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Comparison of the retention behavior of polyethoxylated alcohols on porous graphitic carbon and polar as well as apolar bonded-silica phases

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Abstract

Porous graphitic carbon (Hypercarb S) is presented as a suitable packing for the analysis of polyethoxylated alcohol surfactants by using organic solvents. The separation mechanism is different from that found in normal-phase liquid chromatography and reversed-phase liquid chromatography. This packing permits to analyse simultaneously polyethylene glycol and polyethoxylated alcohol mixtures under gradient elution using water–acetonitrile then acetonitrile–dichloromethane mixtures as mobile phase with evaporative light scattering detection. © 1998 Elsevier Science B.V.

Keywords: Stationary phases, LC; Mobile phase composition; Porous graphitized carbon; Surfactants, non-ionic; Polyethoxylates

1. Introduction

Polyethoxylated alcohols (PEAs) and polyethoxylated alkylphenols (PEAPs) are widely used as non-ionic surfactants. They are synthesized by condensation of ethylene oxide (EO) units on a long-alkyl chain alcohol or alkylphenol. Indeed these surfactants are complex mixtures in which the distribution of oligomers (due to the number of EO units) varies over a considerable range. Furthermore, the alcohol or alkylphenol can be a mixture enhancing the complexity of chromatographic fingerprint. Moreover these surfactant mixtures can contain polyethylene glycols (PEG) as by-products without surfactant properties.

The characterisation of these surfactants is difficult due to the complex mixture and the lack of chromophores in PEGs and PEAs. Avoiding a necessary time-consuming derivatization for a UV detection, universal detection is thus needed and only evaporative light scattering detection (ELSD) is commonly used in HPLC analysis of surfactant with gradient elution.

Many papers have described various surfactant analyses by chromatography; these have been detailed in two recent reviews [1,2]. It has been confirmed that for these compound families generally a separation according to the number of EO units, N_{eo}, can be performed by normal-phase liquid chromatography (NPLC). The capacity factors of oligomers vary as follows:

$$\log k' = \log \beta_{eo} + N_{eo} \log \alpha_{eo} \quad (1)$$

where α_{eo} is the ethylene oxide selectivity and $\log \beta_{eo}$ is the extrapolated value related to the retention of the corresponding hydrocarbonaceous end group of PEAs or PEAPs. In NPLC, the value of the slope $\log \alpha_{eo}$ is always positive.

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On the other hand, it appears that the retention mechanism observed in reversed-phase liquid chromatography (RPLC) with hydro–organic mobile phase is more difficult to describe. RPLC is more suitable for separation principally according to the hydrophobic moiety, but sometimes in addition according to the number of EO units. By increasing the number of EO units, retention can increase according to Eq. (1) ($\log \alpha_{eo} > 0$, [3,4]), or decrease ($\log \alpha_{eo} < 0$, [1,4–7]), but can also remain unchanged [4,6,8]. The elution order depends on the nature of organic modifier as well as on the ratio of organic modifier–water and on the nature of the apolar stationary phase. Moreover, few papers have shown resolutions of both oligomeric series (PEAs or PEAPs and PEGs) in NPLC and RPLC [1,2].

Supercritical fluid chromatography with polar stationary phase can resolve surfactant and PEG mixtures, but the two distributions are overlapped [8].

The aim of this work is to evaluate porous graphitic carbon (Hypercarb S) for surfactant analysis. This phase possesses a rigid, planar surface in addition to high electronic and charge transfer interactions. It has been reported to be useful for the separation of solutes with closely related structures and which are often aromatic planar [9–11] and cyclic non-planar [12,13] compounds, but it has been little used for oligomeric and homologous compound analysis.

