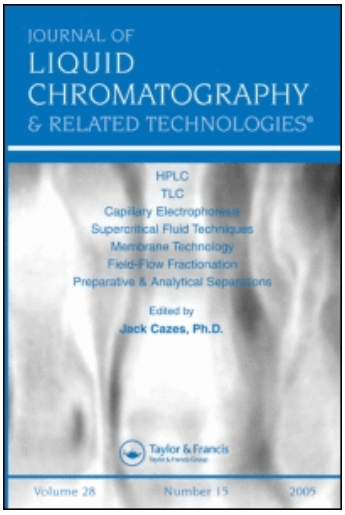

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

HPLC Analysis of Nonionic Sufactants. V. Ethoxylated Fatty Acids

Abraham Aserin[a]; Nissim Garti[a]; Moshe Frenkel[a]
[a] Casali Institute of Applied Chemistry School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, ISRAEL

To cite this Article Aserin, Abraham , Garti, Nissim and Frenkel, Moshe(1984) 'HPLC Analysis of Nonionic Sufactants. V. Ethoxylated Fatty Acids', Journal of Liquid Chromatography & Related Technologies, 7: 8, 1545 — 1557
To link to this Article: DOI: 10.1080/01483918408074065
URL: http://dx.doi.org/10.1080/01483918408074065

JOURNAL OF LIQUID CHROMATOGRAPHY, 7(8), 1545-1557 (1984)

HPLC ANALYSIS OF NONIONIC SURFACTANTS – PART V; ETHOXYLATED FATTY ACIDS

Abraham Aserin, Nissim Garti and Moshe Frenkel
Casali Institute of Applied Chemistry
School of Applied Science and Technology
The Hebrew University of Jerusalem
Jerusalem 91904, ISRAEL

ABSTRACT

High performance liquid chromatography technique was used in order to achieve separation and identification of product composition of nonionic surfactants of ethoxylated fatty acids.

Lichrosorb SI-60 (10μm) column, under gradient elution of mixture of isopropanol, methanol and n-hexane (50°C) and UV detector at 220 nm, were used for best separation of ethylene oxide (EO) adducts of fatty acids consisting of up to 20 EO units.

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 fatty acids resulting from addition of bromine to the double bond of the hydrophobic chain were also separated without a need for change in elution conditions or derivatization.

INTRODUCTION

Ethoxylation of fatty acids with ethylene oxide or polyethylene glycols, in the presence of a variety of alkaline catalysts, yields a mixture of polyethylene glycol monoesters, polyethylene glycol diesters and free polyethylene glycols. A variety of such adducts can be obtained depending on molar ratio of EO to fatty acids used in the reaction (1-2).

Attempts to analyze the fatty acid adduct by chromatographic methods have been carried out by several authors. GLC analysis was done after chemical decomposition of the crude product by using the

 0148-3919/84/0708-1545$3.50/0

mixed acetic anhydride and p-toluene sulfonic acids. In this way the hydrophobic fatty acids composition was determined, but no information could be gathered on the internal EO adduct distribution (3). Aitzetmüller (4) was the first to report on the use of HPLC technique to analyze a commercial product of ethoxylated fatty acids. A most complicated chromatograph having typical pattern was shown but no identification of the peaks was given. Similarly, fingerprints of the product mixture were presented by Brüschweiler using its 3,5-dinitrobenzoyl chloride derivatives (5). More qualitative analysis were carried out by Nakamura and Matsumoto (6). The samples were acetylated prior to chromatography in order to decrease the materials adsorption on the column. The molar distribution of EO adducts in the range of 30 EO units was directly proportional to the reaction time. Several mobile phases were tested and their effect on the reaction time and the detector response were examined. The chromatogram was quite complex and no identification of the peaks was shown.

The following study demonstrates elution of fatty acid ethylene oxide adducts from various commercial sources without a need for either prior chemical treatment or derivatization. In addition, peaks identification was achieved by quantitative separation followed by their identification using chemical ionization mass-spectrometry.

