak. The density was ramped at 0.020 g/mL/min to 0.400 g/mL, then ramped at 0.010 g/mL/min to 0.600 g/mL, and finally ramped at 0.005 g/mL/min to 0.650 g/mL. This three-part density program was used to approach asymptotic ramping to improve component resolution across a wide range of molecular-weight components. The final density was held for 15 min. Chromatograms were recorded on a Hewlett-Packard model 3396 integrator in the default mode.

High-temperature gas chromatography was conducted on a high-temperature, polyimide-coated, fused-silica "SimDist-CB" capillary column capable of being programmed to 400°C (Chrompack, Middleburg, The Netherlands). This column was 10 m by 0.32 mm i.d. with a 0.1-μm bonded film. The gas chromatograph used was a Hewlett-Packard model 5880A (Hewlett-Packard, Palo Alto, CA). Parameters with this column were an initial temperature of 100°C, initial time 2 min, then programmed at 4°C/min to 375°C and held at that temperature for 15 min. The injector was maintained at 350°C and the FID at 400°C. Carrier gas was helium with a 7.5-psi head pressure and a flow of approximately 2.5 mL/min through the column. Injected samples were 1 μL with a split ratio of 30:1. Chromatograms and area percent reports were obtained by using the peak integration mode of operation.

Samples of commercially available alcohol ethoxylates representing several suppliers were used for this work. These samples were selected to provide simple, two-alcohol mixtures (samples 1, 2 and 3), complex four-alcohol mixtures (samples 4 and 5), and mixtures with high average moles of ethylene oxide (samples 3 and 4). This choice of representative samples provided a range of characteristics with which to evaluate advantages and disadvantages of SFC and HTGC, including the following. i) C_{12}/C_{13} (6.6), a mixture of C_{12} and C_{13} alcohol ethoxylates with an average of 6.6 moles of ethylene oxide (supplier's analysis). ii) C_{12}/C_{14} (10.6), a mixture of C_{12} and C_{14} alcohol ethoxylates with an average of 10.6 moles of ethylene oxide (supplier's nominal value). iii) C_{14}/C_{15} (12.3), a mixture of C_{14} and C_{15} alcohol ethoxylates with an average of 12.3 moles of ethylene oxide (supplier's analysis). iv) C_{12}–C_{15} (11.3), a mixture of C_{12}, C_{13}, C_{14} and C_{15} alcohol ethoxylates with an average of 11.3 moles of ethylene oxide (supplier's analysis). v) C_{12}–C_{18} (8.8), a mixture of C_{12}, C_{14}, C_{16} and C_{18} alcohol ethoxylates with an average of 8.8 moles of ethylene oxide (supplier's analysis).

Two derivatization procedures were used in this work: Acetylation, by means of acetic anhydride and pyridine, and silylation, with bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine. In both procedures, 100-mg aliquots of the alcohol ethoxylate surfactant were transferred to clean 1-dram screw cap vials. Five hundred μL of derivatizing reagent and 500 μL of pyridine were added to the samples. The vials were closed with teflon-lined caps and heated at approximately 60°C for 30 min with occasional shaking of the vials. Excess reagent was removed at approximately 50°C in a nitrogen stream (taken almost to dryness). Derivatized samples were dissolved in 2 mL of chloroform for analysis.

Quantitative characterizations of surfactant samples, calculated as the underivatized nonionics, were obtained by calculating weight percent distributions, mean-molecular weights, and average moles of ethylene oxide from FID response data by using the ECN theory described above. Based on this theory, the expected FID effective carbon (EC) response for a fatty alcohol ($R\text{-}CH_2OH$) equals the contribution from the R group, plus 0.5 ECs for the alcohol carbon, plus 1.0 EC for each mole of ethylene oxide (2.0 for the carbons and −1.0 for the ether oxygen). Acetylated derivatives are expected to have an FID response equal to the R contribution plus the EO contribution plus 1.5 ECs for the acetate group. The silylated derivatives are expected to have an FID response equal to the R plus EO contribution plus 3.69 ECs for the trimethylsilyl group. Therefore, a molar response factor (MRF) for each component equals the component MW (underivatized) divided by the component ECN as prepared for analysis:

$$\text{Corrected areas (weight basis)} = \text{FID area (percent)} \times \text{MRF}$$

$$\text{Component weight percent} = (\text{corrected area} \times 100)/\text{sum of corrected areas}$$

$$\text{Component moles per 100 g (moles)} = \text{component weight percent}/\text{component MW}$$

$$\text{Sample mean-molecular weight (MMW)} = \Sigma(C_1\ \text{wt\%} + C_2\ \text{wt\%} + \ldots)/\Sigma\ \text{moles}\ (C_1 + C_2 + \ldots)$$

$$\text{Alcohol MMW} = \Sigma\ \text{moles (C12 components} \times \text{MwC12OH} + \text{C13 components} \times \text{MwC13OH} + \ldots)/\Sigma\ \text{moles (C12 components} + \text{C13 components} + \ldots)$$

$$\text{Average moles of ethylene oxide} = (\text{sample MMW} - \text{alcohol MMW})/44.05$$

RESULTS

A capillary SFC chromatogram of the separation of a C_{12}/C_{13} (6.6) alcohol ethoxylate is shown in Figure 2. A quick comparison of the results shown in Figures 1 and 2 easily demonstrate the superiority of SFC over conventional capillary GC for the analysis of these materials. Based on the effective carbon theory, SFC data indicated this sample to have an average of 7.0 moles of ethylene oxide.

