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Comparison of ethoxylated alcohols and polyethylene glycols by high-performance liquid chromatography and supercritical fluid chromatography using evaporative light-scattering detection☆

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ABSTRACT

Ethoxylated alcohols are surfactants whose oligomer distributions are conventionally determined by high-performance liquid chromatography. However, this method cannot resolve individual oligomers with a high degree of ethoxylation. Further, normal- and reversed-phase liquid chromatography cannot give the fingerprints for both the ethoxylated alcohols and polyethylene glycols, the synthetic residues without surfactant properties. Supercritical fluid chromatography coupled with evaporative light-scattering detection was developed for the analysis of these mixtures which do not contain chromophores.

INTRODUCTION

Commercial surfactant compounds [C_nH_{2n+1}-$(OCH_2CH_2)_xOH$] are complex mixtures because of the various numbers of ethylene oxide units declared by the manufacturer. They are synthesized by condensation of ethylene oxide units on a long chain alcohol ($C_nH_{2n+1}OH$) and, as a result, the oligomer index (x) varies over a considerable range [x = 2–40 ethylene oxide (EO) units for BC–X (see Experimental part)]. Further, when the starting alcohol is an isomeric mixture, the chromatographic fingerprint becomes more complex. Moreover, these surfactant mixtures can contain polyethylene glycols (PEGs), synthetic residues without surfactant properties. McClure [1] proposed a method using chemical derivatization to eliminate terminal hydroxyl groups from the surfactant mixtures. However, these groups undergo derivatization, thus altering the chromatographic properties. Zeman [2] used a back-flushing technique in order to elute PEGs. These compounds are strongly adsorbed on polar stationary phases. In addition to the difficulty of obtaining a good separation of individual ethylene oxides, detection is problematic. For non-UV-absorbing compounds, hydroxyl groups derivatized with 3,5-dinitrobenzoyl chloride allow, for example, UV detection [3,4], but, this involves a supplementary step in the analysis. With alkylphenol ethoxylated oligomers, Bear [5] and Ahel and Geiger [6] pointed out that the UV response depends on the number of ethylene oxide units, and this behaviour makes quantitative analysis difficult. Moreover, the differential refractometer is not adapted to the study of these mixtures because only an isocratic analysis is possible, which causes the peaks occuring near the end of the chromatogram to be deformed and too weak. Gradient elution is possible with flame ionization detection (FID) [1,7,8], but for very small amounts it is not sensitive enough for a proper analysis. For these reasons, the evaporative

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light-scattering detection (ELSD) appeared to be the best choice for this type of study [9,10] because the instrumentation is universally available and the method is sensitive (20 ng) and compatible with gradient elution.

Supercritical fluid chromatography (SFC) with capillary columns has been used as a complementary technique in the analysis of PEGs because of its capacity for new selectivities, hence circumventing the limitations of high-performance liquid chromatography (HPLC). However, surfactants having high molecular weights were not resolved. Moreover, simultaneous analysis of the two families (ethoxylated alcohols and PEGs) was not mentioned, and the analysis times were long [11–13]. Giorgetti *et al.* [14] applied packed columns to analyses of surfactants containing chromophores. In SFC on packed columns it appeared necessary to add polar modifiers to the supercritical fluid to elute these compounds. This allows the neutralization of residual silanol groups on bonded silica. This is the reason why FID cannot be used for the non-UV-absorbing compounds. Thus ELSD seems to be a quasi-universal detection method for SFC on packed columns [15]. Hagen *et al.* [16] recently used ELSD with polymeric particles as stationary phase to resolve PEG 1000, but there was no mention of surfactant analyses.

The aim of this work was to show the superiority of SFC over HPLC and to illustrate the coupling of SFC and ELSD to resolve PEGs and surfactants. Thus we used HPLC and SFC to resolve the ethylene oxide oligomer distributions inside of each of these two families.

EXPERIMENTAL

Apparatus

In HPLC, a Bruker Model LC-31 ternary pump (Merck, Darmstadt, Germany) was coupled with a Sedex 45 evaporative light-scattering detector (Sedere, Vitry-sur-Seine, France).

The SFC apparatus was as follows. Carbon dioxide was pumped with a Waters (Milford, MA, USA) Model M 501 pump. An ethanol cooling bath was used to cool the pump head in order to increase the pump-down efficiency. A polar modifier was added using a Jasco (Tokyo, Japan) Model 2510 pump. The two solvents were mixed at a controlled temperature (Jasco 860-CO oven) in a dynamic mixing chamber (Knauer, Berlin, Germany). An injection valve was placed in the Jasco oven. A Sedex Model 45 evaporative light-scattering detector with the interface adjusted to SFC was used.

