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Analysis of alkylphenol-based non-ionic surfactants by high-performance liquid chromatography

Dan F. Anghel*[,a], Marieta Balcan[a], Anca Voicu[b], Mihai Elian[b]

[a]*Laboratory of Colloids, Institute of Physical Chemistry, Spl. Independentei 202, 79611 Bucharest, Romania*
[b]*Institute of Organic Chemistry, Spl. Independentei 202A, 71141 Bucharest, Romania*

Abstract

Ethoxylated non-ionic surfactants derived from octyl- and nonylphenols were analyzed by normal-phase HPLC. A silica column (Si-100, 5 μm) with gradient elution and UV detection at 280 nm were used for oligomer determination. Baseline separation of the ethylene oxide adducts of alkylphenols with average ethoxymer numbers as high as 40 was achieved. The elution system and the gradient profile used depend on the average ethoxymer number of the surfactant. The method can provide full information for the quantitative calculation of the oligomer distribution from ethoxylated surfactants. The hydrophobic moiety of the surfactants was characterized by reversed-phase chromatography. An octadecylsilica column (RP-18, 5 μm) and methanol–water (8:2, v/v) as eluent were used. The procedure is useful for the rapid identification of surfactants according to the alkylphenyl chain.

1. Introduction

Ethoxylated non-ionic surfactants are effective, multi-purpose and versatile substances. Commercial products are obtained by reaction of the ethylene oxide with a hydrophobe having an active hydrogen atom (*e.g.*, alkylphenols, fatty acids or fatty alcohols) in the presence of a suitable alkaline catalyst [1]. Alkylphenol polyethoxylates usually contain complex mixtures of compounds that have isomerism in the alkyl chain and in the position of substitution, mono- and dialkyl substitution of the aromatic ring, different ethoxymers and free polyethylene glycol (PEG). When full identification and quantification of the components from ethoxylated alkylphenols are required, the analyst is faced with a difficult task. The terms "ethoxymer" and "oligomer" are equivalent; they are used here for a group of individual adducts containing various numbers of ethylene oxide units.

In the past two decades, separational and instrumental methods have made great strides in the field of non-ionic surfactant analysis. The state-of-the-art of thin-layer and paper chromatography (TLC and PC), gas chromatography (GC) and high-performance liquid chromatography (HPLC) has been reviewed by Cross [2].

HPLC is the most ideal technique for the evaluation of the product composition of non-ionic surfactants [3]. Information about the distribution of ethoxymers [3], the average degree of ethoxylation [4,5], the hydrophobic moiety [6–9] and the PEG content [3,10] of the sample can be readily obtained.

In normal-phase HPLC, the oligomers are separated according to their ethylene oxide con-

* Corresponding author.

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tent; the hydrophobic chain has virtually no influence on the chromatographic process [6]. The columns used for such a purpose have as packings bare silica gel [3,4] and bonded stationary phases of the amino [3,5,6], diol [10] or cyano [11] types. Reversed-phase chromatography on octyl- or octadecylsilica [3,6,7] allows the surfactant hydrophobic moiety to be investigated. These columns are also suitable for determining the PEG content of the samples.

Polarity gradient elution and UV detection are mostly employed [3–7,11]. However, fluorescence [12] and mass spectrometric [13,14] detection have also been used. Mass spectrometry can reveal interesting structural information and is very suitable for analysing minute amounts of surfactants from streams and lakes.

This paper describes the use of HPLC in the analysis of non-ionic surfactants. Normal-phase HPLC was applied for the separation, identification and determination of oligomers from commercial samples of alkylphenol polyethoxylates. The behaviour of these surfactants in reversed-phase HPLC and the characterization of their hydrophobic moiety were also investigated.

2. Experimental

2.1. Apparatus

The equipment consisted of a Hewlett-Packard (Boeblingen, Germany) Model 1084B, liquid chromatograph fitted with a variable-wavelength UV detector and a fraction collector. The UV detector was set at 280 nm. Analytical columns (200 × 4.6 mm I.D.) packed with irregular silica (Si-100, 5 μm) or octadecylsilica (RP-18, 5 μm) were purchased from Hewlett-Packard (Waldbronn, Germany). The semi-preparative column (250 × 9.4 mm I.D.) was packed with spherical (5–6 μm) porous silica (Zorbax Sil) obtained from DuPont (Wilmington, DE, USA).

