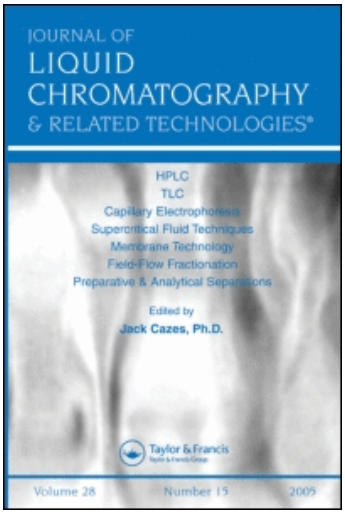

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Martin, N.(1995) 'Analysis of Non-ionic Surfactants by HPLC Using Evaporative Light-Scattering Detector', Journal of Liquid Chromatography & Related Technologies, 18: 6, 1173 — 1194
To link to this Article: DOI: 10.1080/10826079508009283
URL: http://dx.doi.org/10.1080/10826079508009283

JOURNAL OF LIQUID CHROMATOGRAPHY, 18(6), 1173-1194 (1995)

ANALYSIS OF NON-IONIC SURFACTANTS BY HPLC USING EVAPORATIVE LIGHT-SCATTERING DETECTOR

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ABSTRACT

The analysis of surfactants, the basis of numerous surface wetting agents, detergents, emulsifiers, cosmetic products... is frequently carried out by liquid chromatography. Unfortunately, the analyses are very complex because of the use of gradients and the lack of suitable chromophore.
The object of this study by HPLC using an evaporative light-scattering detector was to select chromatographic conditions that characterize the majority of the different non-ionic surfactants (ethoxylated, oxypropylated, propoethoxylated, ethopropoxylated), according to their hydrophobic and hydrophilic parts.

INTRODUCTION

Surfactants are widely used for a variety of purposes, including surface wetting agents, detergents, emulsifiers, cosmetic products. Adducts of ethylene oxide or

propylene oxide and fatty alcohols or acids are important nonionic surfactants commercially used for many years.

Several publications and litterature reviews are available that describe techniques developed for surfactant analysis. Difficulties are often encountered in many analytical methods due to the complex nature of the mixture and the lack of adequate detection capabilities. HPLC methods have been developed for the separation of non-ionic surfactants according to :

- their alkyl chain lengths using a refractometer in isocratic conditions (1),
- and the distribution of ethylene oxide or propylene oxide in adducts of ethylene oxide or propylene oxide with fatty alcohol (2)(3), with alkylphenol (4 - 7) or with fatty acid (8 - 10).

Lack of suitable chromophores in the most usual surfactants molecules limits the use of UV detectors. For POE or many POE adducts, derivatization is required for sensitive LC detection (11 - 15), but the sample preparation is time-consuming and can lead to sample losses and imprecision. "Universal detectors", such as the refractive index detector (RI) and the evaporative light-scattering detector (ELSD), are most commonly used in HPLC analysis of surfactants but RI precludes the use of gradients. So ELSD has rapidly gained popularity among surfactant analysts, one of its advantages being the possibility of using complex gradients.

The theory of the ELSD has been discussed in several papers (16 - 26). In the light-scattering detector the chromatographic solvent is first nebulized by a gas stream, and the vapor enters a heated tunnel, where the solvent evaporates. The remaining analyte particles pass through a narrow light beam, and the scattered light is collected by a photomultiplier. The response of the ELSD depends on the number and size of the analyte particles. It is a suitable detector for all types of compounds that are relatively non-volatile, like waxes, sugars, lipids, glycerides (27 - 33) and surfactants (34-40).

In our study, the following aliphatic surfactants, synthesized in our research center, were examined :

(a) non-ionic ethoxylated alcohols
(b) non-ionic ethoxylated acids
(c) non-ionic propoxylated alcohols
(d) non-ionic ethopropoxylated alcohols
(e) non-ionic propoethoxylated alcohols.

The chromatographic conditions, optimized to characterize the different surfactants rapidly (<30 mn), are also described.

MATERIAL

Instrumentation :

The HPLC system was composed of an HP series 1051 HPLC pump equipped with the light-scattering detector : Cunow DDL21. The gas used in the ELSD was nitrogen passed through a filter before entering the detector. The detector temperature was 40°C and the nitrogen pressure 2 bars. The photomultiplier sensitivity was adjusted to the value (450 m Volts) of the photomultiplier gain area (400-800 m Volts). The Penelson 2600 program (Perkin Elmer) on a Prolinea 4/33 Compaq was used for data compilation and processing.

Solvents

The mobile phase was an HPLC grade hexane, chloroform and methanol. Water for use in HPLC was purified with a MilliQ reagent water system from Millipore Waters.
All solvents were filtered through a 0.45 µm filter (Millex HV13 Millipore Waters).

Columns

Various stationary phases and columns were used :
- 5 µm Spherisorb NH2 (250mmx4.6mm I.D) (Prolabo)
- 5 µm Intersphere ODS2 (150mmx4.6mm I.D) (Interchim)
- 5 µm Lichrospher 60RP select B (125mmx4mm I.D) (Merck)

RESULTS AND DISCUSSION

Ethoxylated alcohols

The general formula for these alcohol surfactants is $RO(CH_2CH_2O)_nH$ where R is $C_{10}H_{21}$, $C_{12}H_{25}$ or $C_{14}H_{29}$ and the average value for n is 2, 4, 9, 12, 16.

The non-ionic ethoxylates were separated according to the number of ethylene oxide (EO) groups (n) using normal phase chromatography. After trying different types of columns (Lichrosorb Diol, Spherisorb CN et NH2), gradient shapes and various combinations of solvents, the separation was performed with a gradient of hexane/chloroform/methanol in 30 mn (table 1).
The flow rate varied between 1 and 1,2 ml/mn depending on n.

Fig 1/2 shows the HPLC profiles for the ethylene oxide condensate of an alcohol and a fatty alcohol. Using this technique, it is possible to separate components of each product according to n.(fig3a : n<10 and fig3b : n>10). Within each group, components are further separated according to the length of the alkyl chain, i.e C12 and C14. When the alkyl chain is complex (mixture, presence of ramification...), the chromatogram is more complicated (fig4). We obtained the same results as Bear (34) using HPLC/ELSD, but in 30 mn instead of 50 mn. The EO distribution is shown to be between 1 and 30 for n = 16.

Normalized peak areas were used to calculate the average number (n) of the distribution of the oligomers : $n = \Sigma ni Ai / \Sigma Ai$, we observed good repeatability between three injections of the same product (fig5).

Studies have been also carried out with reversed phase chromatography to obtain the simplest chromatographic fingerprint, but showing different alkyl chain lengths present in these polyethoxylated alcohol mixtures. The separation was performed with a Lichrospher 60 RP Select B column in methanol - water (80/20) without gradient elution. The flow rate was 1 ml/mn. Such systems allowed, first, the elution of PEGs, then surfactants according to their alkyl chain length (fig6).