Chromatographic columns

Various stationary phases and columns were used: 5-μm LiChrospher Diol, 125 mm × 4 mm I.D. (Merck); 5-μm Hypersil C_{18}, 150 mm × 4.6 mm I.D. (Shandon, Runcorn, UK); 5-μm Nucleosil C_{18}, 150 mm × 4.6 mm I.D. (Macherey-Nagel, Düren, Germany); 5-μm PLRPS, 150 mm × 4.6 mm I.D. (Polymer Labs., Shropshire, UK); 5-μm Zorbax Sil, 150 mm × 4.6 mm I.D. (DuPont, Wilmington, DE, USA); 5-μm Zorbax Diol, 250 mm × 9.4 mm I.D. (DuPont); and 5-μm Ultrasphere Si, 250 mm × 4.6 mm I.D. (Beckman, Berkeley, CA, USA).

Chemicals and reagents

Carbon dioxide was of B 50 grade (Air Liquide, Paris, France), methanol of HPLC grade (Prolabo) and all other polar modifiers of analytical-reagent grade.

Brij 76, BC-10, BC-20, BC-30 and BC-40 [$C_{16}H_{33}(OCH_2CH_2)_xOH$] are complex industrial mixtures purchased from Nikko Chemicals (Tokyo, Japan). $C_{12}H_{25}(OCH_2CH_2)_9OH$ are industrial mixtures (Diversey, Ozoir la Ferrière, France). Ethylene glycol monohexadecyl ($C_{16}OE_1$), diethylene glycol monohexadecyl ($C_{16}OE_2$), tetraethylene glycol monohexadecyl ($C_{16}OE_4$), hexaethylene glycol monohexadecyl ($C_{16}OE_6$), hexaethylene glycol monodecyl ($C_{10}OE_6$), hexaethylene glycol monododecyl ($C_{12}OE_6$), hexaethylene glycol monotetradecyl ($C_{14}OE_6$) and hexaethylene glycol monooctadecyl ethers ($C_{18}OE_6$) and androsterone were purchased from Fluka (Buchs, Switzerland).

PEG 300, 400 and 1540 waxes were used as stationary phases in gas chromatography.

RESULTS AND DISCUSSION

High-performance liquid chromatography

Normal-phase HPLC is the technique mainly used for surfactant analyses because it furnishes rich fingerprints. Bonded silicas with groups such as diol and amino were used instead of bare silicas

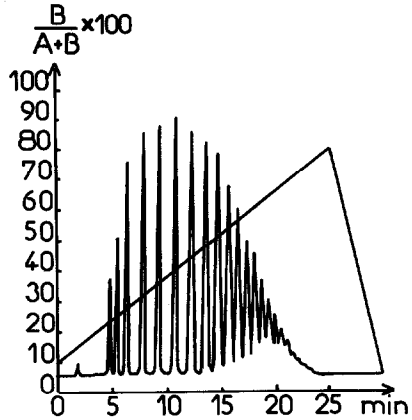

Fig. 1. Brij 76, $C_{18}H_{37}(OCH_2CH_2)_{10}OH$. Chromatographic conditions: column, LiChrospher 100 Diol (125 mm × 4 mm I.D.); mobile phase, linear gradient from 90% to 20% A in 25 min, A = hexane, B = chloroform–2-propanol (98:2); flow-rate, 1 ml min^{-1}; detection, ELSD.

because the activity of the latter depends on the amount of water in the mobile phase, making column equilibration time very long. *n*-Hexane–2-propanol–water mixtures are often used as mobile phases [3,4] because chloroform and dichloromethane cause a baseline drift in UV detection with gradient elution and a decrease in sensitivity. On the other hand, the use of *n*-hexane–dichloromethane–methanol mixtures with ELSD affords different polarities. Dichloromethane can be replaced with chloroform because of its larger donor character, and 2-propanol is easier to use than methanol for regulating retention times. Fig. 1 shows a very good separation of a surfactant mixtures having an octadecyl chain and an average of ten EO (according to the manufacturer). These oligomers without chromophores are detected by ELSD and the gradient elution does not cause baseline drift. In normal-phase elution, mixtures are separated according to the number of EO units (x). The retention of lower molecular weight oligomers increases with increasing number of repeat EO units (Table I). However, normal-phase HPLC has the following four major drawbacks: (1) for high-molecular-weight surfactants, the resolution of oligomers decreases with increase in the number of EO units (Fig. 1); (2) when there are over twenty EO units, these surfactant mixtures are completely adsorbed on a chromatographic support; these mixtures can be desorbed

TABLE I

RETENTION TIMES OF PURE ETHOXYLATED ALCOHOLS HAVING THE SAME ALKYL CHAIN LENGTH

Chromatographic conditions: column, LiChrospher 100 Diol (125 mm × 4 mm I.D.); mobile phase, linear gradient from 90% to 20% A in 25 min, A = hexane, B = chloroform–2-propanol (98:2); flow-rate, 1 ml min^{-1}; detection, ELSD.