Exthoxylated oleic acid were further brominated to obtain dibromostearic derivatives e.g. 9,10 dibromostearoyl-(9)-ethoxylated ester. These new surfactants were also easily eluted by our technique at the same conditions without any need for derivatization.

EXPERIMENTAL

Materials

Ethoxylated fatty acids with various ethylene oxide (EO) units were commercially available products from three different sources: 1. Oleic acid ester with average 4.5, 9 and 13.5 EO units (Mapeg-200, Mapeg-400 and Mapeg-600) were obtained from Mazer Chemicals, Inc. (USA); 2. Oleic acid ester with average 2 and 10 EO units (Myo-2 and Myo-10) were obtained from Nikko Chemicals Co., Ltd. (Japan); and 3. Commercial polyoxyethylene oleate without given specifications concerning the numbers of EO units (G-5507 and G-2143) were purchased

from Atlas Europol A.p.S. (Italy). The addition of bromine to the double bond of the oleic chain was carried out in our laboratory (7). The eluents were isopropanol, methanol and n-hexane HPLC grade from Bio-Lab Laboratories, Ltd. (Israel) and pure anthracene from Riedel-de Haën (Germany).

Procedure Technique

The analyses were performed on Spectra Physics HPLC chromatograph model SP-8000 equipped with a UV SP-770 variable wavelength detector (Schoffel Instrument Corp.) at 220 nm. The column was a commercially available 250 x 4.6 mm packed with Lichrosorb SI-60 (10 μm) purchased from Alltech Associates, Inc.

A gradient elution with isopropanol, methanol and n-hexane was carried out as described in Table 1, at a flow rate of 1 ml/min and a pressure of about 200 psi at 50°C.

The samples were dissolved in 7:93 volume percent (isopropanol: n-hexane) up to 5% w/w. Ten μl of solution were injected using an automatic loop injector.

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

RESULTS AND DISCUSSION

Polyoxyethylene oleyl ester with average 4.5 EO units (Mapeg-200) was injected to the HPLC column after addition of traces of anthracene to the eluents in order to achieve best baseline and to obtain minimum destortion of the chromatogram caused by the gradient elution (8). Figure 1 demonstrates typical chromatogram recorded within 40 minutes. It can be seen that the main peaks are 4 and 5. The mass-spectra analysis confirmed that peak 4 is oleyl ester with 4 EO units (M.W. = 458) while peak 5 consists of 5 EO units. Peak 0 reveals existence of free oleic acid unethoxylated (M.W. = 282). Indeed free acid was determined either by its acid value or GLC techniques. In a similar way identification of the other peaks was

TABLE 1

The Method of Gradient Elution Used for the Separation of Ethoxylated Fatty Acids. (Continuous gradient).

Time (min.)	Isopropanol (Vol.%)	Methanol (Vol. %)	n-Hexane (Vol. %)
0.0	7.0	0.0	93.0
20.0	42.0	10.0	48.0
40.0	65.0	35.0	0.0
60.0	65.0	35.0	0.0
63.0	65.0	0.0	35.0
65.0	7.0	0.0	93.0

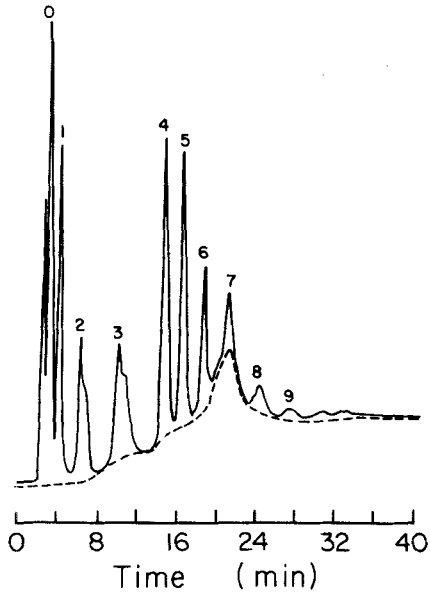

Figure 1: HPLC chromatogram of polyoxyethylene oleyl ester with 4.5 (av.) EO units (Mapeg-200). The peak number corresponds to the number of EO units on the fatty acid chain. The dashed line shows the baseline.