However, as the surfactant system becomes more complicated, a limitation of SFC is revealed. An SFC chromatogram of the separation of a C_{12}/C_{14} (10.6) alcohol ethoxylate is shown in Figure 3. Inspection of the chromatogram reveals an apparent coelution of the C_{14}-0 (unethoxylated alcohol) and C_{12}-1 (1 EO oligomer) components. This coelution was verified by comparison with the chromatograms of other systems. Another aspect of the resolution issue is the gradual loss of resolution with increasing molecular-weight EO oligomers, resulting in coelution of later components. However, SFC is still adequate for quality control analysis of this surfactant. The composition of coeluted peaks can be estimated based on ratios of similar components in early eluting integrated peaks, and a semi-quantitative result can be obtained.

Coelution of the type observed in this example, longer-chain homologues, occurs due to the higher density of the supercritical fluid required to elute these components. At higher mobile phase densities, resolution decreases partly due to higher mobile phase velocity and to the lower

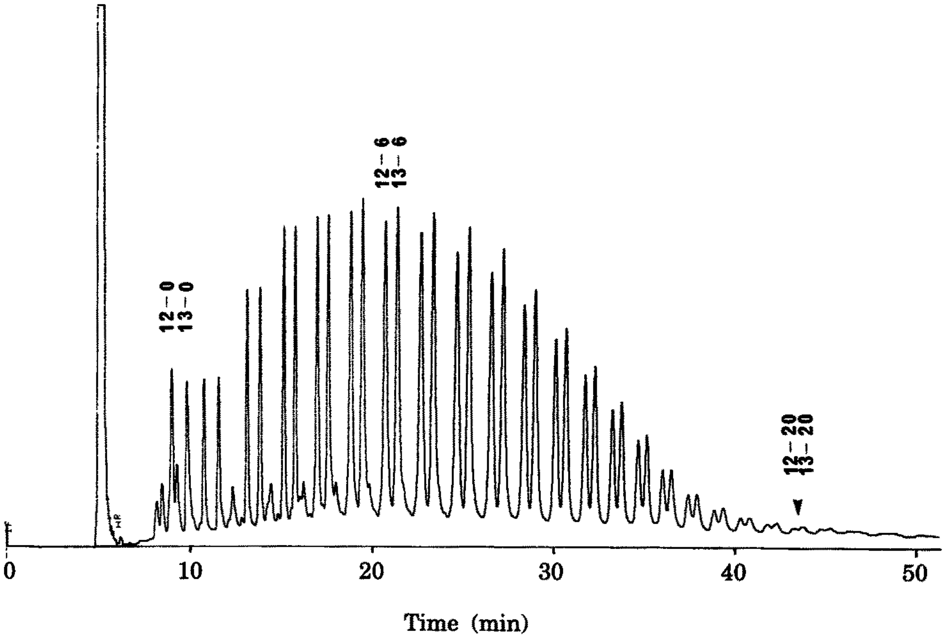

FIG. 2. Capillary SFC chromatogram of a C_{12}/C_{13} alcohol ethoxylate with an average of 6.6 moles of ethylene oxide (supplier's analysis).

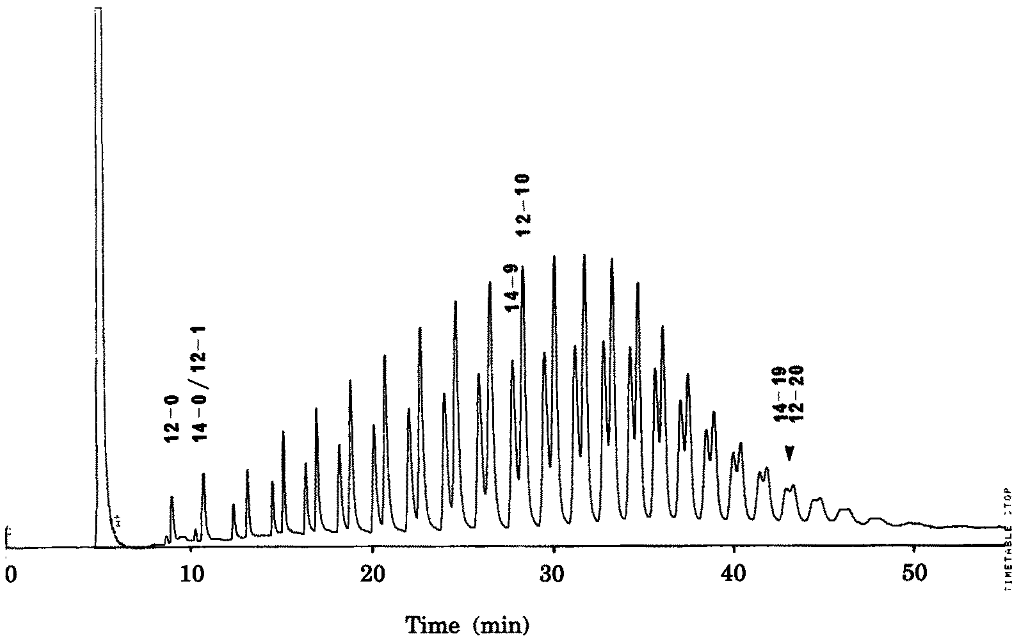

FIG. 3. Capillary SFC chromatogram of a C_{12}/C_{14} alcohol ethoxylate with an average of 10.6 moles of ethylene oxide (supplier's nominal value).

diffusivity in the more dense carbon dioxide (20,21). This results in a lower efficiency of separation.