2. Experimental

2.1. Reagents

Acetonitrile and ethyl acetate (RS for LC) were purchased from Carlo Erba (Milan, Italy), methanol and dichloromethane (Hypersolv grade) from BDH (Poole, UK), and tetrahydrofuran (THF) from Prolabo (Paris, France). Water was produced by an Elgastat UHQ II system (Elga, Anthony, France). The standard ethoxylated alcohols: hexaethylene glycol monodecyl ether ($C_{10}EO_6$), hexaethylene glycol monododecyl ether ($C_{12}EO_6$), hexaethylene glycol monotetradecyl ether ($C_{14}EO_6$), hexaethylene glycol monohexadecyl ether ($C_{16}EO_6$), hexaethylene glycol monooctadecyl ether ($C_{18}EO_6$), diethylene glycol monododecyl ether ($C_{12}EO_2$), tetraethylene glycol monododecyl ether ($C_{12}EO_4$), nonaethylene glycol monododecyl ether ($C_{12}EO_9$) were purchased from Fluka (Buchs, Switzerland). Two complex industrial mixtures were analysed: BC-10 ($C_nH_{2n+1}(OCH_2CH_2)_m$ OH, with *n* equal to 16 or 18 and an average *m* value of 10 EO) was purchased from Nikko Chemicals (Tokyo, Japan), Triton X-100 (polyethylene glycol *tert.*-octylphenyl ether with average value of 9–10 EO) was purchased from Sigma (St. Louis, MO, USA) and polyethylene glycol 400 (PEG 400) was purchased from Fluka.

2.2. Apparatus

Chromatography was carried out using a Beckman (Fullerton, CA, USA) Model 128 System Gold binary pump, a Rheodyne (Cotati, CA, USA) Model 7125 injection valve, a Shimadzu (Kyoto, Japan) C-R3A integrator, and a Sedere (Vitry/Seine, France) Model Sedex 45 evaporative light scattering detector (ELSD). The usual ELSD settings were as follows: drift tube, 27°C; nebulizer gas pressure, 2.2 bar. This universal detector is needed for the simultaneous analyses of UV absorbing and transparent compounds in mixture because its response does not depend on the presence of a functional group in the sample and the narrow spread of the response factors enables quantification with an acceptable degree of approximation [8,14,15].

In order to obtain a satisfactory quantification of solutes, it was necessary to optimise the evaporation temperature of the drift tube because solid particles of solutes scatter light better and so give a greater sensitivity than liquid droplets of solutes [16]. The detection of the standard ethoxylated alcohols with a low number of EO units and low boiling temperature was greatly improved with a low drift tube temperature (the response peak area for $C_{12}EO_2$ was 100-fold higher at 27°C than at 54°C) while the effect of temperature was much less marked for standard ethoxylated alcohols with a higher number of EO units (the response peak area for $C_{12}EO_9$ was only doubled between these two temperatures).

LC–MS was used to identify each chromatographic peak. The mass spectrometer was a Perkin-Elmer Sciex API 300 (Foster City, CA, USA) where ionisation was obtained by using heated nebulizer

under the following conditions: needle current, 3 μA; temperature, 350°C; orifice, 90 V; focus ring, 300 V. The mass spectrometer was calibrated with standard polypropylenes.

The porous graphitic carbon column was a Hypercarb-S column (100×4.6 mm I.D., particle size 7 μm) from Hypersil (Runcorn, UK). Reversed-phase columns were: Lichrospher 100 RP-18 (125×4.6 mm I.D.) from Merck (Darmstadt, Germany); Zorbax ODS (150×4.6 mm I.D.) from DuPont (Wilmington, DE, USA); Asahipak ODP 50 (150×4.6 mm I.D.) from Asahi Chemical Industry (Kawasaki, Japan). The normal-phase column was a Lichrospher 100 Diol (250×4 mm I.D.) from Merck.

The influence of the temperature on the retention time has been studied for the Hypercarb S column in a gradient elution mode. The columns were thermostated with a Croco-CIL column oven (CIL-Cluzeau, Ste-Foy-la-Grande, France). An increase in temperature involves a weak decrease (about 0.05 min/°C) in retention. It was for this reason that all the reported separations were carried out at ambient temperature. The flow-rate was 1 ml/min.

3. Results and discussion

3.1. Study of the retention behavior

3.1.1. Influence of the mobile phase composition

It has already been reported that fatty alcohols can be eluted with methanol–water (80:20) on Hypercarb [12] and are more retained on this porous graphitic carbon (PGC) phase than on an octadecyl silica phase. Moreover, it has been noted that a non-ionic surfactant such as polysorbate 80 is highly adsorbed on the PGC surface, and owing to this property it has been proposed to add this surfactant as a modifier to deactivate PGC support and decrease the high retention of aromatic compounds observed on this support [9].