Compound	Retention time (min)
$C_{16}H_{33}OE_1$	2.99
$C_{16}H_{33}OE_2$	4.51
$C_{16}H_{33}OE_4$	7.38
$C_{16}H_{33}OE_6$	10.65

with a considerable increase in the alcohol content in the mobile phase (methanol, ethanol, 2-propanol, etc.), but all species are eluted as a single peak without any resolution under such elution conditions; (3) the same chromatographic system is not able to resolve PEGs and ethoxylated alcohol mixtures; and (4) Table II shows that normal-phase chromatography cannot resolve alkyl chain homologues with common degrees of ethoxylation.

Consequently, studies [4] have been carried out in reversed-phase chromatography to obtain the simplest chromatographic fingerprint but showing different alkyl chain lenghts present in these polyethoxylated alcohol mixtures. Such systems allowed, first, the elution of PEGs, then surfactants according to their alkyl chain length in methanol–water without gradient elution (Fig. 2). The retention times of the second and third chromatographic peaks corresponded to those of the $C_{16}OE_6$ and

TABLE II

RETENTION TIMES OF PURE ETHOXYLATED ALCOHOLS HAVING THE SAME NUMBER OF EO UNITS

Chromatographic conditions as in Table I.

Compound	Retention time (min)
$C_{10}H_{21}OE_6$	10.99
$C_{12}H_{25}OE_6$	10.93
$C_{14}H_{29}OE_6$	10.71
$C_{16}H_{33}OE_6$	10.65
$C_{18}H_{37}OE_6$	10.47

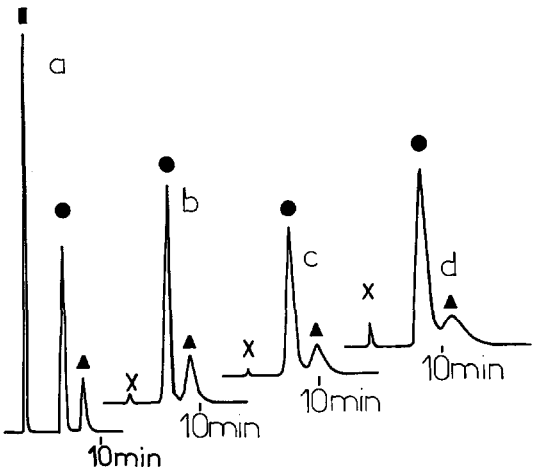

Fig. 2. (a) ■ = PEG 300; ●,▲ = BC-7; ● = BC7–C_{16}; ▲ = BC7–C_{18}. (b) × = Unknown; ●,▲ = BC-20; ● = BC20–C_{16}; ▲ = BC20–C_{18}. (c) × = Unknown; ●,▲ = BC-30; ● = BC30–C_{16}; ▲ = BC30–C_{18}. (d) × = Unknown ●,▲ = BC-40; ● = BC40–C_{16}; ▲ = BC40–C_{18}. Chromatographic conditions: column, Nucleosil C_{18} (150 mm × 4.6 mm I.D.); mobile phase, methanol–water (19:1); flow-rate, 1 ml min^{-1}; pressure, 104 atm; detection, ELSD.

$C_{18}OE_6$ standards, respectively, indicating that the starting alcohol is a mixture. The reversed-phase system allows an easy separation according to the number of methylene units (Fig. 3). Moreover, several studies [17] showed, contrary to the normal-phase system, good resolutions of PEGs with the reversed-phase system but poor surfactant fingerprints (Fig. 4). The results were similar with many apolar adsorbents using alkyl, TMS, C_8 or C_{18}

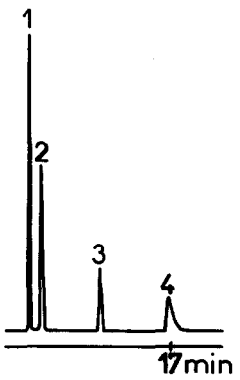

Fig. 3. 1 = PEG 300; 2 = $C_{10}OE_6$; 3 = $C_{14}OE_6$; 4 = $C_{18}OE_6$. Chromatographic conditions: column, Hypersil C_{18} (150 mm × 4.6 mm I.D.); mobile phase, methanol–water (9:1); flow-rate, 1 ml min^{-1}; pressure, 49 atm; detection, ELSD.