TABLE 1

Gradient Elution Program for Normal Phase HPLC of Non-Ionic Ethoxylated Alcohols

Time (min)	Hexane (%)	Chloroform (%)	Methanol (%)
0	76	19	5
10	72	18	10
20	64	16	20
30	56	14	30

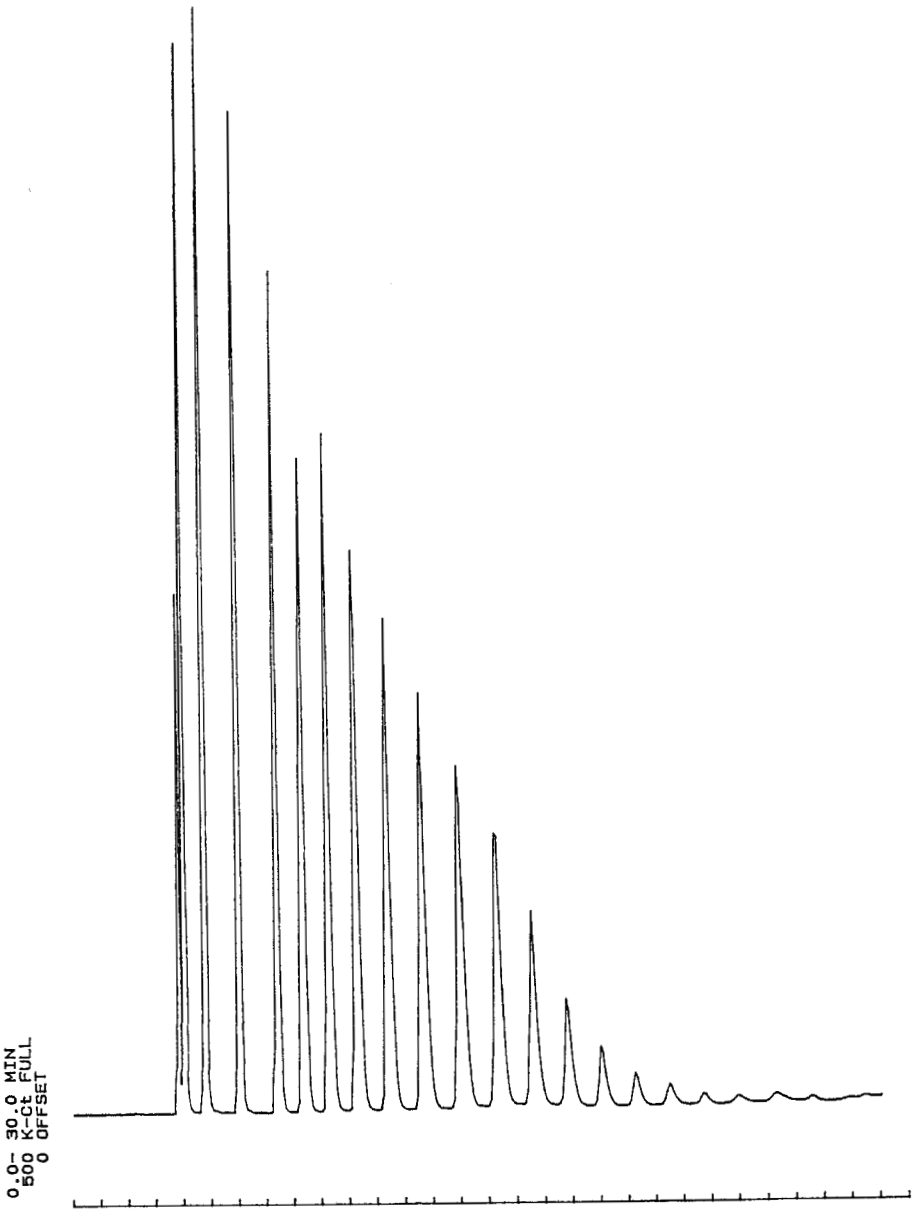

FIGURE 1 : HPLC profile for the ethylene oxide condensate of an alcohol

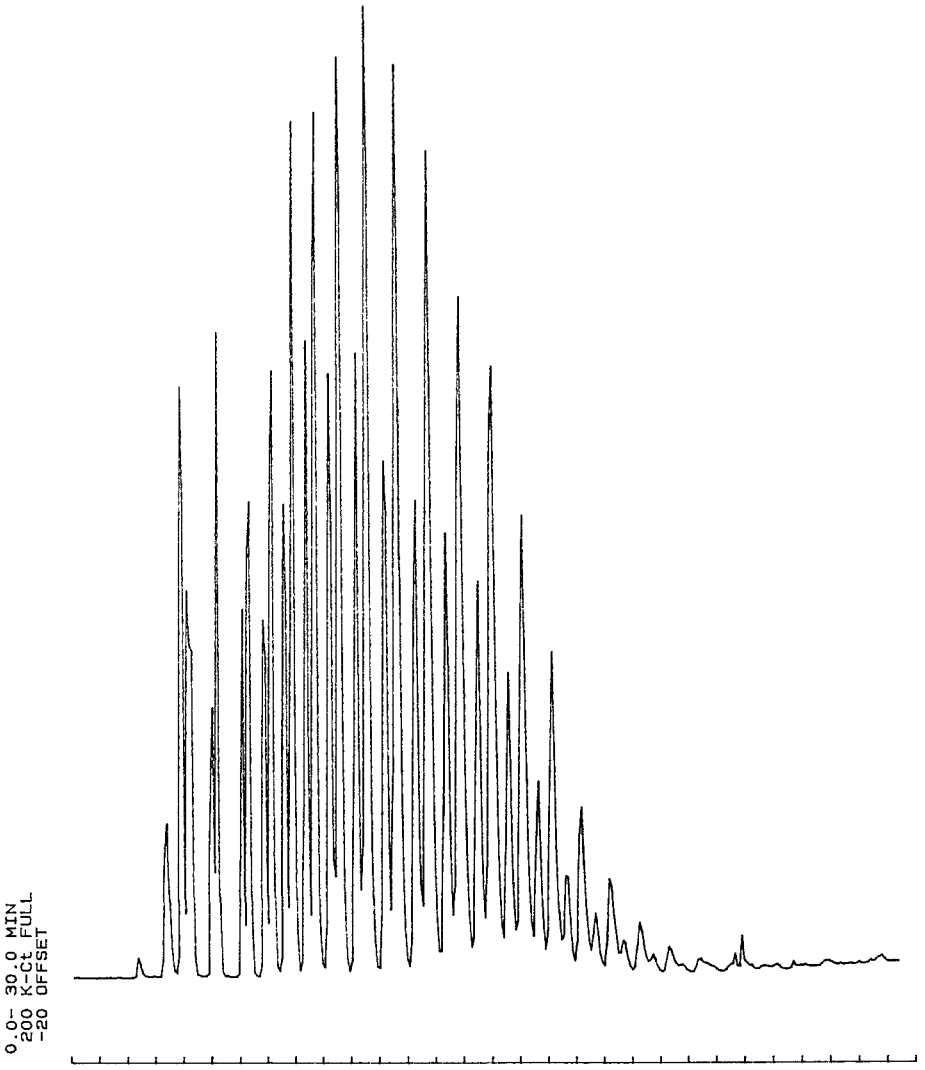