In order to assess the chromatographic behaviour of PEAs and PEAPs on Hypercarb, the retention of some standard ethoxylated alcohols such as $C_{12}EO_n$ [$C_{12}H_{25}(OCH_2CH_2)_nOH$; $n=2$, 4, 6, 9] and C_nEO_6 [$C_nH_{2n+1}(OCH_2CH_2)_6OH$; $n=10$–18 even] was first investigated with different mobile phases.

As expected, these solutes are more highly retained on PGC support than on an octadecyl bonded phase. The elution strength of the aqueous–organic eluent was too weak to elute these compounds on Hypercarb S column but sufficient to elute them on octadecyl bonded silica column. Therefore, the following mixtures dichloromethane–methanol, dichloromethane–acetonitrile and ethyl acetate–acetonitrile in various proportions were evaluated as mobile phase.

Table 1 summarizes the results of a linear regression analysis of plots of $\log k'$ versus the volume fraction φ of the less-polar solvent in the mobile phase corresponding to the equation:

$$\log k' = a - m\varphi \quad (2)$$

In the studied φ range where each solute was eluted in a satisfactory analysis time, a good linearity is observed, with a correlation coefficient better than

Table 1
Linear regression analysis of $\log k' = a - m\varphi$ (Eq. (2)) for different $C_{12}EO_n$ and C_nEO_6 standards analyzed on a Hypercarb S column

Solute	Mobile phase						Solute	Mobile phase					
	Ethyl acetate–acetonitrile $0.50<\varphi<0.70$		Dichloromethane–acetonitrile $0.30<\varphi<0.55$		Dichloromethane–methanol $0.40<\varphi<0.60$			Ethyl acetate–acetonitrile $0.60<\varphi<0.80$		Dichloromethane–acetonitrile $0.45<\varphi<0.70$		Dichloromethane–methanol $0.50<\varphi<0.70$	
	a	*m*	*a*	*m*	*a*	*m*		*a*	*m*	*a*	*m*	*a*	*m*
$C_{12}EO_2$	0.90	1.18	0.88	1.67	1.39	2.91	$C_{10}EO_6$	0.77	0.88	1.08	2.00	1.80	3.50
$C_{12}EO_4$	1.14	1.21	1.23	1.94	1.84	3.32	$C_{12}EO_6$	1.32	1.16	1.54	2.23	2.34	3.92
$C_{12}EO_6$	1.32	1.16	1.54	2.23	2.34	3.92	$C_{14}EO_6$	1.72	1.19	2.07	2.58	2.82	4.22
$C_{12}EO_9$	1.72	1.36	2.00	2.67	3.08	4.82	$C_{16}EO_6$	2.21	1.34	2.61	2.93	3.31	4.52
							$C_{18}EO_6$			3.11	3.18	3.90	4.98

φ is the volume fraction of dichloromethane or ethyl acetate in the mobile phase. Correlation coefficient better than 0.9988.

0.998. For all compounds the value of the slope was negative, i.e. the retention of C_nEO_6 and $C_{12}EO_n$ decreases when the less-polar solvent content increases. Such variation is characteristic of the RPLC mode [17]. However, as the three mobile phases do not contain water, the term of non-aqueous reversed-phase liquid chromatography (NARPLC) is more appropriate than RPLC to describe the retention mode of these solutes on PGC.

Table 1 shows that for a given standard and a given value of φ the capacity factor is higher when ethyl acetate–acetonitrile replaces dichloromethane–acetonitrile. So, dichloromethane is a stronger solvent than ethyl acetate. When dichloromethane–methanol replaces dichloromethane–acetonitrile, methanol has a greater elution strength than acetonitrile when φ is higher than 0.4–0.5, and a lower one when φ is less than 0.4–0.5. The value of intercept a corresponds to the theoretical value of log k' for each compound using the pure more-polar solvent of each mixture as mobile phase. So, for PEAs and PEAPs on PGC, pure acetonitrile was a stronger solvent than pure methanol. These results were the reverse of those obtained for different homologous series ($C_nH_{2n+1}Z$ where Z=H, Cl, OH) in RPLC with octadecyl silica columns for which aqueous–organic eluent with acetonitrile was a stronger eluent than with methanol, but pure methanol was a stronger eluent than acetonitrile [18]. Table 1 shows that the absolute value of slope m was greater with dichloromethane–methanol and dichloromethane–acetonitrile mixtures than with an ethyl acetate–acetonitrile mixture. Thus, during the analysis of PEAs or PEAPs, if a gradient elution mode is required to decrease the analysis time and improve the sensitivity of the more retained compounds, ethyl acetate–acetonitrile gradients will not cover as wide a solvent strength range, therefore some compounds may not elute with this gradient.