The column temperatures were 30°C for the Si-100 column and 40°C for the RP-18 and semi-preparative columns. These temperatures were imposed by the volatility of the eluents used. The flow-rates for analytical and semi-preparative separations were of 1 and 3 ml/min, respectively.

The operating conditions for determining the oligomer distributions of alkylphenol polyethoxylates (APEs) by normal-phase HPLC are given in Table 1. Reversed-phase separations were carried out with methanol–water (80:20, v/v) as eluent.

2.2. Chemicals

HPLC eluents were prepared by careful purification of analytical-reagent grade ethanol, methanol, 2-propanol and diethyl ether (Reactivul, Bucharest, Romania). The alcohols were fractionally distilled. Diethyl ether was washed free from peroxides with iron(II) sulphate solu-

Table 1
Eluents and gradients used to determine the distribution of oligomers in ethoxylated alkylphenol surfactants

No.	Average ethoxy units	Eluent A	Eluent B	Gradient
1	1–10	*n*-Hexane–diethyl ether (80:20, v/v)	*n*-Hexane–diethyl ether–dioxane–2-propanol–water–acetic acid (20:30:40:10:1:0.5, v/v)	5–95% B in 45 min
2	1–20	*n*-Hexane–diethyl ether (80:20, v/v)	*n*-Hexane–diethyl ether–dioxane–ethanol–2-propanol–water–acetic acid (10:15:50:20:5:1:0.25, v/v)	10–95% B in 40 min
3	10–40	*n*-Hexane–2-propanol (40:60, v/v)	Ethanol–water (80:20, v/v)	10–95% B in 45 min

tion, dried over sodium and fractionated prior to use. A narrow-cut hexane fraction was purchased from VEGA Petrochemicals (Ploiesti, Romania). It contained 80% *n*-hexane, the remainder being hexane isomers, *n*- and isopentanes and heptanes. The hexane fraction was submitted to fractional distillation and only the fraction boiling at 61°C was used. Dioxane was obtained from Petrochemical Works Savinesti (Savinesti, Romania). It was kept over potassium hydroxide for 1 week and then fractionally distilled. The fraction boiling at 101°C was employed. The purity of all the solvents was checked by UV spectrophotometry against water, using 1-cm light path cells. *n*-Hexane, methanol, ethanol and 2-propanol were accepted as eluents only if they showed >95% transmission at 280 nm. The threshold transmissions at 280 nm for diethyl ether and dioxane were of 90% and 85%, respectively. Acetic acid was purchased from Reactivul and used as received. Doubly distilled water having a conductivity lower than 1.5 μS was employed. In order to remove the particulate matter, the eluents were passed through 0.7-μm glass microfibre filters (Gelman Science, Ann Arbor, MI, USA).

The surfactants studied were commercial samples of the ethoxylated octylphenol (OPE_n) and nonylphenol (NPE_n) types from Detergentul (Timisoara, Romania) or Petrochemical Works Brazi (Ploiesti, Romania) and were used as received. The alkyl chain of these surfactants is highly branched, being the dimer of isobutene (2-methyl-1-propene) and the trimer of propene, respectively.

2.3. Ethoxymer standards

The oligomers separated during a run were identified with the aid of homogeneously ethoxylated alkylphenol standards. Triethylene glycol monononylphenyl ether ($NPEO_3$), octaethylene glycol monononylphenyl ether ($NPEO_8$) and triethylene glycol monooctylphenyl ether ($OPEO_3$) were obtained by reaction of the corresponding alkylphenol with the appropriate ethylene glycol in the presence of dicyclohexylcarbodiimide. Details of the synthesis and purification have been given elsewhere [15]. As higher ethoxymer standards are difficult to synthesize and purify, they were obtained from the polydisperse ethoxylated alkylphenols by semi-preparative HPLC. *n*-Hexane–2-propanol (40:60, v/v) (eluent A) and ethanol–water (80:20, v/v) (eluent B) were used with a linear gradient from 10 to 95% B in 45 min. Six fractions corresponding to ethoxylation degrees of 10–15 were collected and the products recovered by removing the solvent. All samples were subjected to analytical HPLC, and confirmation of their identity was done by IR and ^1H NMR spectrometry. Fig. 1 shows the chromatograms of $NPEO_3$, $OPEO_3$, $NPEO_8$ and $NPEO_{15}$. The compounds are almost free from impurities and