Resolution of the C_{14}-0 and C_{12}-1 components is achieved by derivatization of the surfactant. The same C_{12}/C_{14} (10.6) alcohol ethoxylate acetylated provides the chromatogram shown in Figure 4. In this chromatogram, the C_{14}-0 and C_{12}-1 components are now resolved. In addition, there is a slight improvement in resolution of the higher molecular-weight oligomers when compared to the separation of the underivatized sample. However, adequate resolution and, thus, accurate integration, is still not achieved for all components. The data obtained from this SFC chromatogram indicated this sample to have an average of 10.2 moles of EO.

Figure 5 shows the capillary SFC separation of a slightly higher molecular weight surfactant, a silylated C_{14}/C_{15} (12.3) alcohol ethoxylate sample. This chromatogram shows adequate resolution for integration of components through the 23 EO oligomers. The presence of 24 and 25 EO oligomers are indicated; however, these components are not adequately resolved for integrations. Based on SFC data, this sample has an average of 11.9 moles of ethylene oxide.

Figure 6 compares SFC data for the C_{12}/C_{14} (10.6) alcohol ethoxylate sample underivatized, acetylated and silylated. Essentially, identical weight-percent distributions are obtained with all three samples. Similar results were obtained for the C_{12}/C_{13} and C_{14}/C_{15} samples. One can conclude that derivatization does not alter alcohol ethoxylate samples and, in spite of minor issues with resolution, SFC is useful for the characterization of these surfactants. When the surfactant becomes more complicated, the resolution of the alcohol ethoxylates shows a major limitation of capillary SFC. Figure 7 shows the SFC chromatogram of an acetylated C_{12}–C_{15} (11.3) alcohol ethoxylate sample. It is apparent that (except for the C_{12}-0 component) the C_{12} and C_{15} alcohol ethoxylates coelute. Also, the resolution of the C_{13} and C_{14} alcohol ethoxylate oligomers degrade completely above 20 moles of EO. Therefore, quantitation of this sample is ambiguous. One solution is to assume that all four alcohols have similar EO distributions. The average moles of EO can then be estimated based on the C_{13} and C_{14} alcohols and ethoxylated oligomers. Based on this assumption, this sample was estimated to have an average of 10.5 moles of EO. Similar results were obtained by SFC for a silylated C_{12}–C_{18} (8.8) alcohol ethoxylate (Fig. 8). With this sample the C_{12}-0 and C_{12}-1 ethoxylate components are resolved. However, the higher molecular-weight C_{12} EO oligomers coelute with the C_{18} alcohol and ethoxylated components, leading to ambiguity in quantitation. Again, one solution is to assume that all four alcohols have similar EO distributions. The average moles of EO can be estimated based on the C_{14} and C_{16} alcohols and ethoxylated oligomers. Based on this method, this sample was estimated to have an average of 9.0 moles of EO.

These same five samples were then examined by HTGC (Figs. 9–13). The HTGC chromatogram of the silylated C_{12}/C_{13} (6.6) alcohol ethoxylate mixture is shown in Figure 9. Separation of individual components with essentially baseline resolution through 22 EO oligomers is demonstrated. In comparison, the SFC separation of an underivatized sample of the same surfactant (Fig. 2) shows a loss of resolution for the 21 and 22 EO oligomers. However, HTGC has its own limitation. Comparing the SFC chromatogram of Figure 2 with the HTGC chromatogram of Figure 9, one sees that SFC detects trace amounts of 23 EO oligomers, but there is no evidence of these components in the HTGC chromatogram. Trace levels of higher molecular-weight components should not contribute significantly to the average molecular weight of this sample. HTGC data indicated this