In Table 1, the two extrapolated a values of log k' in pure acetonitrile obtained from dichloromethane–acetonitrile and ethyl acetate–acetonitrile mixtures were not the same. This result suggests that the linear relationship between log k' and φ observed on the limited range of binary composition is not valid over the complete range. As shown in RPLC [17], a quadratic relationship would enable the true value to be obtained when φ is close to zero. However the true value of k' is so high that the exact value is without experimental interest and the values of a yielded in Table 1 show principally that the interactions of PEAs with PGC were stronger than with an octadecyl bonded silica.

3.1.2. Methylene selectivity

The retention of homologous series C_nEO_6 for a given mobile phase increases with increasing number of carbon number N_c of the hydrocarbonaceous moiety as follows:

$$\log k' = \log \beta_{me} + N_c \log \alpha_{me} \quad (3)$$

where the slope log α_{me} and the intercept log β_{me} represent, respectively, the methylene selectivity and the retention of polar residue EO_6. Table 2 yields the values log β_{me} and log α_{me} at various mobile phases.

The values of methylene selectivity are lower with the two mixtures containing dichloromethane than with the ethyl acetate mobile phase, thus showing a greater elution strength of dichloromethane for alkyl chain on PGC. Moreover log α_{me} decreases as the less-polar solvent content φ increases. This decrease of the interaction of the methylene group with the support when the less-polar solvent content increases is also observed in RPLC [19]. This decrease in methylene selectivity is less marked with ethyl acetate–acetonitrile mixture. Thus a gradient elution with this mixture cannot involve a significant variation in the retention of alkyl chain.

Furthermore, for a similar retention [$k'(C_{14}EO_6)$= 5.88 on Zorbax ODS using acetonitrile–water (95:5) as mobile phase and 6.15 on Hypercarb S, using dichloromethane–acetonitrile (50:50)], log α_{me} is 0.12 on Zorbax ODS, whereas it is higher (0.18) on Hypercarb S, thus showing a stronger interaction of alkyl chain on PGC. These results confirm those reported in the literature [12].

The intercept log β_{me} represents the retention of EO chain when N_c is zero. The negative value (about −1.7) of this parameter reflects repulsive interactions between this polar moiety, i.e. PEG and Hypercarb S, whatever the organic mobile phase. Thus to obtain some retention for PEG on Hypercarb it was necessary to use a mobile phase with a lower elution strength such as water–organic modifier mixtures.

Table 2
Influence of the carbon number N_c on the homologous series C_nEO_6 retention on a Hypercrb S column

φ	Mobile phase					
	Ethyl acetate–acetonitrile		Dichloromethane–acetonitrile		Dichloromethane–methanol	
	Log α_{me}	Log β_{me}	Log α_{me}	Log β_{me}	Log α_{me}	Log β_{me}
0.45			0.178	−1.589		
0.50			0.181	−1.744	0.166	−1.614
0.55			0.173	−1.767	0.161	−1.749
0.60	0.188	−1.628	0.161	−1.727	0.151	−1.818
0.65	0.190	−1.710	0.159	−1.821		
0.70	0.188	−1.727	0.159	−1.976	0.139	−1.979
0.75	0.183	−1.720				
0.80	0.178	−1.707				

Linear regression analysis of $\log k' = \log \beta_{me} + N_c \log \alpha_{me}$ where φ is the volume fraction of dichloromethane or ethyl acetate in the mobile phase. $N_c = 10–18$ even. Coefficient correlation better than 0.9993.

