HPLC Analysis of Nonionic Surfactants. Part IV. Polyoxyethylene Fatty Alcohols

A. ASERIN, M. FRENKEL and **N. GARTI**, Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

ABSTRACT

A high performance liquid chromatographic technique (HPLC) was applied to analyze nonionic surfactants of ethylene oxide (EO) adducts. Pattern analyses of EO adducts (ethers), with 2, 10 and 20 average EO units, were carried out using a Lichrosorb SI-60 (10 μm) column (4.6 mm inner dimension (id) × 25 cm) under the following conditions: mobile phase—mixture of isopropanol, methanol and n-hexane (gradient): temperature of 50 C: UV detector at 220 nm. No derivatization of the compounds was needed. An improved baseline, in spite of gradient elution, was achieved by adding negligible amounts of anthracene to the eluents. Brominated ethoxylated alcohols, resulting from the addition of bromine to the hydrophobic chain of the ethoxylated fatty alcohol, did not require any changes in the elution conditions.

INTRODUCTION

Adducts of ethylene oxide and fatty alcohols are important nonionic surfactants commercially used for many years as emulsifiers. Surfactants are mostly long-chain molecules with both a hydrophilic and lipophilic nature and are nonvolatile and, therefore, difficult to elute by gas liquid chromatography (GLC), Several attempts have been made to separate mixtures of the ethoxylated alcohol oligomers using thin layer chromatography (TLC) methods (1-3) and, to some extent, even GLC methods (4,5).

The use of a high pressure liquid chromatographic technique (HPLC) seems to be most adequate for the separation of such mixtures. In 1975, Nakamura and Matsumoto (6) showed that the EO oligomers of commercially available short-chain alcohols derived by acetylation could be separated by HPLC of acetate derivatives. When fatty alcohol oligomers were analyzed, the separation was difficult and subject to error. Nozawa (7) used 3,5-dinitrobenzoyl chloride for the derivatization of ethoxylated fatty alcohols with an average of 2 and 7 ethylene oxide units, in order to improve separation and detectability. The derivatization reduces the hydrophilic character of the molecule and increases its detectability. Allen and Linder (8) used phenyl isocyanate derivatives and an ultraviolet (UV) detector for separating mixed carbon number ($R=C_{12}$ through C_{18}) alcohol ethoxylates. McClure (9) describes an HPLC method for the separation and quantitative determination of EO adducts. In his method, dodecyl alcohol, ethoxylated with 1-30 units, was separated using an acetylation technique to reduce the hydrophilicity of the molecule and a rotating disc flame ionization detector (FID) for optimal detection.

This paper describes an HPLC method for separating both oleyl and dibromostearyl alcohols ethoxylated with 1-30 EO units (Scheme 1) without the need for any derivatization. This paper is the first study showing a good separation of the adducts without prechemical treatments of the samples to be analyzed being necessary.

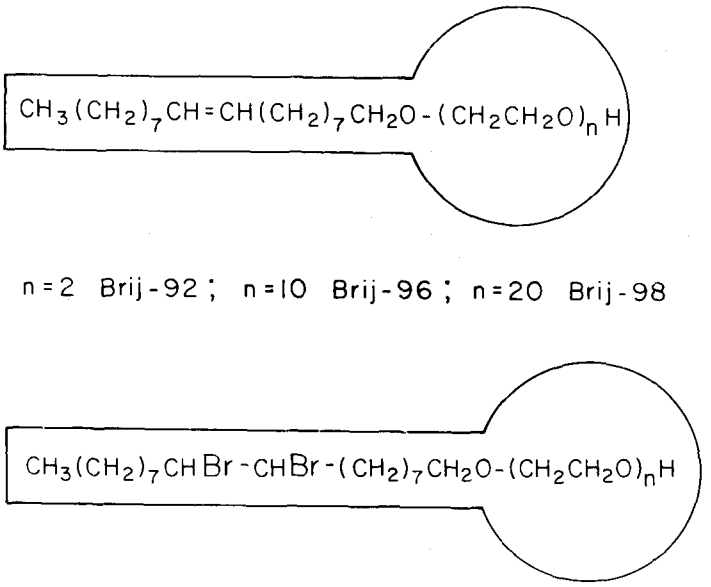
EXPERIMENTAL PROCEDURES

Materials

Oleyl alcohols ethoxylated with an average of 2, 10 and 20 ethylene oxide units, were commercially available from Altas Europol A.p.S. The addition of bromine to the double bond of the oleic chain was carried out in our laboratory (10). The eluents were n-hexane, isopropanol and methanol HPLC grade from Bio-Lab Ltd. Laboratories (Israel) and pure anthracene from Riedel-de Haen (Germany).