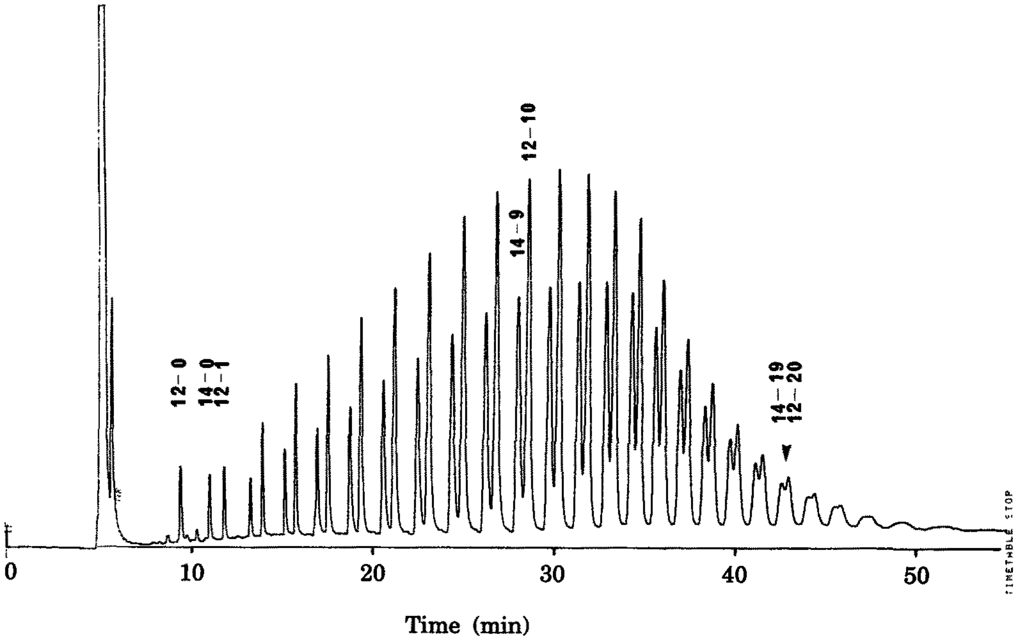

FIG. 4. Capillary SFC chromatogram of an acetylated C_{12}/C_{14} alcohol ethoxylate with an average of 10.6 moles of ethylene oxide (supplier's nominal value).

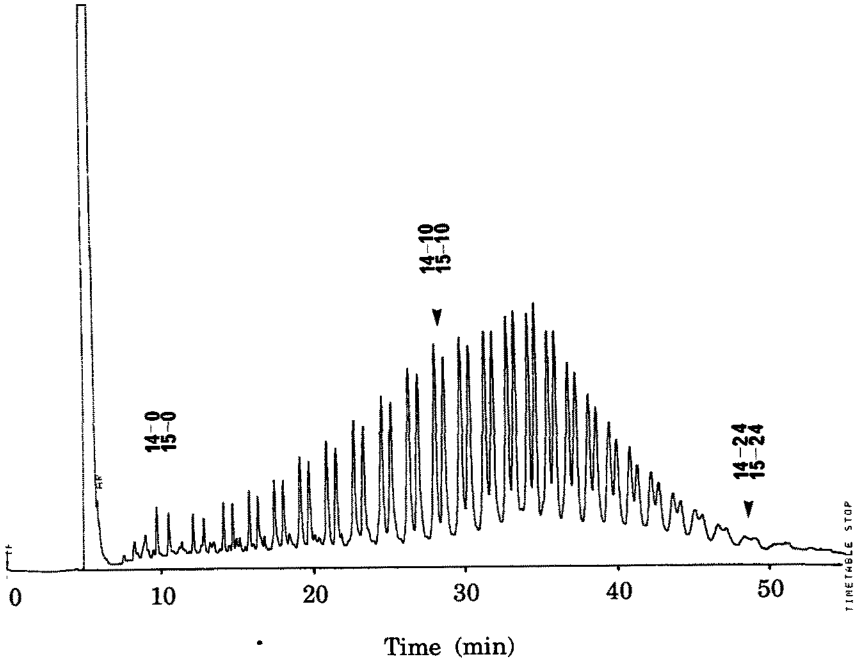

FIG. 5. Capillary SFC chromatogram of a silylated C_{14}/C_{15} alcohol ethoxylate with an average of 12.3 moles of ethylene oxide (supplier's analysis).

sample to have an average of 7.4 moles of EO (7.0 by SFC).

Table 1 compares the weight percent distributions obtained with the C_{12}/C_{13} (6.6) sample by SFC and HTGC. Although the SFC data are skewed to lower moles of ethylene oxide, the distributions readily characterize the type of sample. The calculated sample and alcohol moiety mean-molecular weights, and average moles of ethylene oxide allow quick comparison of this sample with other commercial or experimental surfactants. Similar results are obtained with the other alcohol ethoxylate samples.

The HTGC chromatogram of the silylated C_{12}/C_{14} (10.6) alcohol ethoxylates is presented in Figure 10. Baseline resolution is achieved through the 21 EO oligomers as

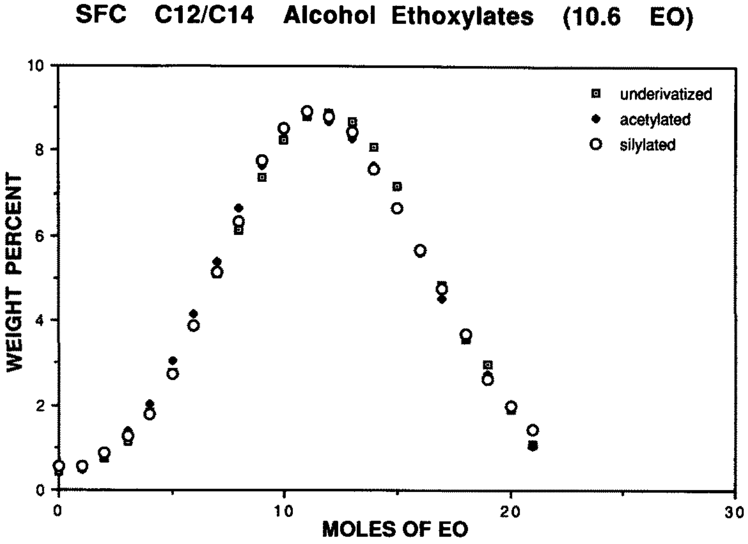

FIG. 6. Comparison of capillary SFC data of a C_{12}/C_{14} alcohol ethoxylate underivatized and derivatized.