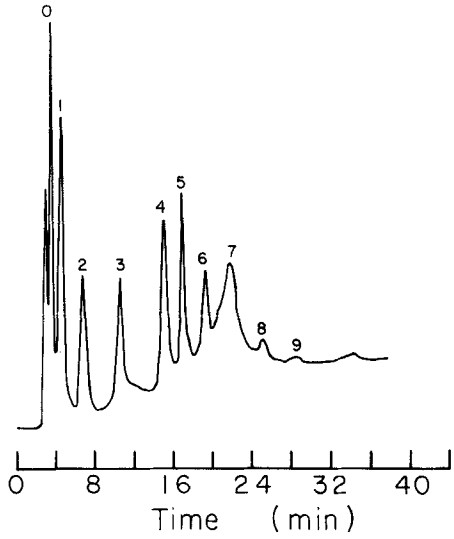

Figure 2: HPLC chromatogram of 9,10 dibromostearoyl-polyoxyethylene ester with 4.5 (av.) EO units.

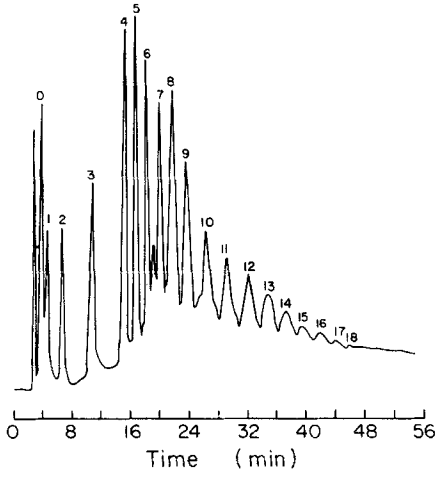

Figure 3: HPLC chromatogram of oleic acid (9) ethoxylated (Mapeg-400).

TABLE 2

Peaks Area Distribution of the Ethoxylated Oleic Acids Esters

Number of the peak in the Chromatogram	Relative area of the peaks (%)						
	Mapeg 200 (4.5 EO)	Mapeg 400 (9 EO)	Mapeg 600 (13.5 EO)	Myo 2 (2 EO)	Myo 10 (10 EO)	G 5507	G 2143
0	8.05	4.51	4.44	6.70	0.92	3.17	0.80
1	8.58	3.30		11.82	1.66	4.28	0.83
2	13.10	3.32		25.83	1.89	5.00	2.65
3	15.79	5.00		23.50	3.25	8.58	3.39
4	17.79	7.53	1.86	15.53	5.93	12.87	5.31
5	16.73	7.90	2.20	9.32	6.82	9.77	7.04
6	9.60	8.19	2.99	5.06	8.35	5.24	7.33
7	3.87	8.37	5.19	2.19	8.74	2.86	7.60

8	3.55	8.92	6.90	9.48	7.94	8.01
9	1.82	7.82	7.01	9.96	11.98	8.49
10	0.90	6.44	7.26	8.53	10.25	9.40
11		5.73	7.53	7.72	8.34	9.69
12		5.30	7.66	7.14	5.80	9.53
13		5.02	7.82	6.75	3.89	8.17
14		4.35	8.07	5.15		5.62
15		3.08	7.91	3.48		3.61
16		2.51	7.56	2.01		1.57
17		1.70	5.81	1.30		0.52
18		0.47	4.29	0.59		0.30
19			2.90	0.30		
20			1.69			
21			0.90			

obtained by chemical ionization mass-spectrometry. The numbers on top of each peak in the chromatogram stands for the number of EO units in the adduct, as confirmed by mass-spectra analysis. The dashed line in Figure 1 shows the baseline after addition of anthracene to the eluents to equalize its absorbance at 220 nm (8).

Figure 2 shows the chromatogram of Mapeg-200 after bromination in order to obtain 9,10-dibromostearoyl-polyoxyethylene ester with an average 4.5 EO units.

By doubling the number of EO units from 4.5 to 9 (molecular weight of ethoxylated chain 400;Mapeg-400) a more complicated chromatogram is obtained. Figure 3 illustrates that most isomers consist of 4 to 9 EO units. Nevertheless, one can see the appearance of all derivatives from peak 0 to 17 with excellent separation resolution.