Procedure Technique

The analyses were performed on a Spectra Physics model SP-8000 HPLC chromatograph equipped with an SP 770 variable wavelength UV-detector at 220 nm. The separation was achieved on a 25 cm × 4.6 mm id column prepacked with 10 μm Lichrosorb SI-60 purchased from Alltech As-



SCHEME 1. Structure of ethoxylated oleyl and 9,10-dibromostearyl alcohols.

sociates, Inc., Arlington Heights, IL.

The gradients elutions with n-hexane, isopropanol and methanol were carried out as described in Table I at a flow rate of 1 mL/min and a pressure of ca. 200 psi at 50 C.

Each component of the mixture eluted from the column was trapped, using a fraction collector, and analyzed by chemical ionization (CI) mass spectrometry (CIMS, DuPont model 21-490B, single focusing) equipped with a commercial double source CI/EI (electron impact) in an inert atmosphere of isobutane.

The samples were dissolved in 7 wt% isopropanol and 93 wt% hexane (up to 5% w/w). Ten μL of solution were injected, using an automatic loop injector.

RESULTS AND DISCUSSION

Oleyl alcohol with 2 average EO units (Brij 92) was eluted using 7 wt% isopropanol in hexane. Figure 1 shows a typical chromatogram in which the peaks marked 0, 1, 2, 3 and 4 correspond to the number of EO units on the fatty alcohol chain. Fraction collector and CI mass spectra were used to obtain pure compounds and to confirm their structure immediately after their elution from the detector.

A similar chromatogram (Fig. 2) was obtained when brominated stearyl alcohol ethoxylated (which was found to be a useful surfactant) was injected under the same conditions (Table IA).

The injection of Brij 96, having an average of 10 EO units, under the same conditions was unsatisfactory, as only 6 peaks were detected. Increasing the isopropanol fraction in the hexane using a gradient elution from 7 wt% to 60 wt% in 1 hr improved resolution (Fig. 3). A satisfactory separation of 11 peaks is observed as a result of the gradual increase of the eluent hydrophilicity. The solvent gradient (Table IB) caused a shift of the baseline because commercial hexane does absorb some UV light at 220 nm. In addition, Brij 96, consisting of an average of 10 EO units, should probably contain, several more higher molecular-weight compounds that were not eluted. Methanol was added to the eluent mixture in order to elute the more hydrophilic higher molecular-weight components of the mixture. To eliminate the shift of the baseline, anthracene was added to the solvent to equalize its absorbance at 220 nm. Figure 4 demonstrates the improvement of the chromatogram in the baseline, separation ability and number of peaks eluted. Up to 20 peaks were detected, compared with 11 under the previous conditions, indicating that at least 20 EO units exist in the mixture. The fact that such a complicated oligomeric mixture is separated without any derivatization, and with almost optimal baseline, indicates that traces of anthracene are valuable for such separations. The conditions for best separation are summarized in Table IC. The addition of 2 bromine atoms to the double bond of the oleyl chain did not significantly affect the chromatogram, except that peak 13 rose after bromination (Fig. 5). This phenomenon is not yet clear.

When Brij 98, having an average of 20 EO units, was separated under similar conditions, a very complicated chromatogram was obtained with excellent resolution of 27 peaks (Figure 6).

Table II summarizes the relative areas of the various peaks as measured from the chromatograms of Brij 92, Brij 96 and Brij 98. The areas were measured, substracting any baseline shifts. The largest peaks in the case of Brij 92 (commercially claimed to consist of an average of 2 EO units) are those having 0-3 units. In Brij 96, the main components contained 7-11 EO units, whereas, in Brij 98, the main ones were those containing 18-21 EO units.