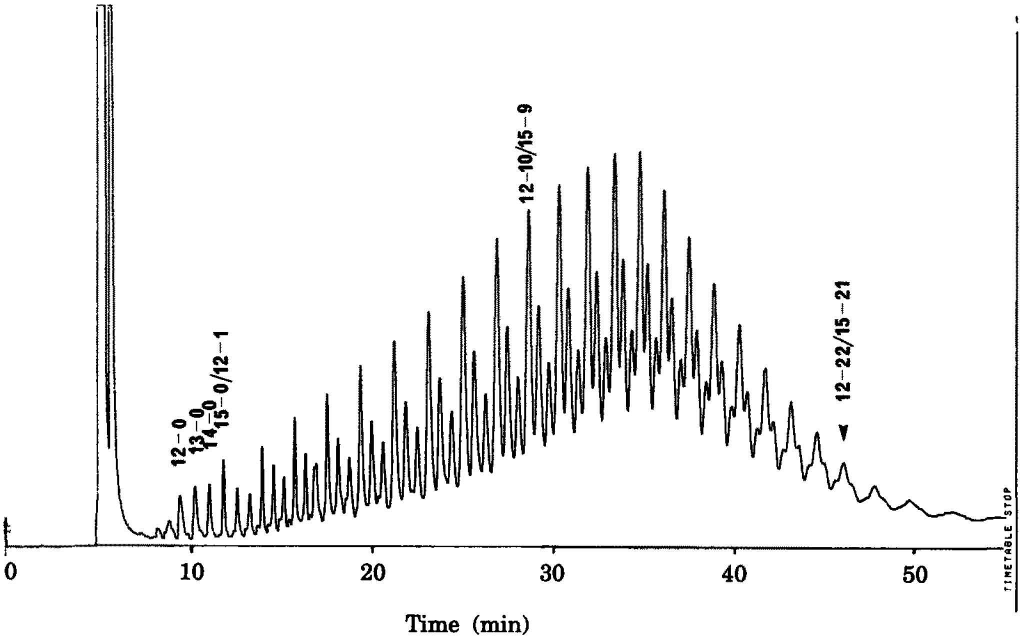

FIG. 7. Capillary SFC chromatogram of an acetylated C_{12}–C_{15} alcohol ethoxylate with an average of 11.3 moles of ethylene oxide (supplier's analysis).

compared to SFC separation of an acetylated sample of the same surfactant (Fig. 4), where there is only a slight indication of separation between the two 21 EO oligomers. The HTGC fails to detect the low levels of 22 through 24 EO oligomers observed in the SFC chromatogram. Again, however, HTGC data resulted in a higher average level of ethoxylation than SFC (10.9 moles of EO by HTGC and 10.2 by SFC).

Similar results were obtained with the HTGC separation of a silylated C_{14}/C_{15} (12.3) alcohol ethoxylate sample (Fig. 11). Separation of individual components with essentially baseline resolution was achieved through the 21 EO oligomers. In comparison, the SFC separation of the same sample (Fig. 5) shows some loss of resolution for the 21 EO oligomers, but indicated the presence of 22 through 25 EO oligomers not seen in the HTGC chromatogram. HTGC data indicated this sample to have an average of 11.8 moles of ethylene oxide (11.9 by SFC).

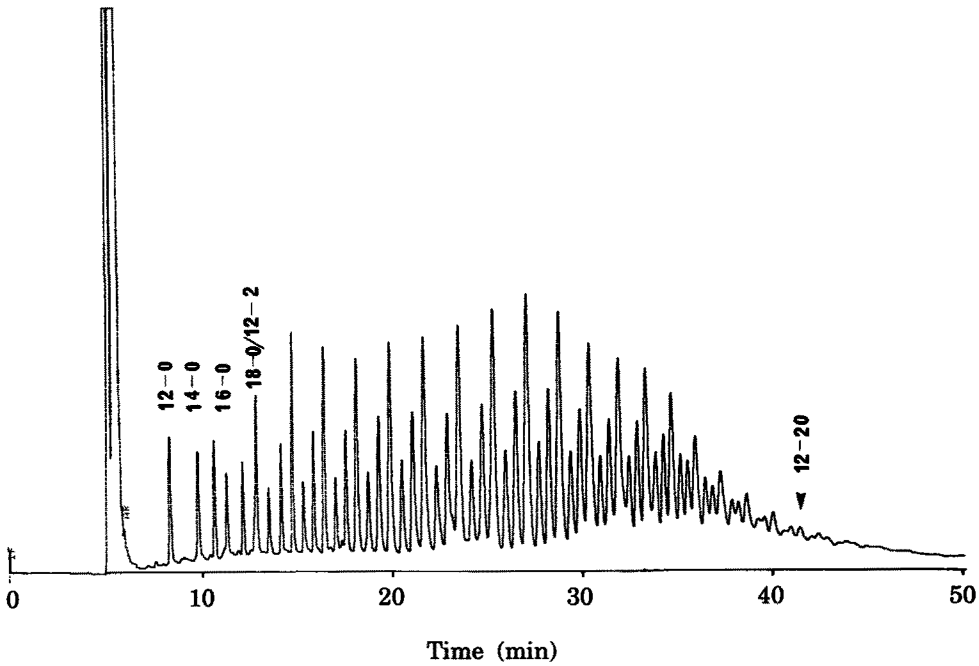

FIG. 8. Capillary SFC chromatogram of a silylated C_{12}–C_{18} alcohol ethoxylate with an average of 8.8 moles of ethylene oxide (supplier's analysis).