FIGURE 2 : HPLC profile for the ethylene oxide condensate of a fatty alcohol

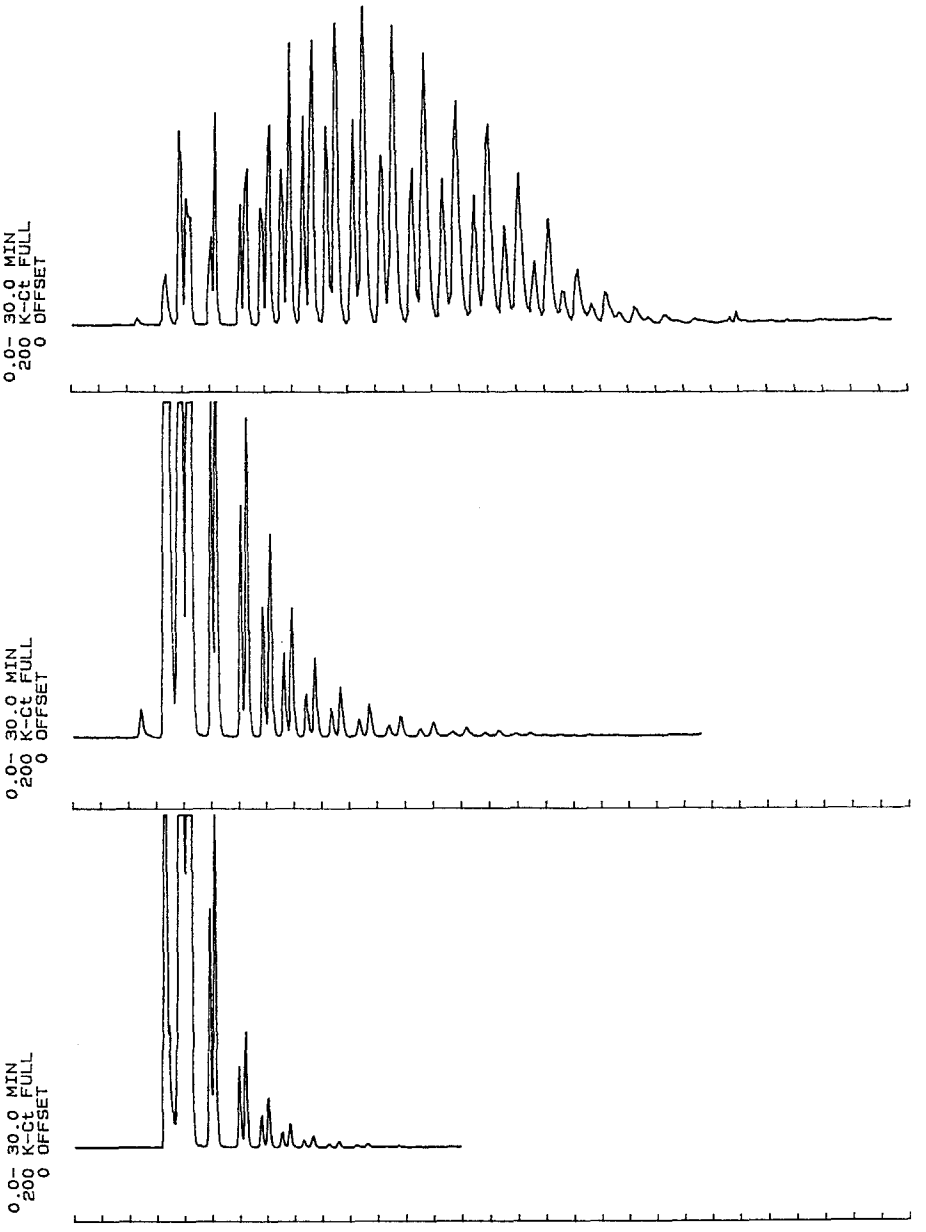

FIGURE 3a : HPLC profiles for the ethylene oxide condensate of fatty alcohols (n<10)

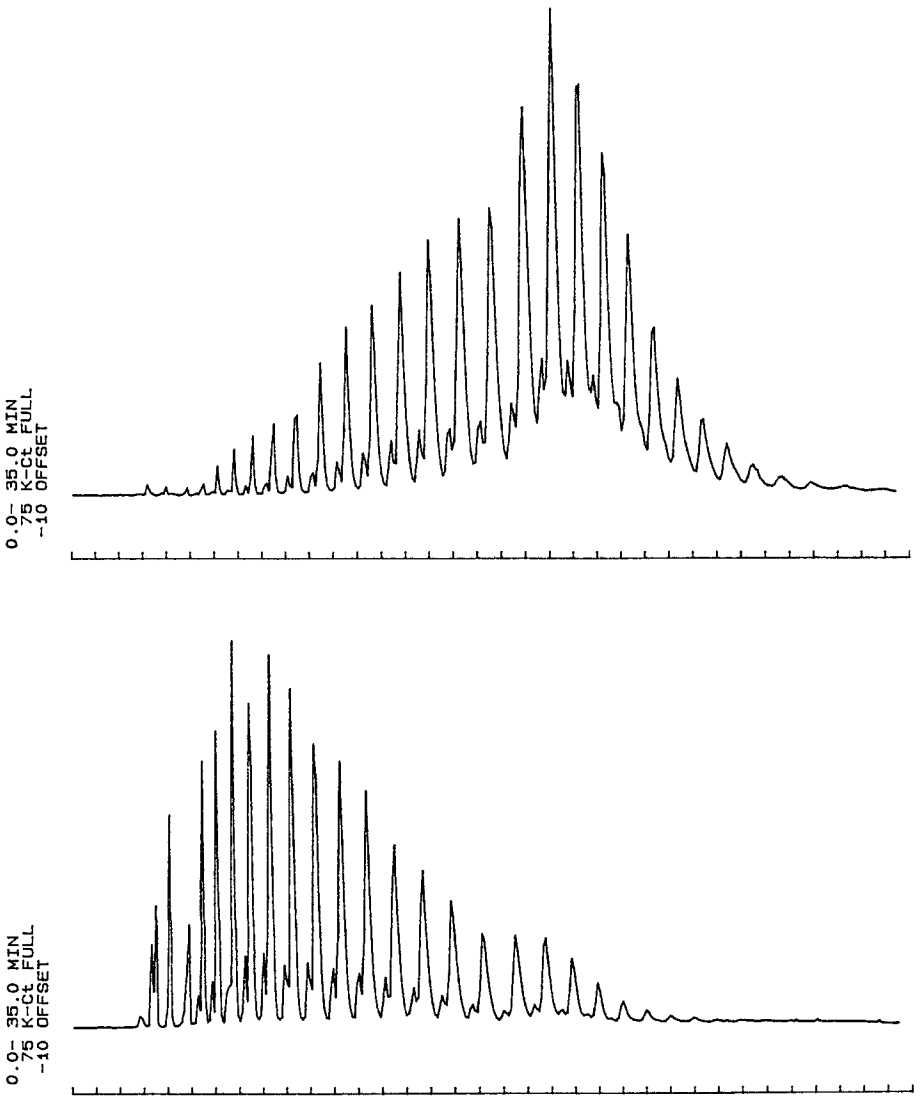

FIGURE 3b : HPLC profiles for the ethylene oxide condensate of fatty alcohol (n>10)