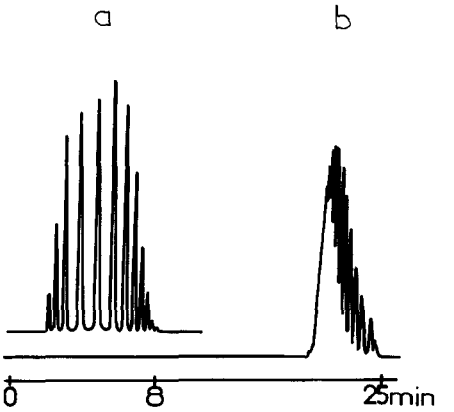

Fig. 4. Chromatograms of (a) PEG 400 and (b) $C_{12}H_{25}(OCH_2CH_2)_9OH$. Chromatographic conditions: column, PLRP-S (150 mm × 4.6 mm I.D.), mobile phase, linear gradient from 10% to 90% A in 30 min, A = acetonitrile, B = water; flow-rate, 1 ml min^{-1}; detection, ELSD.

types of bonded silicas or polymeric particles. The advantage of combined HPLC–ELSD, as shown in Fig. 2, is the possibility of performing a fast determination of each component. Indeed, Ahel and Giger [6] and Bear [5] pointed out the dependence between the polyethoxylated alkylphenol UV response and the number of EO units, whereas the PEGs cannot be detected. ELSD is universal in that all of these ethoxylated products have similar response factors, as shown in Fig. 5. When methanol–water mixtures are used as the eluent and solvent, linear calibration graphs, log (peak area) = f[log (concentration)] are parallel for PEGs and surfactants and also for androsterone, which is a different component used as a reference. The quantitative analysis of one family of mixtures can be achieved with a precision of less than 20% [18].

If the eluent and solvent are a dichloromethane–methanol mixture, a similar response for the same oligomer series can be observed, except for androsterone and PEG 300 (Fig. 6). Androsterone is a solid whereas PEG 300 is a liquid and the other families are waxy. When nebulization occurs, the particle size of drops may be affected by mobile phase characteristics such as density, viscosity, surface tension and velocity, thus explaining the differences in response curves observed. After evaporation of the organic solvent (dichloromethane–methanol) and just before detection, the microparticles probably return to an aspect close to their physical state,

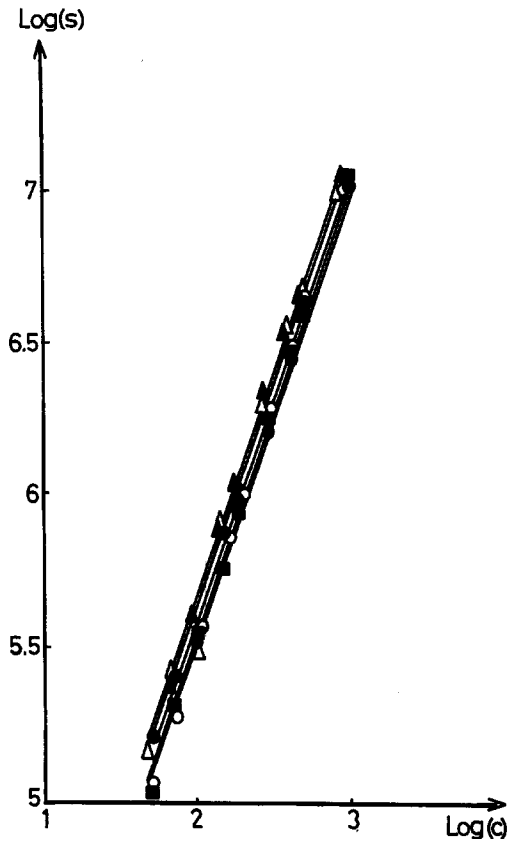

Fig. 5. Linear calibration graph log (peak area) *vs.* log (concentration). ● = BC-7; ▲ = BC-40; ■ = PEG 300; ○ = PEG 1540; △ = androsterone. Chromatographic conditions: column, LiChrospher 100 Diol (125 mm × 4 mm I.D.); mobile phase, methanol–water (4:1); flow rate, 1 ml min^{-1}; detection, ELSD.

which is not the case in an aqueous solution. Because liquid microparticles scatter less light than oily or solid particles, the androsterone response is greater than that of PEG 300.

In HPLC, we can conclude that in the normal-phase mode it is possible to obtain low-molecular-weight oligomer distributions, whereas surfactants with more than 10–15 EO units could not be resolved and PEG mixtures could not be eluted. In the reversed-phase mode, it was possible to evaluate PEGs and surfactants quantitatively, even those with high molecular weights. PEG mixtures were better resolved than in the normal-phase mode, although the surfactant fingerprints were poor (Table III). To obtain richer chromatograms, we therefore decided to investigate SFC with packed columns coupled with ELSD.