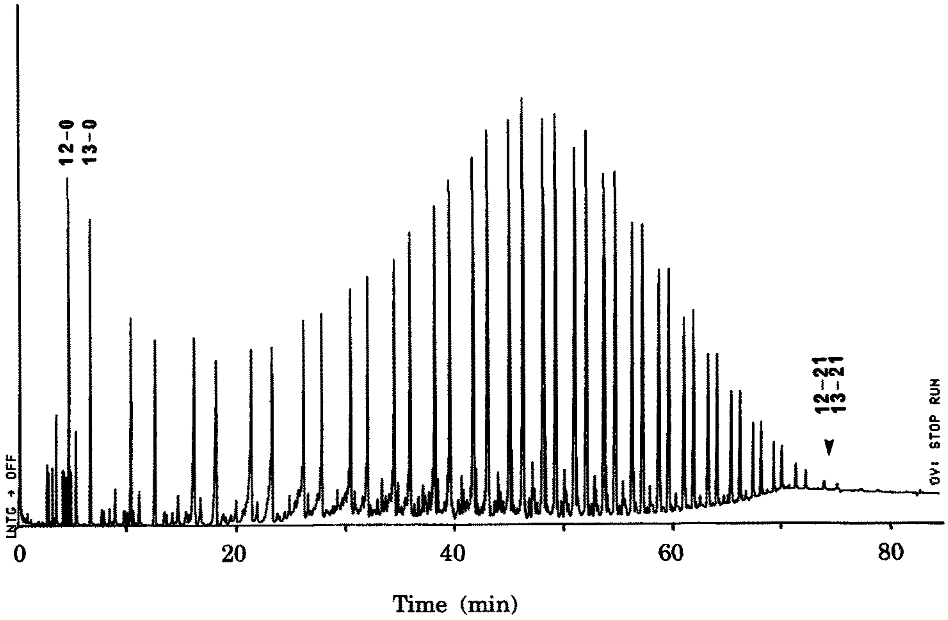

FIG. 9. Capillary HTGC chromatogram of a silylated C_{12}/C_{13} alcohol ethoxylate with an average of 6.6 moles of ethylene oxide (supplier's analysis).

The HTGC chromatogram of the silylated C_{12}–C_{15} (11.3) alcohol ethoxylate sample is shown in Figure 12. In comparison to the SFC chromatogram of an acetylated sample of the same surfactant (Fig. 7), the advantages and disadvantages of HTGC *vs.* SFC are clearly shown. HTGC provides essentially baseline resolution of all four alcohols through the 21 EO oligomers. SFC is not capable of resolving the C_{12} and C_{15} alcohol EO components, and there is a general loss of component resolution of the higher EO oligomers. However, SFC has the advantage of eluting high molecular-weight oligomers not seen in HTGC separations. HTGC data indicated that this sample has an average of 11.0 moles of ethylene oxide (10.5 by SFC). Similarly, an HTGC chromatogram of the silylated C_{12}–C_{18} (8.8) alcohol ethoxylate (Fig. 13) also indicated the advantage of HTGC compared to an SFC separation of

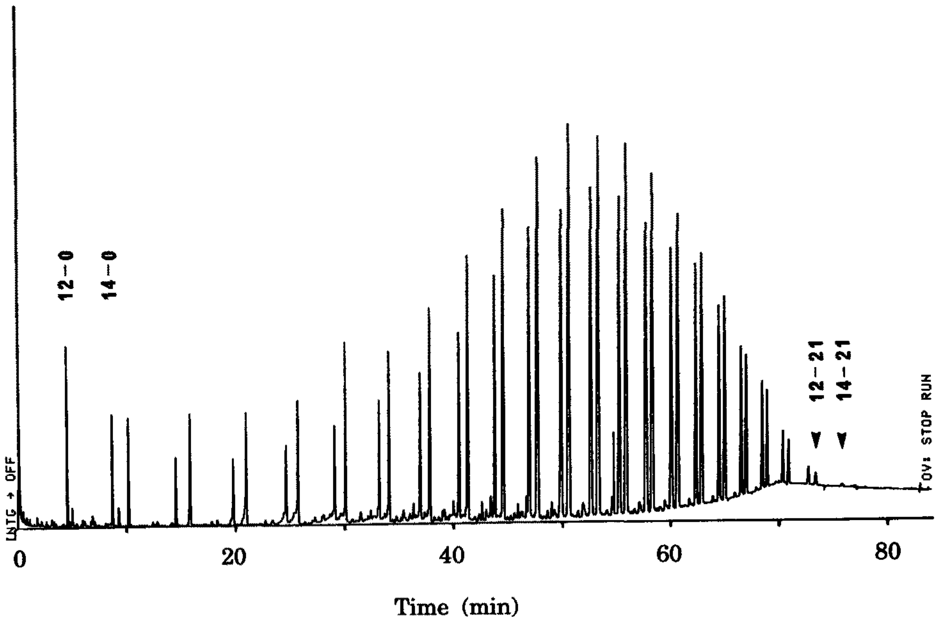

FIG. 10. Capillary HTGC chromatogram of a silylated C_{12}/C_{14} alcohol ethoxylate with an average of 10.6 moles of ethylene oxide (supplier's nominal value).