3.1.3. Ethylene oxide selectivity.

The retention of oligomeric series $C_{12}EO_n$ for a given mobile phase increases with increasing number of ethylene oxide N_{eo} of the polar moiety, following Eq. (1). The values of log α_{eo} and log β_{eo} are given in Table 3. Like the values α_{me}, the values α_{eo} decrease as the less-polar solvent content φ increases whatever the mobile phase. This decrease is smaller with the ethyl acetate mobile phase, thus showing the limited interest of using this mixture in gradient elution. For φ given, log α_{eo} depends on the mobile phase and the lowest value was always obtained with a dichloromethane–acetonitrile mixture. Log β_{eo}, which represents an extrapolated value related to the hypothetical retention of the end group on the polyethylene chain decreases more strongly than log α_{eo} with increasing φ. For a value of φ higher than 0.45, a comparison of log β_{eo} values shows that methanol has an elution strength for the hydrocarbonaceous moiety higher than acetonitrile, and that dichloromethane is a stronger eluent than ethyl acetate. This confirms the results in Section 3.1.1.

On a Diol column with different hexane–ethanol mixtures as mobile phase, a linear relationship according to Eq. (1) between log k' and the EO number is also observed. Table 4 recapitulates the different values of slope and y-intercept obtained for the same oligomeric series. A positive value of log α_{eo} ($\alpha_{eo} > 1$) is noticed as with the PGC system. However, in the NPLC mode on Diol support, log α_{eo} increases as the less-polar solvent content φ increases, unlike the behaviour on PGC. Moreover,

Table 3
Influence of the ethylene oxide number, N_{eo}, on the retention of the oligomeric series $C_{12}EO_n$ on a Hypercarb S column

φ	Mobile phase					
	Ethyl acetate–acetonitrile		Dichloromethane–acetonitrile		Dichloromethane–methanol	
	Log α_{eo}	Log β_{eo}	Log α_{eo}	Log β_{eo}	Log α_{eo}	Log β_{eo}
0.30			0.117	0.162		
0.35			0.108	0.102		
0.40			0.100	0.034	0.132	−0.028
0.45	0.106	0.155	0.092	−0.033	0.117	−0.140
0.50	0.102	0.128	0.089	−0.112	0.104	−0.262
0.55	0.102	0.070	0.080	−0.117	0.090	−0.372
0.60	0.103	−0.009			0.077	−0.483
0.65	0.100	−0.061				
0.70	0.098	−0.105				

Values of the slope and the intercept of the linear relationship $\log k' = \log \beta_{eo} + N_{eo} \log \alpha_{eo}$ on Hypercarb S, where φ is the volume fraction of dichloromethane or ethyl acetate in the mobile phase. $N_{eo} = 2, 4, 6, 9$. Correlation coefficient better than 0.9991.

Table 4
Values of the slope and the intercept of the linear relationship $\log k' = \log \beta_{eo} + N_{eo} \log \alpha_{eo}$ on a Diol column with a hexane–ethanol mixture as mobile phase where φ represents the volume fraction of hexane

φ	Log α_{eo}	Log β_{eo}	r
0.80	0.059	−0.680	0.9993
0.85	0.068	−0.571	0.9998
0.90	0.085	−0.496	0.9997
0.925	0.099	−0.457	0.9993
0.95	0.116	−0.333	0.9998

log β_{eo} values in NPLC are very small, showing thus a weak interaction of the alkyl moiety of solutes, unlike the values on PGC. Furthermore, this value in NPLC increases as the less-polar solvent φ increases in contrast to the values on PGC.

In a pure RPLC mode with an aqueous–organic eluent, for an oligomeric series, the expected value for log α_{eo} is negative and the one for log β_{eo} is positive. In this case, the surfactant interacts by its apolar moiety with the apolar chain of the support, whereas its polar ethylene oxide moiety remains in the polar mobile phase. On octadecyl bonded silicas the mechanism seems more complex and dependent on the choice of the support as well as on the composition of the mobile phase, as described by Kudoh [4]. In Fig. 1a Fig. 1b it was noticed that with different mobile phases having a similar elution strength, three different supports: Zorbax ODS (with monolayer bonding without end capping), LiChrospher RP-18 (with polymeric bonding on silica) and Asahipak ODP 50 (octadecyl bonded polymer without silanol groups) have carried along an opposite sign for the slopes in Eq. (1). With an acetonitrile–water mixture (Fig. 1a), the retention on Zorbax ODS increases as N_{eo} increases according to Eq. (1) (slope >0 and $\alpha_{eo}=1.22$ while the opposite holds true with Asahipak (slope <0 and $\alpha_{eo}=0.92$); the value α_{eo} is nearly 1 ($\alpha_{eo}=0.97$) with LiChrospher RP-18. So no significant variation of retention was observed by increasing N_{eo}. With methanol–water (Fig. 1b) on LiChrospher RP-18 and Asahipak ODP 50, no selectivity according to N_{eo} is observed because the value α_{eo} is close to 1, whereas α_{eo} is 1.05 on the Zorbax ODS phase. It can be concluded that retention is weakly dependent on N_{eo}.