Supercritical fluid chromatography

Above 31°C and 73 bar, carbon dioxide has become a popular supercritical fluid because of its particular combining qualities with analytes and stationary phases. Other studies of PEGs [16] and non-ionic surfactants [19] have been done using apolar or slightly polar capillary columns with carbon dioxide as the mobile phase. These showed that surfactants and PEGs with low molecular weight can be resolved. However, the selectivity of the surfactant mixtures decreases with an increasing number of EO units, whereas PEG mixtures are totally adsorbed on the chromatographic support. In order to elute polar compounds, it is necessary to add

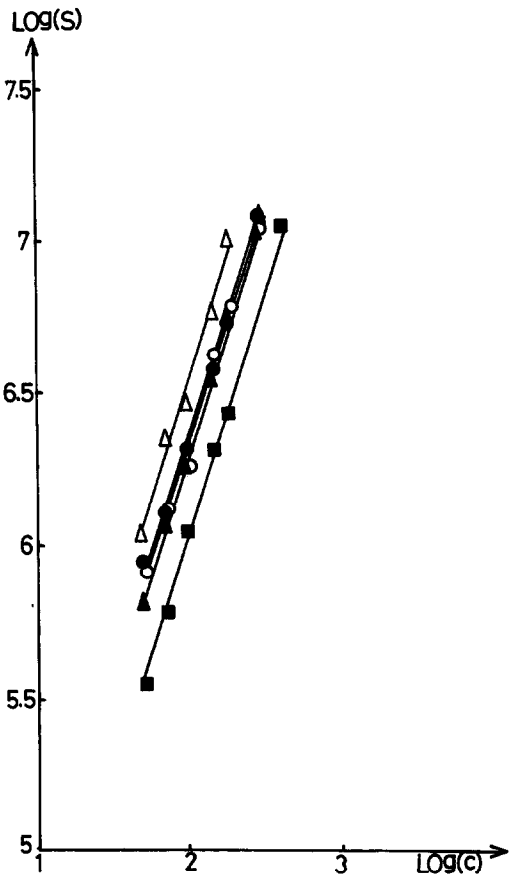

Fig. 6. Linear calibration graph, log (peak area) *vs.* log (concentration). ● = BC-7; ▲ = BC-40; ■ = PEG 300; ○ = PEG 1540; △ = androsterone. Chromatographic conditions: column, LiChrospher 100 Diol (125 mm × 4 mm I.D.); mobile phase, dichloromethane–methanol (9:1); flow-rate, 1 ml min^{-1}; detection, ELSD.

TABLE III

SUMMARY OF ANALYSES OF ETHOXYLATED ALCOHOLS AND PEGs BY HPLC

Mode	Compound	n	x	Separation	Little or no separation	No separation
Normal phase	$C_nH_{2n+1}(OCH_2CH_2)_xOH$	Constant	Variable	×		
	$C_nH_{2n+1}(OCH_2CH_2)_xOH$	Variable	Constant		×	
	$H(OCH_2CH_2)_xOH$		Variable			×
Reversed-phase	$C_nH_{2n+1}(OCH_2CH_2)_xOH$	Constant	Variable		×	
	$C_nH_{2n+1}(OCH_2CH_2)_xOH$	Variable	Constant	×		
	$H(OCH_2CH_2)_xOH$		Variable	×		

modifiers to the carbon dioxide, which is incompatible with the flame ionization detector.

Columns packed with octadecyl-bonded silicas were also investigated by Giorgetti *et al.* [14], and these studies showed excellent non-ionic surfactant separations, but no separations of highly ethoxylated surfactants and PEGs were obtained. To reduce the residual silanol groups on this type of apolar adsorbent, Hagen *et al.* [16] used columns of polymeric particles with carbon dioxide–methanol as the mobile phase. They observed excellent separations of PEG 1540 with baseline resolution, although no work was carried out on surfactant mixtures.

Following these results, we decided to carry out investigations by adopting the chromatographic system used in normal-phase HPLC in SFC. Carbon dioxide–methanol was used as the mobile phase instead of *n*-hexane–chloroform–2-propanol and bare or diol-bonded silicas were used as stationary phases. Modifiers were chosen according to their suitability for obtaining the best elution and resolution for both families of PEGs and surfactants. ELSD with SFC was shown to be compatible [12,14,15] using different modifiers as in the following examples.