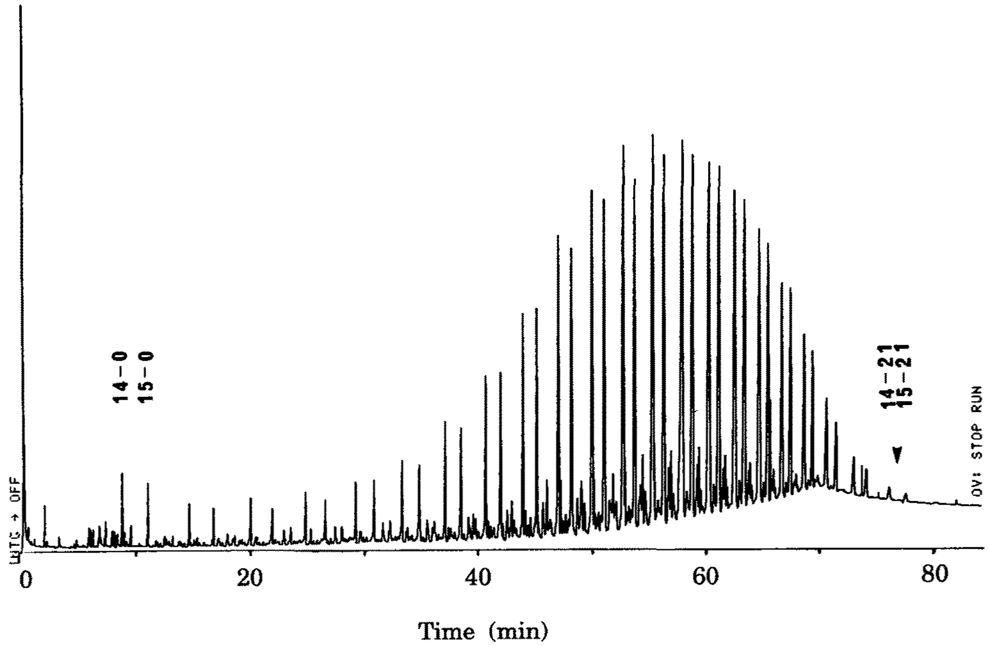

FIG. 11. Capillary HTGC chromatogram of a silylated C_{14}/C_{15} alcohol ethoxylate with an average of 12.3 moles of ethylene oxide (supplier's analysis).

the same sample. The HTGC chromatogram showed essentially baseline resolution for all four alcohols through 21 EO oligomers. SFC was not capable of resolving the C_{12} and C_{18} alcohol EO oligomers.

The average moles of ethylene oxide calculated for each of the alcohol ethoxylate samples examined by SFC and HTGC are presented in Table 1. Four of the five samples show a lower average value as determined by SFC *vs.* HTGC. Two possible explanations for this difference are sample discrimination in the SFC injection valve (22), due to incomplete transfer of higher molecular-weight components from the sample rotor into the column, and inaccurate integration of peak areas, due to incomplete resolution of higher molecular-weight components.

These SFC and HTGC data were compared to the corresponding data obtained from ^{13}C nuclear magnetic

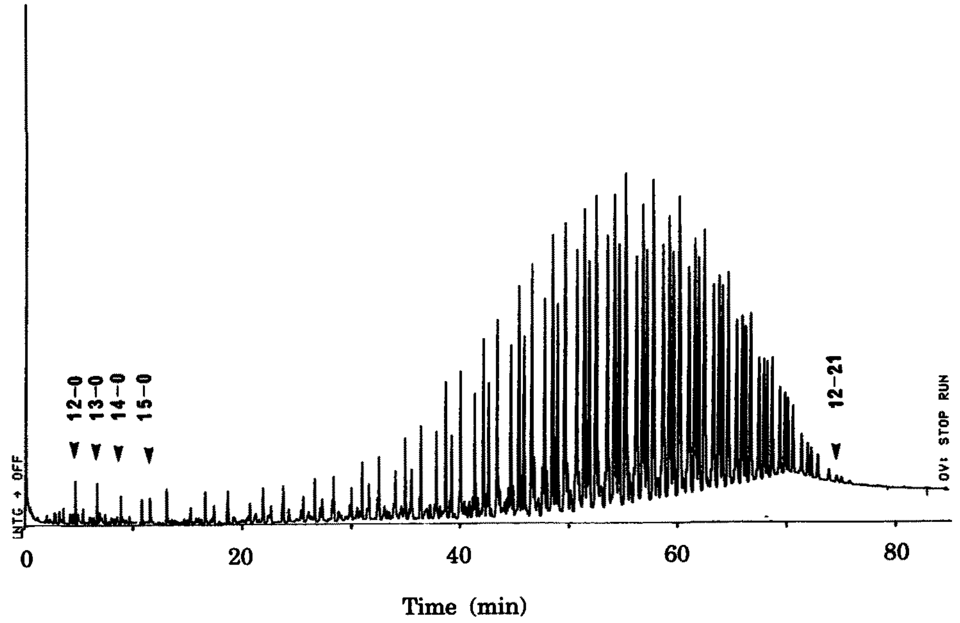

FIG. 12. Capillary HTGC chromatogram of a silylated C_{12}–C_{15} alcohol ethoxylate with an average of 11.3 moles of ethylene oxide (supplier's analysis).