It was impossible to identify existence of diesters probably due to their very high molecular weight. Therefore, Table 2 presents calculations of products distribution based on peak area. The diester isomers, although most probably exist in the product, were not taken under consideration. Table 2 shows that the commercial products are named according to the main isomers that have the highest accuracy in the compound. The areas were measured substracting any baseline shifts.

Evidently from Figure 4 it can be seen that the bromination does not drastically change the chromatogram fingerprints in spite the fact that the peaks are less pronounced due to the bromine addition to the chromophoric group.

Increasing the number of EO units to 13.5 caused the chromatogram to be quite difficult to interpret (see Figure 5 for Mapeg-600 and Figure 6 for the brominated Mapeg-600). Twenty one peaks were obtained. The most common isomers were 12-16 with good agreement with the manufacturer claim.

In order to evaluate the commercial materials and to find possible differences in their product distribution, two other ethoxylated oleyl esters with average 2 and 10 EO units were injected under similar conditions. As expected the product with two EO units (Myo-2; see Figure 7) will contain less EO units then the one with 4.5 EO (see Figure 1) therefore the main adducts will

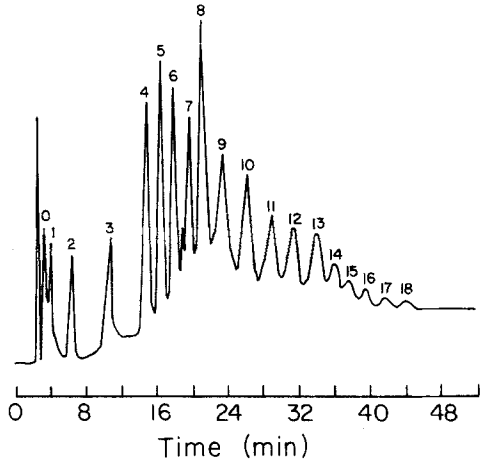

Figure 4: A typical HPLC chromatogram of 9,10 dibromostearoyl-polyoxyethylene ester with 9 (av.) EO units.

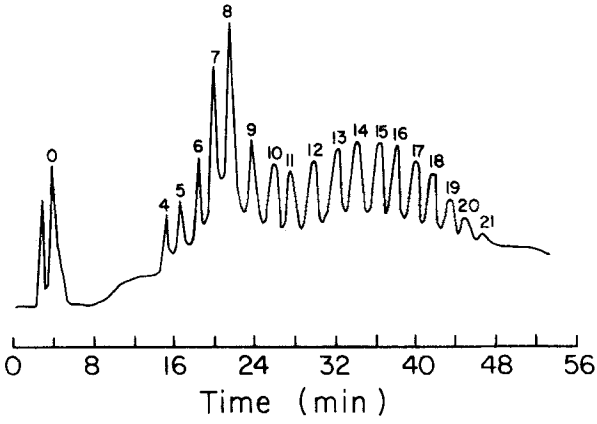

Figure 5: HPLC chromatogram of polyoxyethylene oleyl ester with 13.5 (av.) EO units (Mapeg-600).

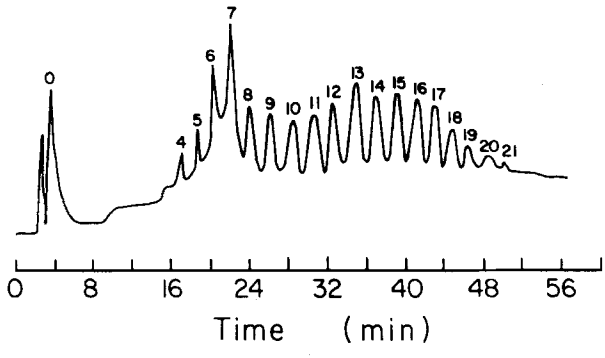

Figure 6: HPLC chromatogram of 9,10 dibromostearoyl-polyoxyethylene ester with 13.5 (av.) EO units.