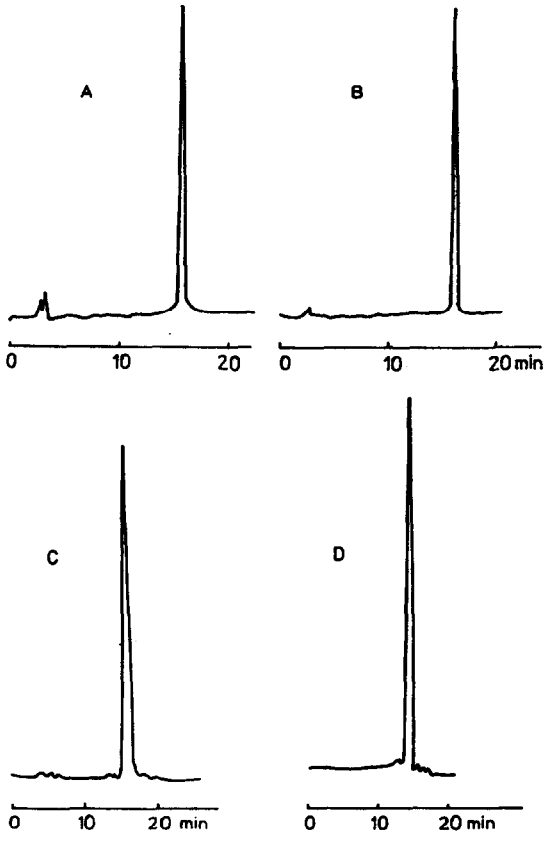

Fig. 1. Gradient elution of ethoxymer standards: (A) $NPEO_3$; (B) $OPEO_3$; (C) $NPEO_8$; (D) $NPEO_{15}$. Eluents and gradients are those in Table 1: for $NPEO_3$ and $OPEO_3$, No. 1; for $NPEO_8$, No. 2; for $NPEO_{15}$, No. 3.

may be used for oligomer identification and determination by HPLC.

2.4. Procedure

Solutions of about 1% (w/v) of commercial surfactant in the less polar solvent A were prepared. For higher ethoxylates, which are not readily soluble in solvent A, small amounts of solvent B were added to assist the dissolution. The volumes injected range from 10 to 50 μl, depending on the ethoxylation degree.

Ethoxymer identification and determination of average ethoxymer numbers were carried out as reported previously [5].

3. Results and discussion

3.1. Ethoxymer separation

In normal-phase chromatography, the most important parameter governing the separation is the adsorbent–solute interaction. The polyoxyethylene chains of non-ionic surfactants interact with the surface hydroxyl groups of silica through hydrogen bonding. The greater the number of oxyethylene units, the tighter will the material be retained and the more molecules of solvent will be required to remove it from the column. This is evident from Fig. 2A, showing the chromatogram of a nonylphenol ethoxylated with 4 mol of ethylene oxide (NPE_4) recorded with isocratic elution. The eluent was a 90:10 (v/v) mixture of eluents A and B listed in the first row of Table 1. The separation has good resolution owing to the column selectivity, but only four ethoxymers are eluted within 1 h. Parameters of the chromatographic process such as capacity factor, selectivity and efficiency are given in Table 2. The selectivity has an almost constant value of 2.2. The capacity factors are 1.63–18.3 and are beyond the optimum range for column efficiency [16]. The column efficiency measured by the height equivalent to a theoretical plate (H) is fairly large. It is evident that with isocratic elution the column operation is not optimum.