Figure 7 illustrates the separation of the brominated

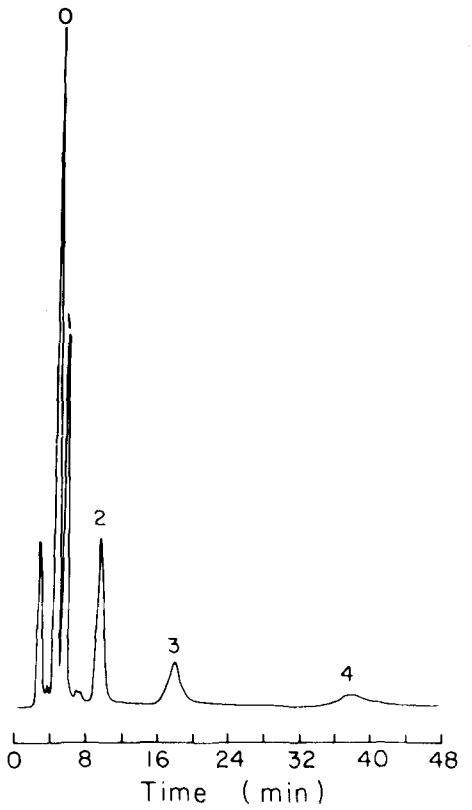


FIG. 1. HPLC chromatogram of oleyl alcohol with 2 (av.) EO units (Brij-92). The peak number corresponds to the number of EO units on the fatty alcohol chain.

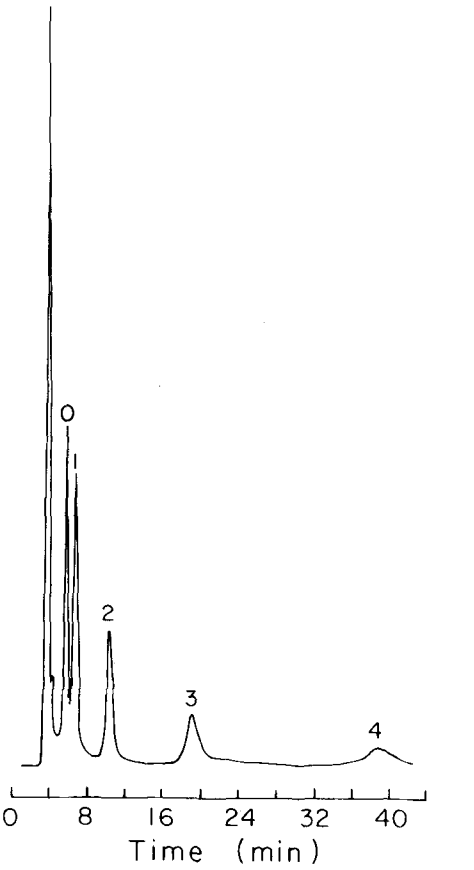


FIG. 2. HPLC chromatogram of 9,10-dibromostearyl alcohol with 2 (av.) EO units.

TABLE I

Elution Conditions for the Separation of Ethoxylated Fatty Alcohols

Method	Time (min)	Isopropanol (wt %)	Methanol (wt %)	Hexane (wt %)
A		7.0	0.0	93.0
B	0.0	7.0	0.0	93.0
	60.0	60.0	0.0	40.0
C	0.0	7.0	0.0	93.0
	20.0	42.0	10.0	48.0
	40.0	65.0	35.0	0.0
D	0.0	7.0	0.0	93.0
	5.0	15.0	0.0	85.0