On bare silicas under isocratic conditions with carbon dioxide–methanol, a very rich chromatographic fingerprint may be obtained for the surfactants (Fig. 7). However, the retention decreases if there is an increase in water content, causing split peaks in the chromatographic signal. The causes of this phenomenon are that two surfactant families have different alkyl chain lengths and that the starting alcohol was not pure. Under the same conditions, PEGs were well eluted when a small amount of water was added to the carbon dioxide–methanol eluent and also the chromatographic signal symmetry increased (Fig. 8). On the other hand, surfactants and PEGs with a high degree of ethoxylation could not be eluted. However, if a small amount of triethylamine is added to the polar modifier, high-molecular-weight polymers such as PEG 1540 (34 EO) may be eluted under isocratic conditions, but the resolution decreases with increasing amounts of triethylamine (Fig. 9). It is interesting to note the peak symmetry, never observed before in HPLC under these isocratic conditions, although the column equilibration times are very long. Moreover, amino adsorption on bare silica seems to be more or less irreversible, thus modifying the stationary phase surface. This polar modifier containing nitrogen is the only one which allows the elution of such high-molecular-weight PEGs. In comparison, diethylamine and pyridine clearly require longer analysis times. In an elution gradient with triethylamine, not only high-molecular-weight surfactants may be eluted but also two different alkyl chain lengths can be confirmed (Fig. 10). The baseline drift observed even without the chromatographic columns was not due to a non-homogeneous eluent mixture, because with on-line UV detection no baseline drift was observed. Nevertheless, increasing the additional gas at the SFC–ELSD interface level makes this phenomenon disappear. This prevents the effluents from the column recondensing at the opening of the nebulizer block, leaving the fused-silica capillary restrictor.

To find a simpler method of analysis, diol-bonded silicas with a supercritical fluid were used again. Using LiChrospher 100 Diol with isocratic elution, a carbon dioxide–methanol mixture offers a differ-

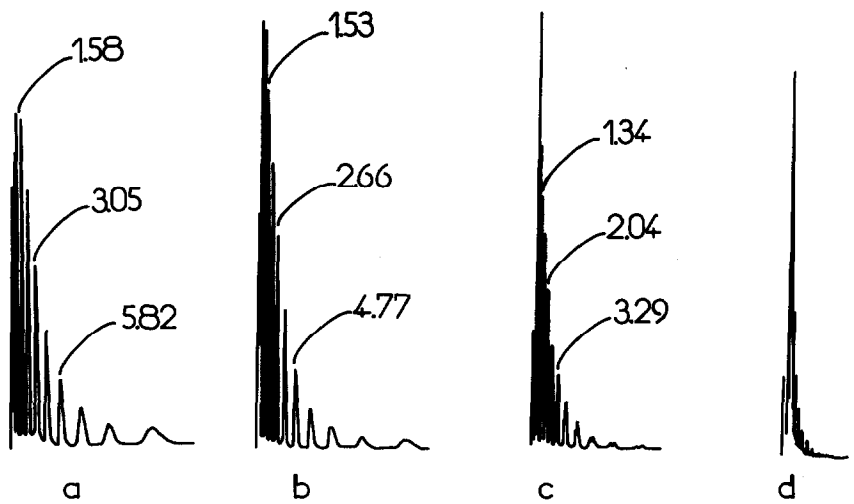

Fig. 7. BC-10: $C_{16}H_{33}(OCH_2CH_2)_{10}OH$. Chromatographic conditions: column, Zorbax Sil (150 mm × 4.6 mm I.D.); flow-rate, 4.2 ml min^{-1}; detection, ELSD. Retention times in minutes. (a) CO_2–CH_3OH (80:20, w/w), pressure 264 atm; (b) CO_2–CH_3OH–H_2O (80:19.5:0.5, w/w/w), pressure 268 atm; (c) CO_2–CH_3OH–H_2O (80:18.76:1.24, w/w/w), pressure 277 atm; (d) CO_2–CH_3OH–H_2O (80:17.56:2.44, w/w/w), pressure 277 atm.