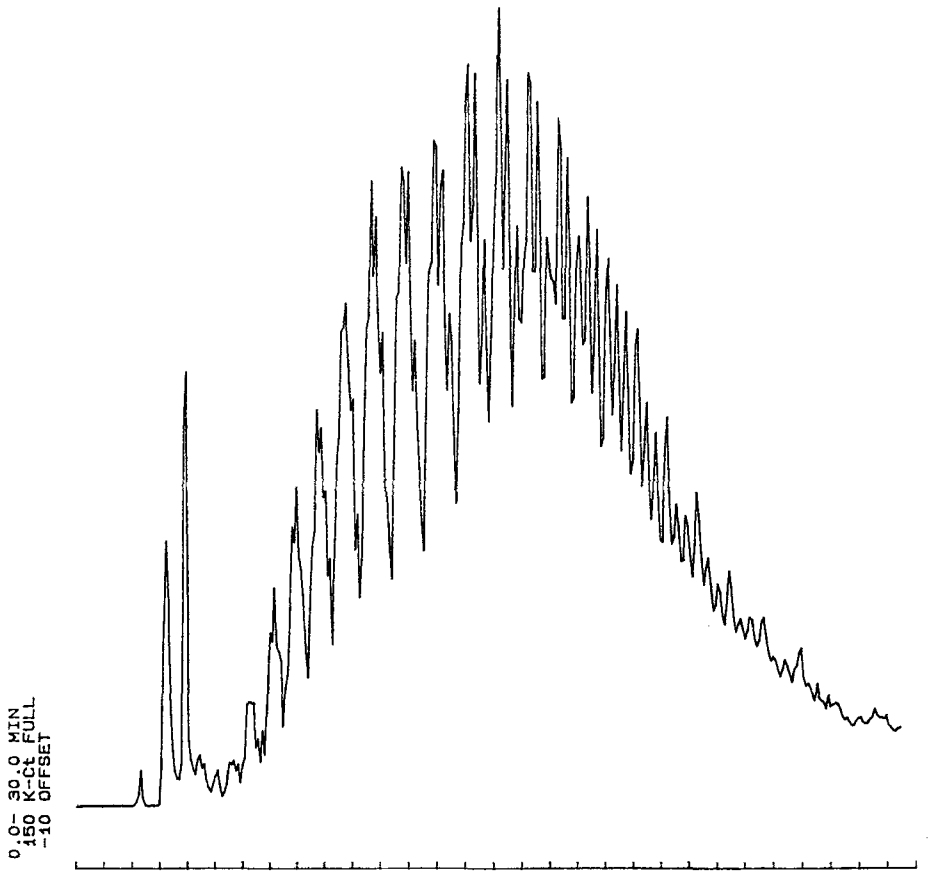

FIGURE 4 : HPLC profile for the ethylene oxide condensate of a fatty alcohol with a complex alkyl chain

Ethoxylated acids

The complete analysis of products from the reactions of fatty acids (FA) with ethylene oxide was even more complicated than for other analogous surfactants. In the reaction mixture not only the presence of main reaction products is to be expected (i.e monoesters (MES) and diesters (DES) with ethylene glycol oligomers), but also the presence of free PEG and fatty acids as by-products.

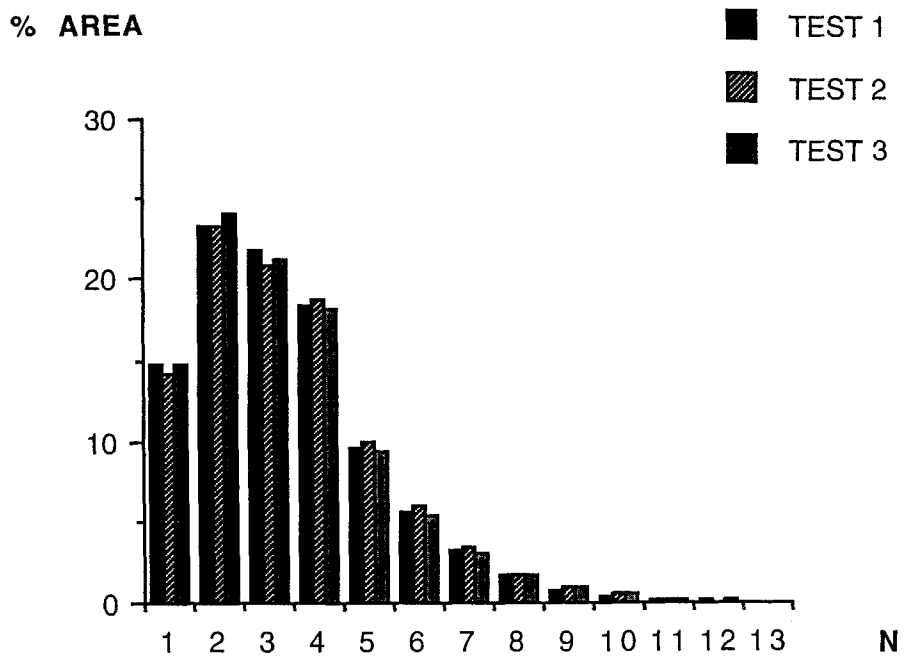

FIGURE 5 : Study of the repeatability of the distribution of the oligomers of an ethoxylated alcohol

Using an NH2 column with a Hexane/chloroform/methanol gradient quite different from that of ethoxylated alcohol (table2), the complete composition of FA ethoxylation products can be determined in 30 mn. Different examples of the complete separation of fatty acid (oleic) ethoxylate of different ethoxylation degrees (n = 6, 9, 15) are shown in fig7. Diester, monoester and PEG are found, just as Zeman observed using a refractometer (9)(10). Diester adduct oligomers remained unresolved in a single peak, whereas the monoester adduct and PEG oligomers are separated into individual oligomers.

Normalized peak areas were used to calculate the percent composition of each di, monoester and PEG. We observed good repeatability between 4 injections, and the percent of DES decreased when n rose (table 3), as Zeman observed (9).