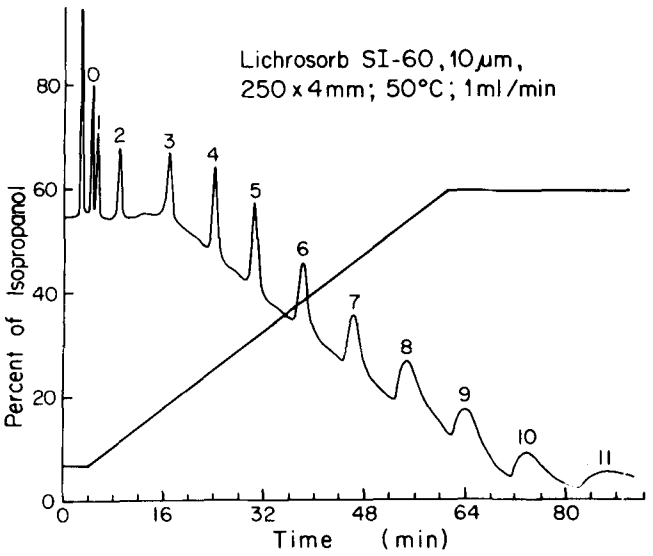


FIG. 3. HPLC chromatogram of oleyl alcohol with 10 (av.) EO units (Brij-96) obtained by gradient elution. (See Table IB).

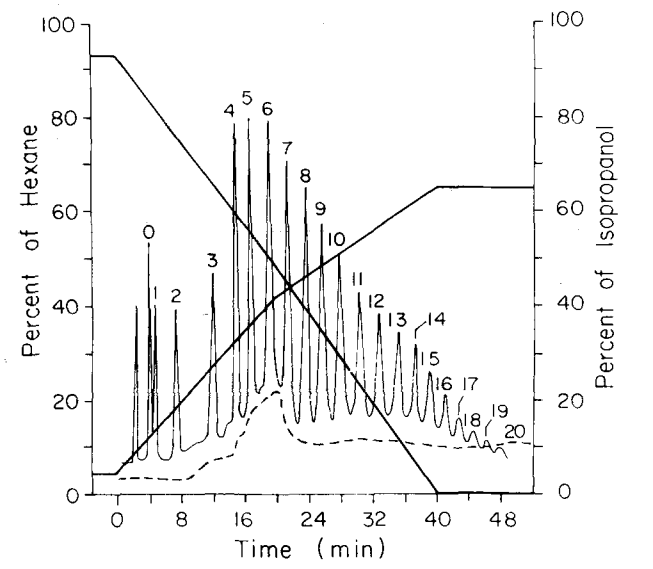


FIG. 4. HPLC chromatogram of oleyl alcohol (10) ethoxylated (Brij-96) obtained by gradient elution (see Table IC) and addition of traces of anthracene. The dashed line shows the baseline.

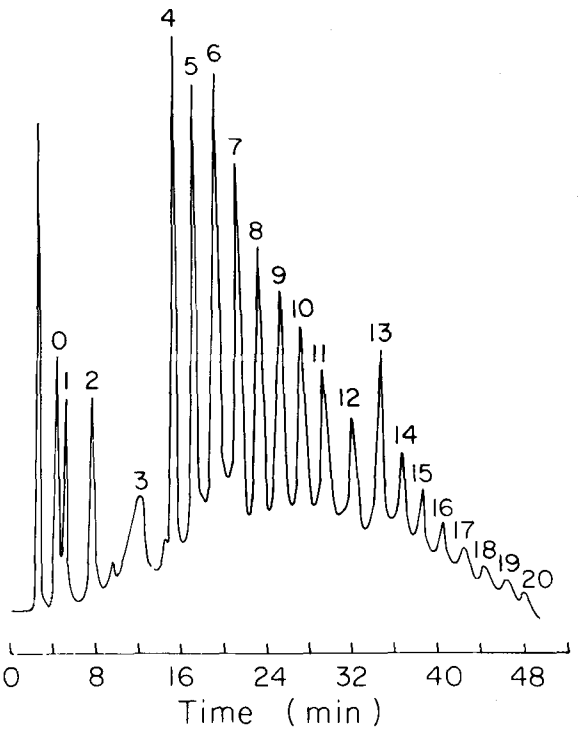


FIG. 5. A typical HPLC chromatogram of 9,10-dibromostearyl alcohol (10) ethoxylated.