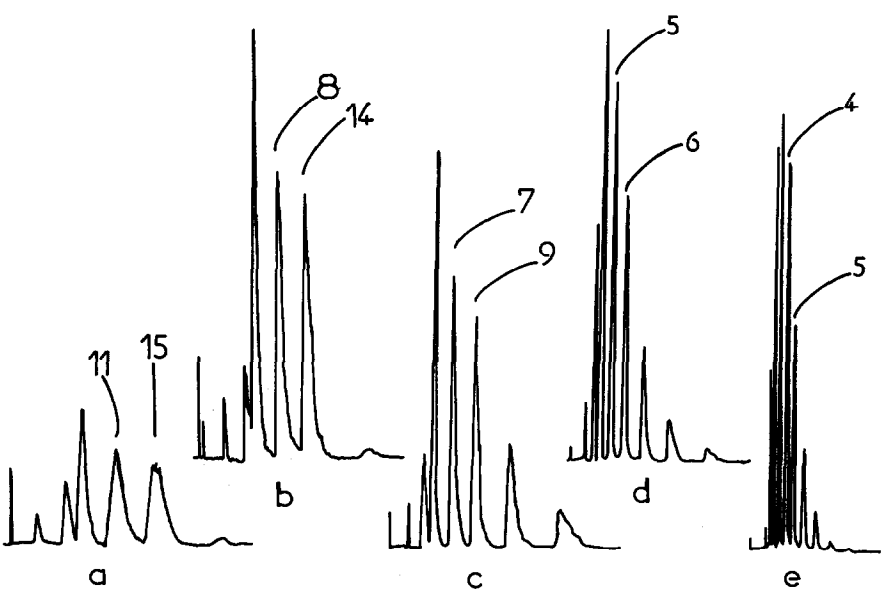

Fig. 8. PEG 400. Chromatographic conditions: column, Zorbax Sil (150 mm × 4.6 mm I.D.); flow-rate, 4.2 ml min^{-1}; detection, ELSD. Retention times in minutes. (a) CO_2–CH_3OH (80:20, w/w) pressure 264 atm. (b) CO_2–CH_3OH–H_2O (80:19.75:0.25, w/w/w), pressure 264 atm; (c) CO_2–CH_3OH–H_2O (80:19.5:0.5, w/w/w), pressure 268 atm; (d) CO_2–CH_3OH–H_2O (80:18.76:1.24, w/w/w), pressure 277 atm; (e) CO_2–CH_3OH–H_2O (80:17.56:2.44, w/w/w), pressure 274 atm.

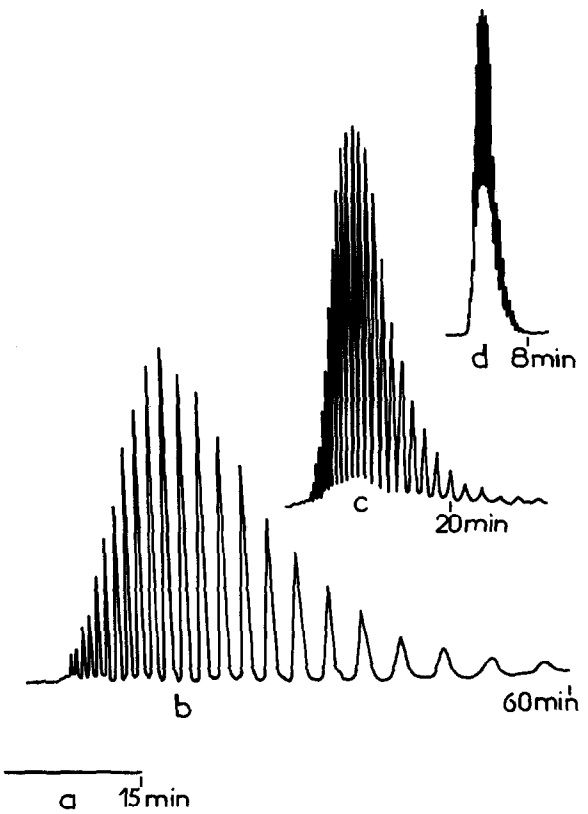

Fig. 9. PEG 1540. Chromatographic conditions: column, Ultrasphere Si (250 mm × 4.6 mm I.D.); flow-rate, 4.2 ml min^{-1}; detection, ELSD. (a) CO_2–CH_3OH–H_2O (80:18.77:1.23, w/w/w), pressure 272 atm; (b) CO_2–CH_3OH–H_2O–$(C_2H_5)_3N$ (80:18.68:1.23:0.09, w/w), pressure 272 atm; (c) CO_2–CH_3OH–H_2O–$(C_2H_5)_3N$ (80:18.60:1.22:0.18, w/w), pressure 288 atm; (d) CO_2–CH_3OH–H_2O–$(C_2H_5)_3N$ (80:18.43:1.21:0.36, w/w), pressure 280 atm.