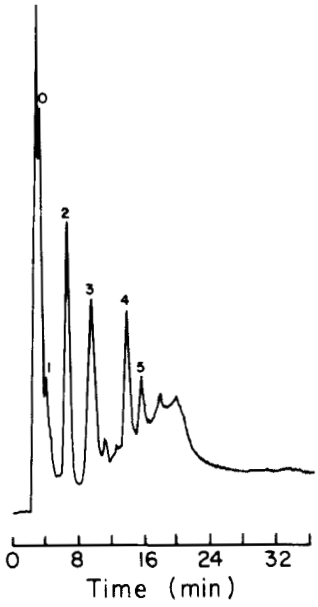

Figure 7: HPLC chromatogram of oleic acid (2) ethoxylated (Myo-2).

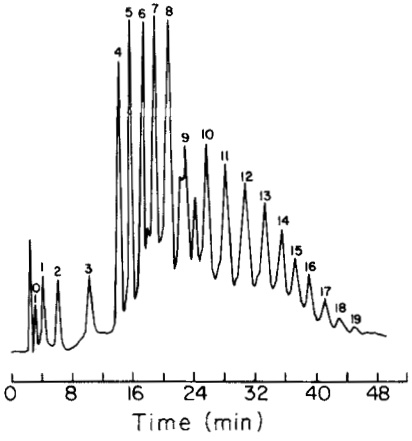

Figure 8: HPLC chromatogram of oleic acid (10) ethoxylated (Myo-10).

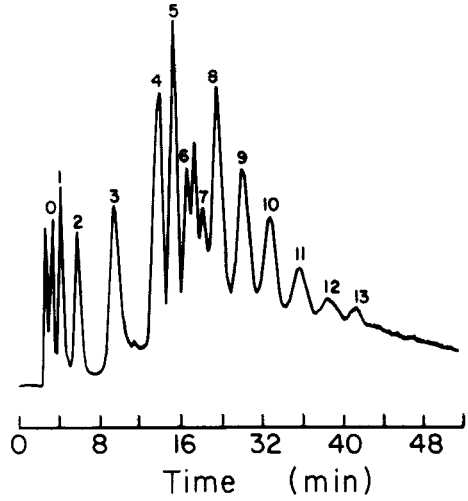

Figure 9: HPLC chromatogram of commercial polyoxyethylene oleate (G-5507).

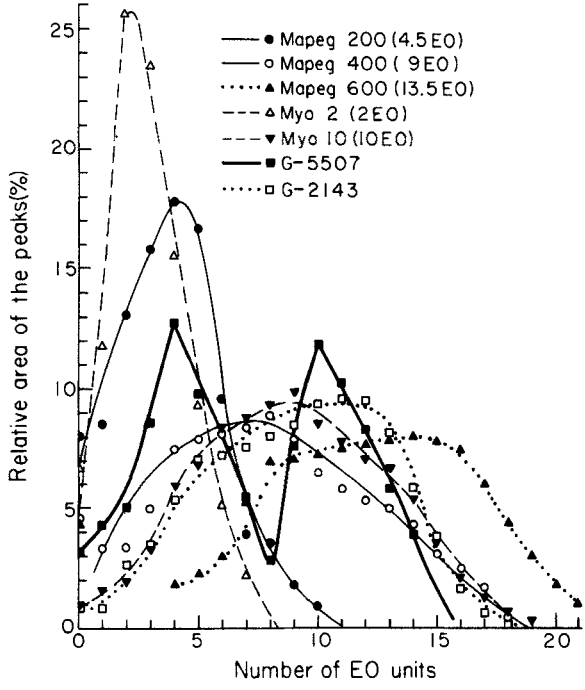

Figure 10: Illustration of the relative area distribution of the peaks versus the number of ethylene oxide units.