On PGC, the retention mechanism is unique: it interacts together with the apolar moiety of the surfactant as in RPLC mode and with the ethylene oxide moiety as in NPLC mode, and these two interactions are enhanced when the less-polar content decreases.

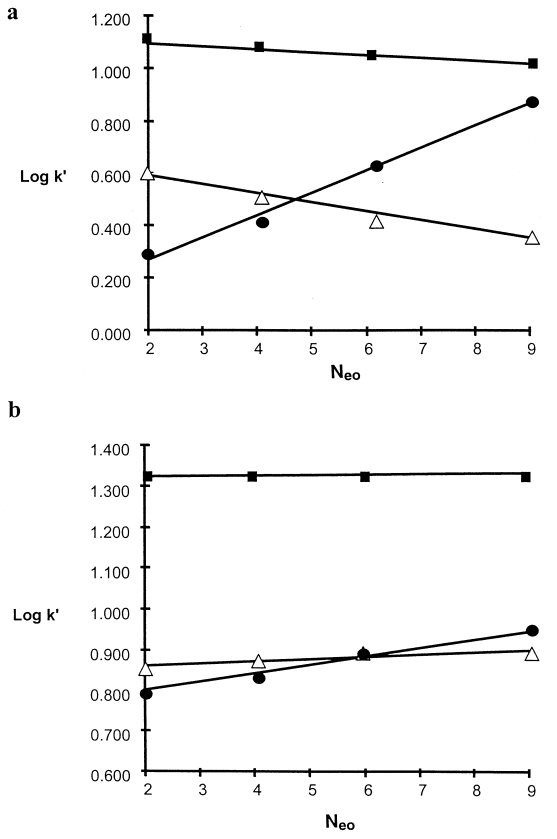

Fig. 1. Influence of the number of EO units (N_{eo}) on the retention in reversed-phase chromatography. Solutes, $C_{12}EO_n$, with $n=2$, 4, 6, 9; octadecyl bonded phases: LiChrospher RP-18, Zorbax ODS, Asahipak ODP 50. (a) Mobile phase: acetonitrile–water mixtures (65:35) on LiChrospher RP-18 (■), (95:5) on Zorbax ODS (●), (70:30) on Asahipak ODP 50 (△). (b) Mobile phase: methanol–water mixtures (75:25) on Lichrospher RP-18 (■), (80:20) on Zorbax ODS (●), (85:15) on Asahipak ODP 50 (△). Column temperature: ambient.

3.2. Separation of industrial surfactant on Hypercarb

Triton X-100 is a mixture of oligomeric compounds having a branched and aromatic apolar moiety. Isocratic elution involves a poor resolution

of the first oligomers and a too large separation of the last peaks which are detected with a weak sensitivity [7]. A gradient elution is required to obtain a short analysis time with a good separation. A linear gradient elution was carried out with a dichloromethane–acetonitrile mixture (Fig. 2) because this mixture enables, as shown in Table 3, a higher retention of the apolar moiety ($\log \beta_{eo}$) and a decrease of $\log \alpha_{eo}$ when dichloromethane content increases.