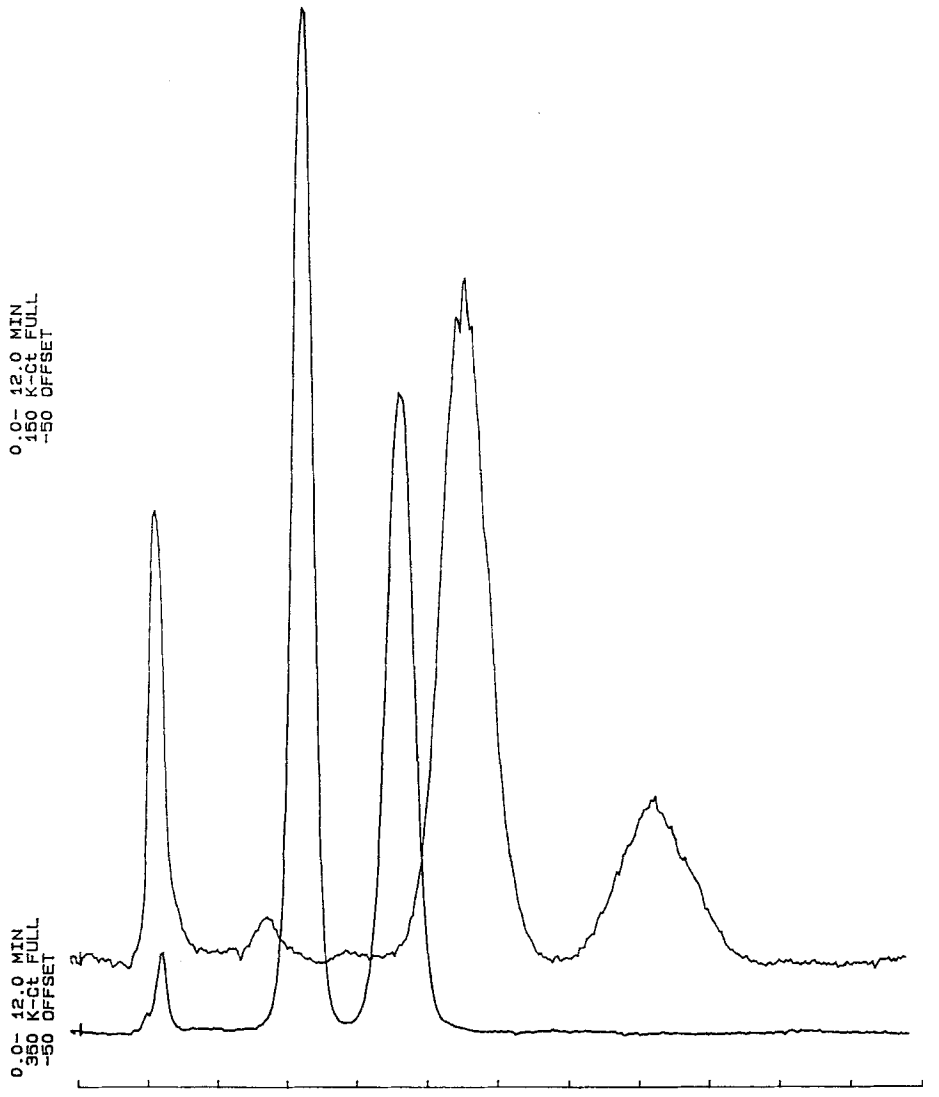

FIGURE 6 : Study of surfactants according to their alkyl chain length

TABLE 2

Gradient Elution Program for Normal Phase HPLC of Non-Ionic Ethoxylated Acids (Area %)

Time (min.)	Hexane (%)	Chloroform (%)	Methanol (%)
0	75	20	5
10	64	16	20
20	50	12.5	37.5
30	50	12.5	37.5

Oxypropylated alcohol and Propoethoxylated or ethopropoxylated alcohols

A sample of an oxypropylated alcohol was analyzed by means of HPLC on an NH2 column and by reversed phase HPLC on a C18 column. With the NH2 column, we observed only one peak.

The distribution of oligomer PO adducts was determined on an Interspher ODS2 C18 column (fig8), using a methanol/water gradient.

Furthermore, the complete analysis of products from the adduct of propylene oxide and ethoxylated alcohol is even more complicated because of the complexity of this mixture. In fact, the propylene oxide reacts partially with the ethoxylated alcohol and with the free PEG. Using the reversed phase chromatography described earlier, it is possible to separate the copolymer PEG/PPG, the free ethoxylated alcohol and the distribution of the propoethoxylated alcohol in 30 mn (fig9). We were able to observe how the distribution of the oligomers between two alcohols (C10 7OE/3OP and 7OE/5OP) evolved (fig10).

In contrast, the adduct of ethoxylene oxide and propoxylated alcohol was studied using the normal phase chromatography described earlier for ethoxylated alcohols. In this case it is possible to separate the copolymer PPG/PEG and the distribution of the ethopropoxylated alcohol. We observed the evolution of the distribution of the oligomers between 4 ethopropoxylated alcohols (C10 2OP/3,5,8,10OE) (fig11). In fact, using the reversed phase chromatography described earlier for the propoxylated alcohols and by comparing the result with that obtained from the injection of an ethoxylated alcohol (fig12), we also saw the formation of free ethoxylated alcohol, a by-product of the adduct of ethylene oxide and free alcohol .