TABLE II

Peaks Area Distribution of Ethoxylated Oleyl Alcohols

Number of the peak	Relative area of the peak (% of total)		
	Brij-92	Brij-96	Brij-98
–	5.57	2.98	3.70
0	22.79	3.36	1.49
1	14.70	2.97	1.22
2	17.99	4.88	0.67
3	16.64	5.46	0.94
4	6.47	6.63	1.22
5	4.40	6.68	1.35
6	3.23	6.74	1.35
7	2.61	6.98	1.93
8	1.79	7.92	2.00
9	1.35	6.84	2.10
10	0.81	6.70	2.23
11	0.72	6.35	2.60
12	0.54	5.81	2.70
13	0.36	5.53	2.97
14		4.51	4.30
15		3.62	4.61
16		2.66	5.38
17		1.86	6.06
18		1.32	6.75
19		0.65	6.98
20		0.39	6.85
21			6.58
22			5.88
23			5.31
24			4.73
25			4.09
26			2.68
27			1.23

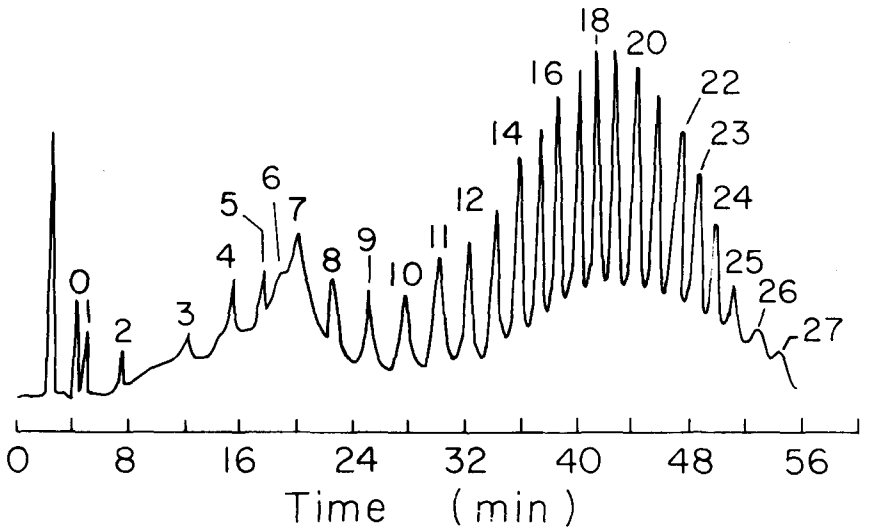


FIG. 6. HPLC chromatogram of oleyl alcohol with 20 (av.) EO units (Brij-98).

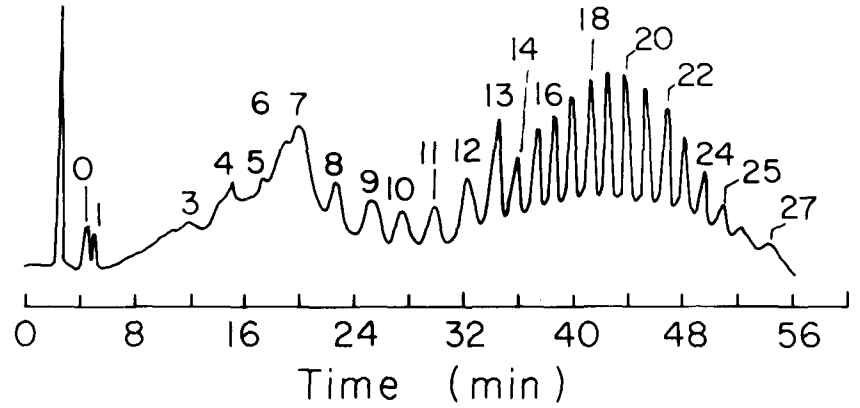


FIG. 7. HPLC chromatogram of 9,10-dibromostearyl alcohol (20) ethoxylated.