When the surfactant is a mixture of two oligomer series with two different alkyl chains as in BC-10, the used chromatographic system must afford both methylene and EO selectivities in order to obtain good separation of both series. In this case, the selectivity between two homologous compounds (given by the $\log \alpha_{me}$ value) should be larger than the selectivity between two oligomer compounds (given by the $\log \alpha_{eo}$ value). Tables 2 and 3 report that on PGC, the methylene selectivity α_{me} value was about 1.23 times higher than that of ethylene oxide selectivity α_{eo} with ethyl acetate–acetonitrile and dichloromethane–acetonitrile, and about 1.16 times higher with dichloromethane–methanol. For a given elution order of the oligomer series and for similar retentions, on PGC, whatever the nature of the organic mobile phase used, the α_{me}/α_{eo} ratio was always higher than that obtained with an aqueous–organic eluent on an octadecyl silica support such as Zorbax ODS ($\alpha_{me}/\alpha_{eo} = 1.07$ with acetonitrile–water 95:5). Thus the PGC support was investigated as a possible additional column material providing an attractive and alternative separation potential to reversed phase for the LC analysis of an industrial surfactant such as BC-10. Fig. 3 shows the LC elution pattern of BC-10 on a Hypercarb S support with a dichloromethane–acetonitrile gradient. As acetonitrile affords higher values of α_{me}/α_{eo} ratio on PGC than methanol, and in addition, for the reasons explained in Section 3.1.2, a gradient elution has been performed with dichloromethane–acetonitrile rather than ethyl acetate–acetonitrile as mobile phase in order to depict clearly the presence of two oligomeric series in BC-10 surfactant. As tetrahydrofuran was known to have an elution strength similar to dichloromethane on Hypercarb S, a similar gradient elution with tetrahydrofuran–acetonitrile was investigated: a greater retention was obtained and the fingerprint of the industrial surfactant was not better than with dichloromethane–acetonitrile. In Fig. 3, peak assignment was provided by LC–MS. Thus, the presence of two oligomer series with 16 and 18 carbon number was shown in the BC-10 industrial surfactant. Moreover, Fig. 3 reveals the presence of minor compounds eluted in void volume which were identified as PEGs by using LC–MS.

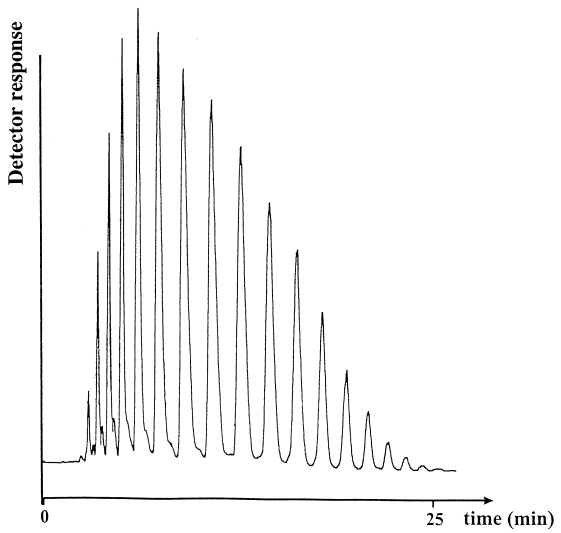

Fig. 2. Chromatogram of Triton X-100 on Hypercarb S (7 μm) column. Mobile phase: acetonitrile (A)–dichloromethane (B), gradient elution with 20% B during 5 min then from 20 to 80% B during 30 min. Flow rate, 1 ml/min; detector, ELSD; column temperature, ambient.

3.3. Separation of PEG and PEAP mixture

PEGs can be present in a surfactant mixture as by-products without surfactant properties. In RPLC these residual compounds are eluted close to the void volume [1,8], while in NPLC they are strongly retained on the polar support [1]. PEGs not retained with organic mobile phase on Hypercarb S (as in Fig. 3) are easily separated on PGC by using an aqueous–organic eluent as on an alkyl bonded phase. In order to analyse the mixture of PEG and PEAP, a gradient elution in two parts (water–acetonitrile then acetonitrile–dichloromethane) enables two nice fingerprints for this mixture to be obtained, as shown in Fig. 4. This chromatogram illustrates the large difference in interactions of both families on PGC. This analysis