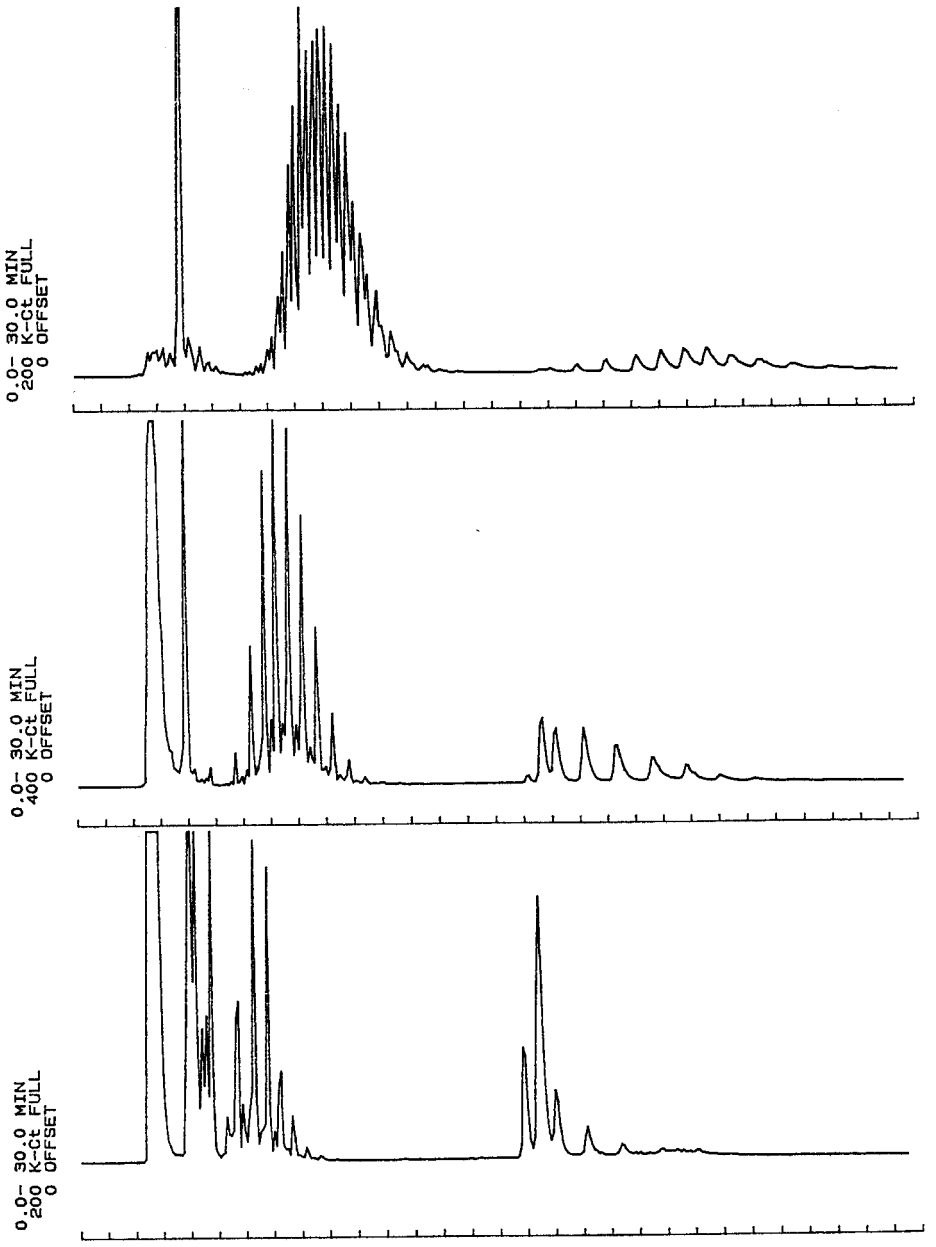

FIGURE 7 : HPLC profiles for the ethylene oxide condensate of fatty acids

TABLE 3

Composition of Ethoxylated Fatty Acids (Area %)

EO moles	% DES	% MES	% PEG
6	48	43	10
6	48	41	11
6	49	40	11
6	50	39	11
9	33	52	15
15	2	91	7