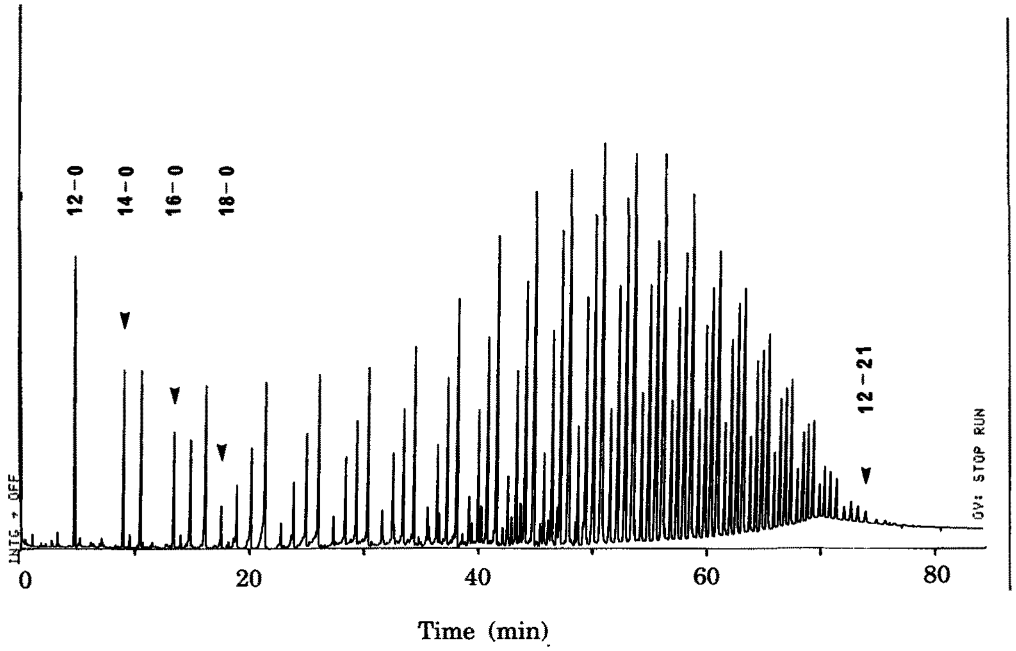

FIG. 13. Capillary HTGC chromatogram of a silylated C_{12}–C_{18} alcohol ethoxylate with an average of 8.8 moles of ethylene oxide (supplier's analysis).

resonance (NMR) analysis of the underivatized surfactants (Table 2) to provide an independent measure of average moles of ethylene oxide in each of the samples. However, the NMR data only provide an average moles of ethylene oxide, and actual distributions are not available by this method (10). Unfortunately, the NMR

TABLE 1

Weight Percent Distributions of C_{12}/C_{13} (6.6) Alcohol Ethoxylates

	SFC		HTGC	
Moles of EO	C_{12}	C_{13}	C_{12}	C_{13}
0	1.00	1.02	1.38[a]	1.69[a]
1	0.84	0.83	1.27[a]	1.26[a]
2	1.36	1.38	1.80[a]	1.80[a]
3	1.92	2.14	1.75	1.38
4	2.72	2.71	1.62	1.72
5	3.54	4.38	2.19	2.27
6	4.11	4.82	2.73	2.71
7	4.42	5.13	3.35	3.47
8	4.44	5.09	4.12	4.27
9	4.44	4.99	4.58	4.86
10	4.03	4.56	4.90	4.96
11	3.45	3.94	4.59	4.64
12	2.83	3.39	4.00	4.03
13	2.23	2.66	3.31	3.35
14	1.80	2.08	2.58	2.61
15	1.34	1.62	1.96	1.97
16	0.94	1.22	1.40	1.37
17	0.68	0.84	0.98	0.92
18	0.48	0.63	0.62	0.57
19	NI[b]	NI	0.34	0.32
20	NI	NI	0.18	0.18
21	NI	NI	NI	NI
22	NI	NI	NI	NI
Sample MMW	504		518	
Alcohol MMW	194		193	
Average moles of EO	7.0		7.4	

[a] Includes identified secondary alcohol components.
[b] NI, Not integrated.

TABLE 2

Calculated Average Moles of Ethylene Oxide

Sample	SFC	HTGC	^{13}C NMR
C_{12}/C_{13} (6.6)	7.0	7.4	6.9
C_{12}/C_{14} (10.6)	10.2	10.9	10.5
C_{14}/C_{15} (12.3)	11.9	11.8	12.8
C_{12}-C_{15} (11.3)	10.5[a]	11.0	11.6
C_{12}-C_{18} (8.8)	9.0[b]	9.8	9.0

[a] Estimate based on C_{13}, C_{14} alcohol ethoxylates.
[b] Estimate based on C_{14}, C_{16} alcohol ethoxylates.

data do not confirm the validity of either the HTGC or SFC data.

Future work will include investigating the possible discrimination in the SFC injection valve and extending the range of HTGC to higher molecular-weight oligomers.

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