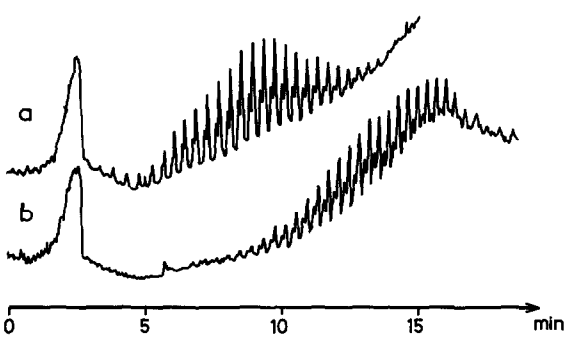

Fig. .10. (a) BC-20, $C_{16}H_{33}(OCH_2CH_2)_{20}OH$; (b) BC-30, $C_{16}H_{33}(OCH_2CH_2)_{30}OH$. Chromatographic conditions: column, Zorbax Sil (150 mm × 4.6 mm I.D.); linear gradient from CO_2–CH_3OH–H_2O–$(C_2H_5)_3N$ (94:5.55:0.4:0.05, w/w) to CO_2–CH_3OH–H_2O–$(C_2H_5)_3N$ (77.2:21.2:1.4:0.2, w/w) in 15 min; flow-rate, 3.46 ml min^{-1}; detection, ELSD.

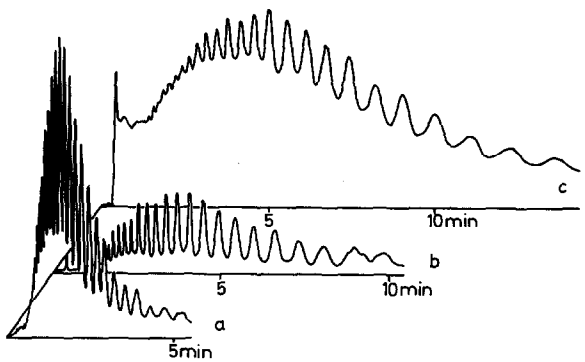

Fig. 11. (a) BC-20, $C_{16}H_{33}(OCH_2CH_2)_{20}OH$; (b) BC-30, $C_{16}H_{33}(OCH_2CH_2)_{30}OH$; (c) BC-40, $C_{16}H_{33}(OCH_2CH_2)_{40}OH$. Chromatographic conditions: column LiChrospher 100 Diol (125 mm × 4 mm I.D.). (a) CO_2–CH_3OH (87:13, w/w), flow-rate 3.88 ml min^{-1}; (b) CO_2–CH_3OH (93:7, w/w), flow-rate 3.88 ml min^{-1}; (c) CO_2–CH_3OH (87:13, w/w), flow-rate 3.88 ml min^{-1}. Detection, ELSD.

ent fingerprint of BC-20, -30 and -40 without peak splitting (Fig. 11). To increase the resolution of this type of separation, a 10-μm Zorbax Diol column (250 mm × 9.4 mm I.D.) was used because of its larger stationary phase volume. In this instance, with a small amount of water, the BC-10 fingerprint was even richer but the peak splitting already observed in Fig. 10 continued. This chromatographic system allows the simple elution of the corresponding PEG 300 and Fig. 12 shows that the two fingerprints are overlapped. It must be noted that triethy-

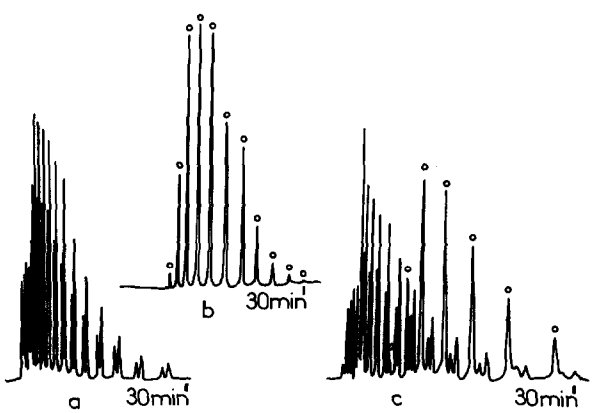

Fig. 12. (a) BC-10, $C_{16}H_{33}(OCH_2CH_2)_{10}OH$; (b) PEG 400; (c) BC-10 + PEG 400. Chromatographic conditions: column, Zorbax Diol (250 mm × 9.4 mm I.D.); mobile phase, CO_2–CH_3OH–H_2O (80:18.76:1.24, w/w/w); flow-rate, 4.2 ml min^{-1}; pressure, 243 atm; detection, ELSD.

lamine is not indispensable with this last bonded adsorbent.

CONCLUSIONS

In SFC, contrary to HPLC, it is possible to obtain richer polyethoxylated alcohol fingerprints and to elute high-molecular-weight polyethoxylated alcohols and PEGs. Both the surfactant and PEG mixtures can be clearly resolved, but the two distributions continue to be overlapped. This problem is currently being studied. Otherwise, SFC with ELSD appears to be well adapted for the analysis of these solutes.

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