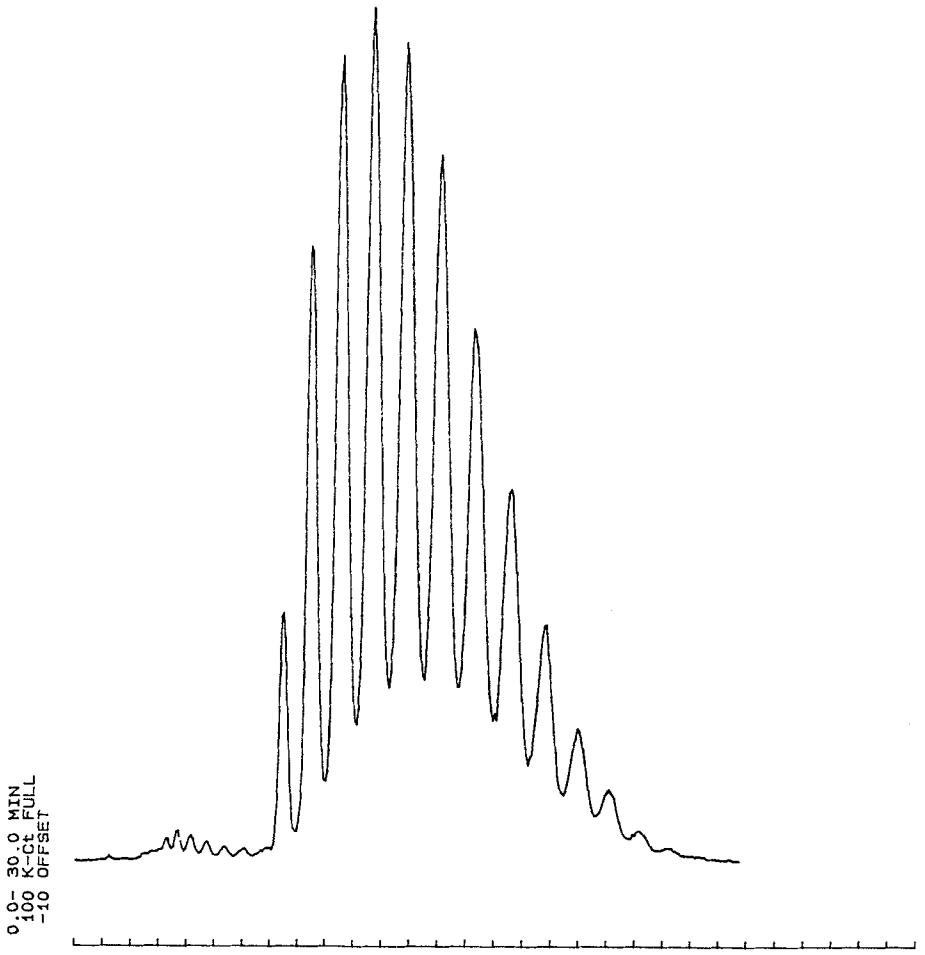

FIGURE 8 : HPLC profile for the propylene oxide condensate of an alcohol

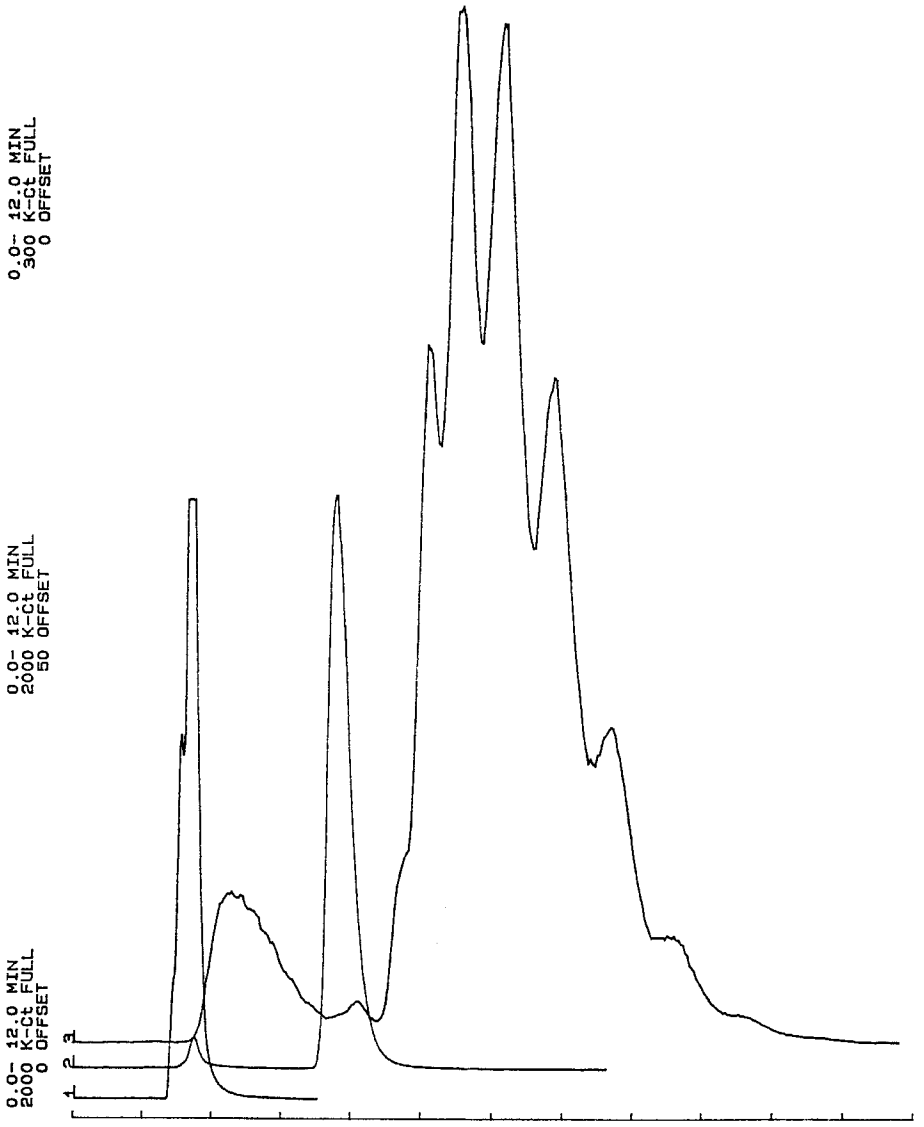

FIGURE 9 : HPLC profile for the propoethoxylated alcohol

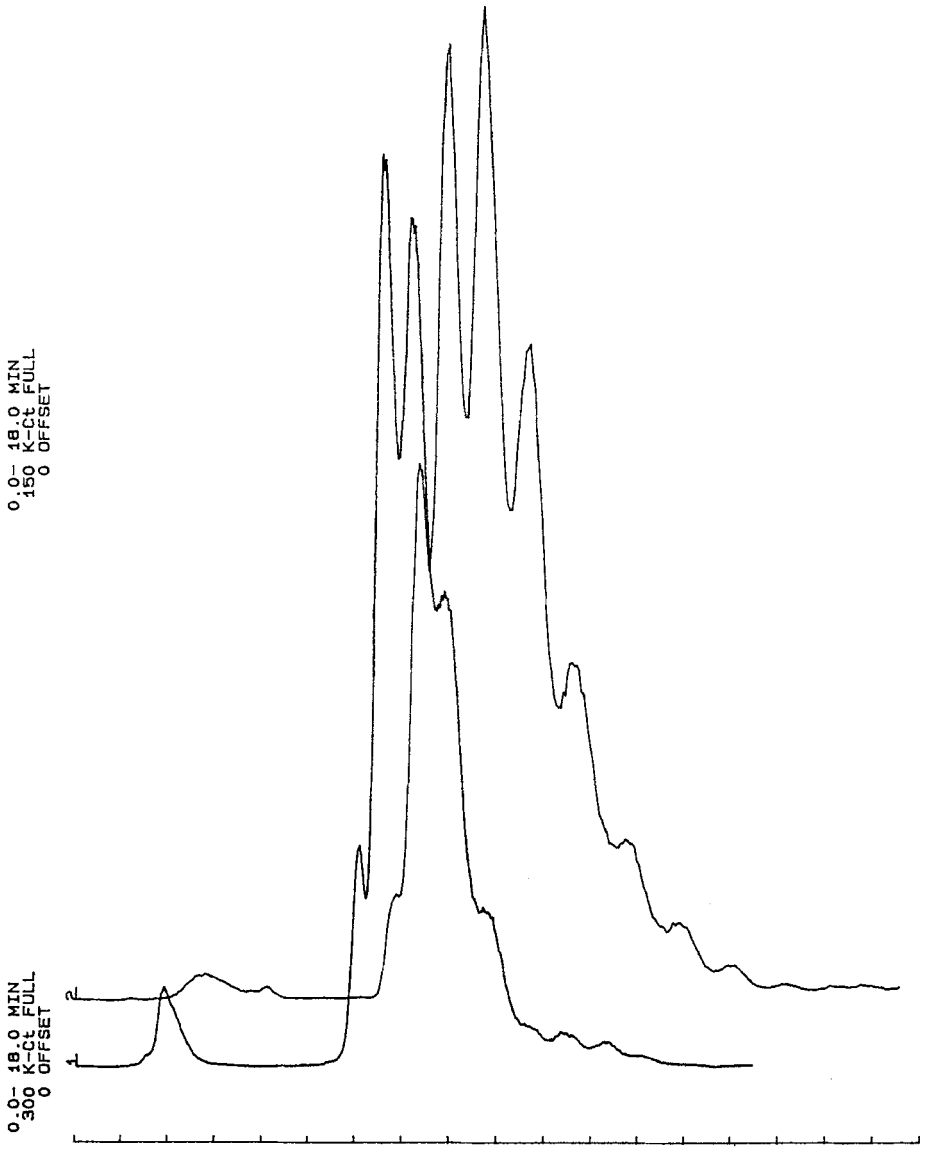

FIGURE 10 : Evolution of the distribution of the oligomers between two alcohols C10 7OE/30P et 70E/5OP