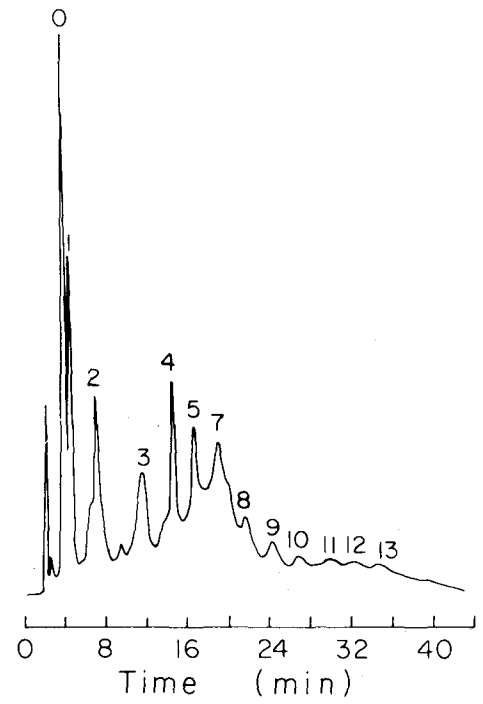


FIG. 8. HPLC chromatogram of Brij-92 using gradient elution (see Table IC).

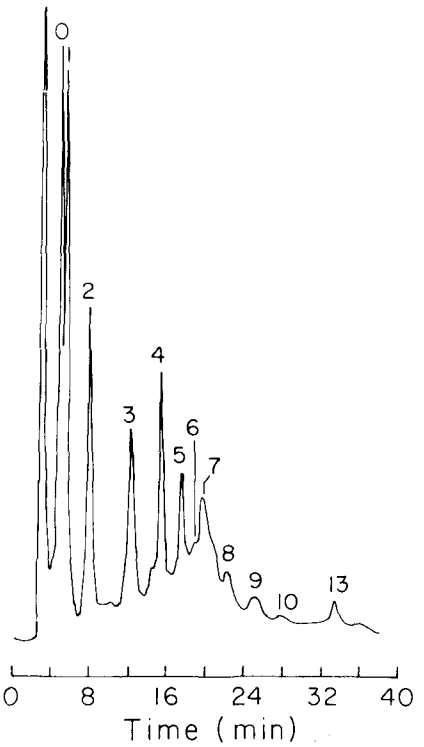


FIG. 9. HPLC chromatogram of 9,10-dibromostearyl alcohol (2) ethoxylated.

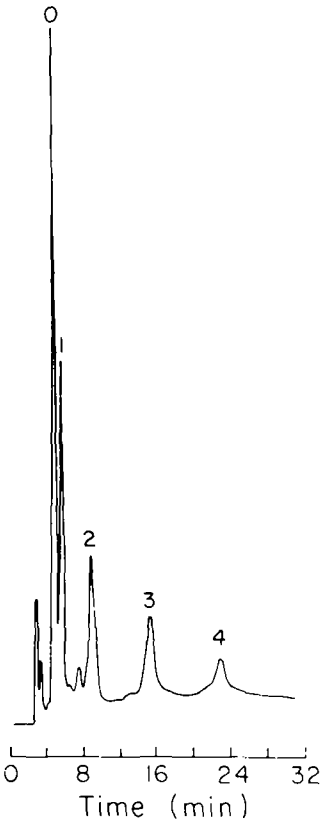


FIG. 10. HPLC chromatogram of Brij-92 using a partial gradient elution.

Brij 98. Peak 13 is again significantly larger than in the non-brominated mixture. Although exactly the same amount of materials were injected in both samples, the peaks height of the brominated materials are lower because bromine was added to the chromophoric group (double bond), decreasing the light absorbance at 220 nm.

Brij 92 (2 average EO units) and the corresponding brominated material (Figs. 8,9) injected under the improved conditions (Table IC) showed the existence of 13 peaks rather than 4, as found under the previous conditions (Table IA). The main peaks were again 0-4 EO units. Yet, peaks 5-13 indicate that the commercial surfactant also contains higher oligomers.

Partial solvent programming, which results in a quick separation of the first 4 peaks of the Brij 92, was performed by increasing the percentage of isopropanol in the hexane from 7-15 wt% within 5 min (Table ID). The fourth component is eluted after only 24 min (Fig. 10) rather than after 40 min, as under the isocratic conditions (Table IA, Fig. 1).

This study shows that separating highly complex mixtures of surfactants containing EO adducts of fatty alcohols, using quite simple and standard techniques that eliminate the need for any derivatization, is possible. This method can be used as an on-line technique for other surfactants as well.

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