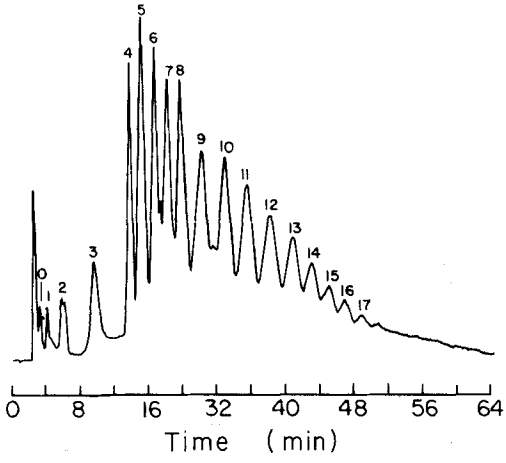

Figure 11: HPLC chromatogram of commercial polyoxyethylene oleate (G-2143).

appear under peak 2 and 3. Similarly, products containing 10 EO (Myo-10) will show quite identical chromatogram to the one with 9 EO units (Mapeg-400); (See Figure 8 and Figure 3).

When commercial surfactant identified only by its HLB (Hydrophilic Lipophilic Balance) value, without any other details or specification on a product's internal distribution one can use the HPLC method to have a full picture of its content. For example, two other commercial products from Atlas Europol (G-5507 HLB=10.4 and G-2143 HLB-12.2) were tested. A clear chromatogram was obtained (Figure 9) revealing that the first emulsifier is probably a mixture of two completely separate products. In order to distinguish between the mixture of the two surfactants and to obtain more accurate product distribution of the mixture a plot of relative area of the peaks versus number of EO units of all separated surfactants, including the G-5507, was demonstrated. It can be seen, for example, that Myo-2 has a maxima at 2 EO units with accordance to the manufacturer's claim. Similarly, all other surfactants have only one maxima revealing consistency of only one isomeric product. The G-5507 shows two peaks of 4 and 10 EO units. The other unknown surfactant G-2143 is probably a single product with average 10 EO units with a typical internal distribution (see Figures 10 and 11). While the second one (G-2143) is probably a single product

with average 10 EO units and typical internal distribution of the EO adducts (Figure 10).

CONCLUSION

The HPLC technique developed in this laboratory allows analysis, both qualitative and quantitative of any commercial ethoxylated fatty acid adducts or ethoxylated fatty alcohols. A simple injection of the crude product to the column, without the need for any pretreatment such as hydrolysis, acetylation of derivatization, is sufficient to obtain excellent separation. In addition, full identification of the adduct peaks was obtained using mass-spectrometry technique.

REFERENCES

1. Goldsmith, H.A., Polyhydric Alcohol Esters of Fatty Acids; Their Preparation, Properties, and Uses, Chem. Rev., 33, 257, 1943.

2. Stakovski, W.B., Huang, S.K. and Liss, R.L., Polyoxyethylene Esters of Fatty Acids, Surfactant Science Series, Vol. 1, Nonionic Surfactants, Schick, M.J., ed., Marcel Dekker, Inc., N.Y., pp. 142, 1966.

3. Tsuji, K. and Konishi, K., Gas Chromatographic Analysis of Ester-type Surfactants by Using Mixed Anhydride Reagent, J. Am. Oil Chem. Soc., 52, 106, 1975.

4. Aitzetmuller, K., Applications of Moving-wire Detectors for the Liquid Chromatography of Fats and Fatty Acid Derived Oleochemicals, J. Chromatog. Sci., 13, 454, 1975.

5. Bruschweiler, H., Analysis of Nonionic Surfactants (Emulsifiers) Using High-Pressure Column Chromatography, Mitt. Gebiete Lebensm. Hyg., 68, 46, 1977.

6. Nakamura, K. and Matsumoto, I., High-Speed Liquid Chromatography in Cosmetic Analysis. I. Analysis of Nonionic Surfactants of Ethylene Oxide Adducts, Nippon Kagaku Kaishi, 8, 1342, 1975.

7. Frenkel, M., Krauz, Z. and Garti, N., Brominated Surfactants as Emulsifiers and Weighting Agents. Part I: Preparation and Surface Properties, Colloids and Surfaces, 5, 353 (1982).

8. Aserin, A., Frenkel, M. and Garti, N., Analysis of Nonionic Surfactants. Part IV: Polyoxyethylene Fatty Alcohols, J. Am. Oil Chem. Soc. (in press).