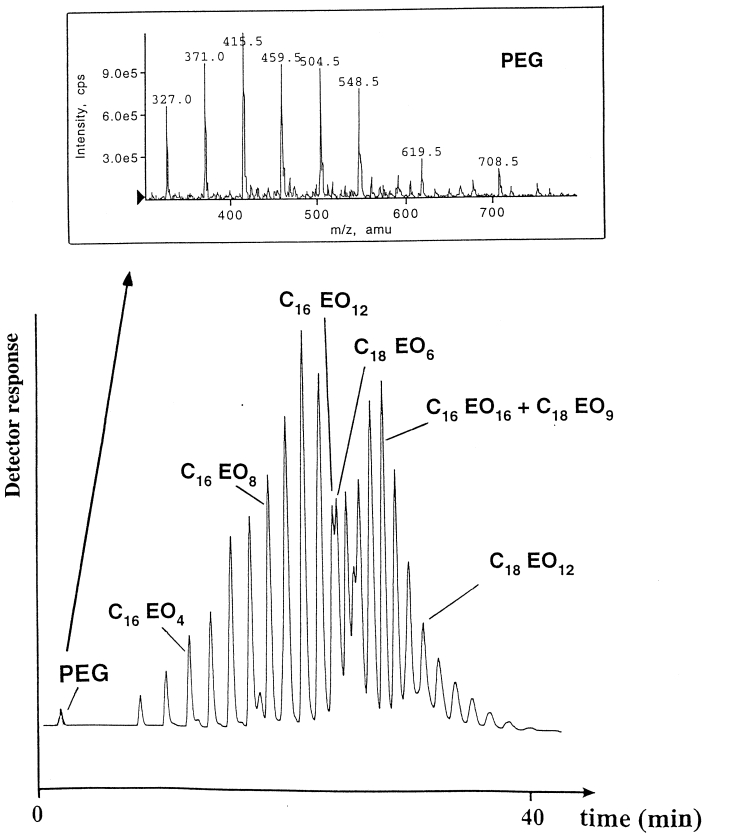

Fig. 3. Chromatogram of BC-10 on Hypercarb S (7 μm) column. Mobile phase: acetonitrile (A)–dichloromethane (B), gradient elution from 20 to 80% B during 30 min. Flow rate, 1 ml/min; detector, ELSD. Column temperature, ambient. For mass spectrometry conditions see Section 2.

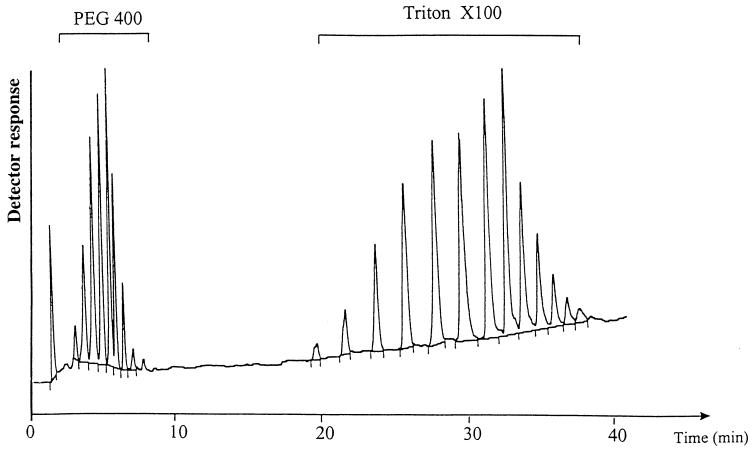

Fig. 4. Chromatogram of a mixture of PEG 400 and Triton X-100 on Hypercarb S (7 μm) column. Mobile phase: water (A)–acetonitrile (B)–dichloromethane (C), gradient elution with A–B mixture from 20% of B to 100% of B during 15 min, then with B–C mixture from 0% of C to 80% of C during 25 min. Flow rate, 1 ml/min; detector, ELSD; column temperature, ambient.

in gradient elution can be realised only with ELSD because PEGs are non-UV absorbing, contrary to Triton X-100.

4. Conclusion

Hypercarb S is a suitable packing for the analysis of polyethoxylated alcohols. The PGC support offers stronger interactions with these compounds than ODS packings. The retention of these non-ionic surfactants on PGC support increases by increasing their hydrocarbonaceous chain length and by increasing their ethylene oxide number, which is not observed in NPLC and in pure RPLC. Moreover, to elute PEAs on a Hypercarb S column it was necessary to use non-aqueous mobile phase.

Gradient elution mode with organic solvents was easily performed on this packing. Both surfactant and PEG mixtures can be clearly resolved on a Hypercarb S column under gradient elution conditions. Moreover, the non-ionic surfactant analysis on a Hypercarb S column enables a better ELSD detection limit for PEAs with low ethylene oxide number than on ODS packings, because the organic mobile phase used with the PGC support was more easily vaporisable than the hydro–organic mobile phase used with ODS packings.

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