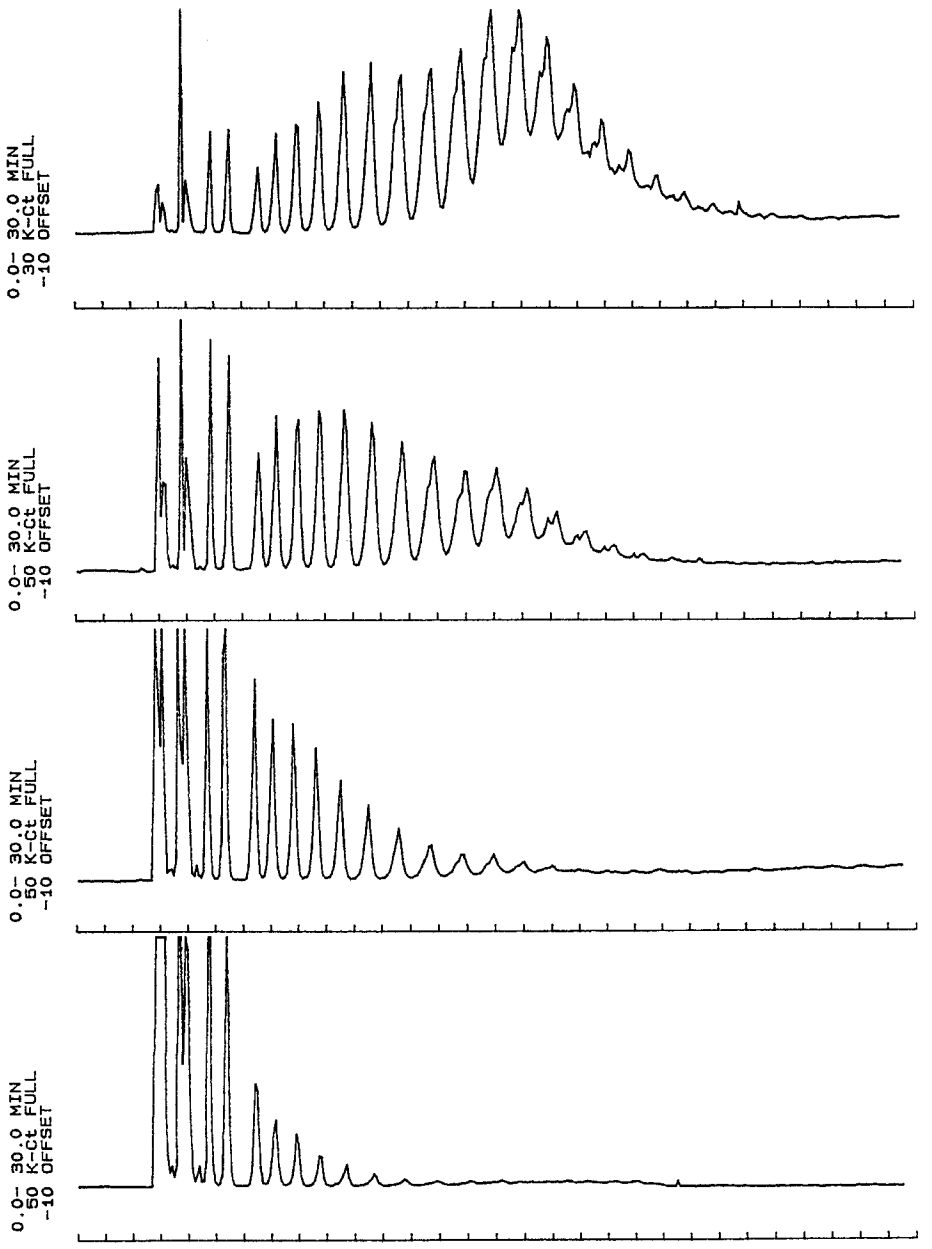

FIGURE 11 : HPLC profiles for ethopropoxylated alcohols C10 2OP/3.5-8-10 OE

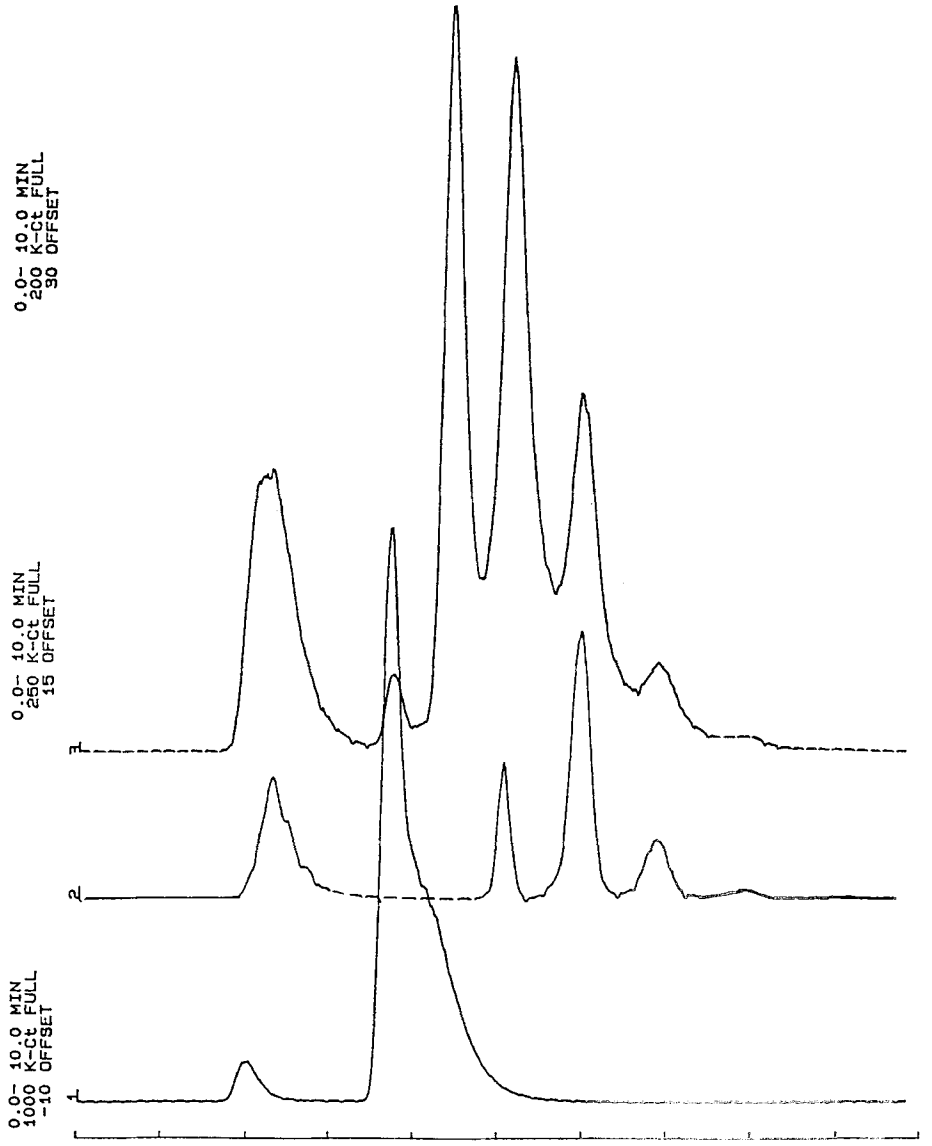

FIGURE 12 : Study of the formation of free ethoxylated alcohol in a ethopropoxylated alcohol

TABLE 4

Gradient Elution Program for Reversed Phase HPLC of Oxypropylated Alcohol

Time (min)	Methanol (Vol %)	Water (Vol %)
0	85	15
20	5	95
30	5	95

Owing to the characteristic chromatographic fingerprints in normal or reversed phase HPLC, several block oligomer POE/PPG or PPG/POE alcohols can be identified.

CONCLUSIONS

The HPLC/ELSD procedures presented here provide separations for a wide range of non-ionic aliphatic surfactants. For routine characterization, normal phase (NH2 column) and reversed phase (C18 column) HPLC are effective for the separation of ethoxylated or propoxylated oligomers.

To our knowledge, chromatography of PPG, POE/PPG or PPG/POE alcohols or POE acids had not been previously performed with HPLC/ELSD for all products and in a short time (<30 mn). HPLC/ELSD methods are sampler and faster than HPLC/RI.

ACKNOWLEDGEMENTS

The author wishes to thank J M. Mercier for the synthesis of surfactants.

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Received: October 3, 1994
Accepted: October 18, 1994