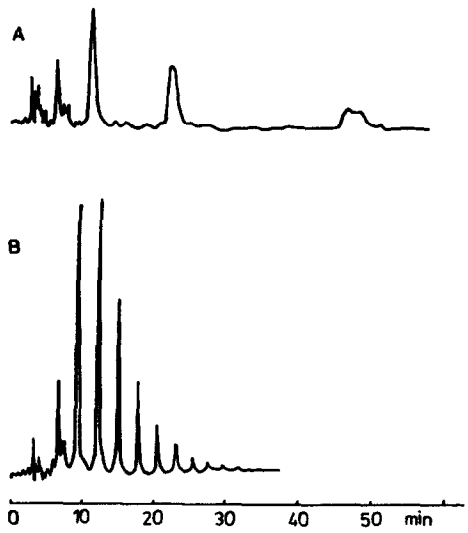

Fig. 2. Separation of NPE_4 ethoxymers with (A) isocratic and (B) gradient elution; Eluent A, *n*-hexane–diethyl ether (80:20, v/v); eluent B, *n*-hexane–diethyl ether–dioxane–2-propanol–water–acetic acid (20:30:40:10:1:0.5, v/v). Isocratic elution, 10% B in A; gradient elution, 5 to 95% B in 45 min.

The column selectivity can be improved by changing the distribution coefficient of the solutes (*i.e.*, during gradient elution). Fig. 2B illustrates the chromatogram obtained on the same NPE_4 sample. It reveals as many as eleven oligomers that are very well separated within 30 min. The parameters of the chromatographic process are considerably improved (see Table 2). The selectivity decreases monotonically and the capacity factor is within the optimum range of values for column efficiency. The height equivalent to a theoretical plate is from several times up to more than an order of magnitude smaller than that obtained under isocratic elution. Although the chromatographic system used was initially proposed for fatty alcohol ethoxylates [17], it provides very good results in the analysis of alkylphenol polyethoxylates also. In addition to NPE_4, several other non-ionic surfactants of the same type were analysed by this method. For example, Fig. 3 shows the chromatogram of NPE_6. The peaks have some inhomogeneities which may be accounted for by nonylphenol isomers. It has been observed that oligomers

Table 2
Selectivity (α), capacity factor (k') and efficiency (H) for isocratic and gradient elution of oligomers from a low ethoxylated nonylphenol (NPE_4)[a]

Oligomer No.	Isocratic[b]				Gradient[c]			
	Retention time (min)	α	k'	H (mm)	Retention time (min)	α	k'	H (mm)
1	6.45	–	1.63	0.169	6.12	–	1.11	0.083
2	11.37	2.22	3.62	0.248	8.69	1.67	1.86	0.093
3	22.55	2.37	8.20	0.142	11.59	1.51	2.81	0.052
4	46.70	2.23	18.37	0.127	14.36	1.35	3.79	0.034
5					17.28	1.28	4.84	0.024
6					20.01	1.22	5.89	0.018
7					22.61	1.17	6.89	0.025
8					24.94	1.13	7.78	0.020
9					26.79	1.10	8.59	0.027
10					29.17	1.08	9.31	0.068
11					30.97	1.08	10.13	0.081

[a] Eluent A, *n*-hexane–diethyl ether (80:20, v/v); eluent B, *n*-hexane–diethyl ether–dioxane–2-propanol–water–acetic acid (20:30:40:10:1:0.5, v/v).
[b] Isocratic elution: 10% eluent B in A.
[c] Gradient elution: 5–95% B in 45 min.

derived from octyl- and nonylphenol show the same chromatographic behaviour. This is additional evidence which supports the previous statement that the hydrophobic moiety does not influence the oligomer separation in normal-phase chromatography [6].

As all the oligomers are baseline separated and removed from the column within a reasonable period of time, the method can be used to determine quantitatively the ethoxymer distribution and the average ethoxylation number of a surfactant sample. Oligomer identifications and detector response factors were obtained with the aid of ethoxymer standards. The case of ethoxylated alkylphenols is the simplest as they bear the chromophore within the molecule. Moreover, they have one chromophore per molecule and the response of the UV detector is independent of the polyoxyethylene chain length [4]. The average ethoxylation numbers of NPE_4, NPE_6 and OPE_6 obtained by HPLC were 4.44, 6.09 and 6.17, respectively. For NPE_6 and OPE_6 samples, good agreement was found between the HPLC results and the ethoxylation degree stated by the producer. For NPE_4 a higher ethoxylation degree was found by HPLC. This demonstrates the ability of HPLC to detect any deficiency appearing during the ethoxylation process.

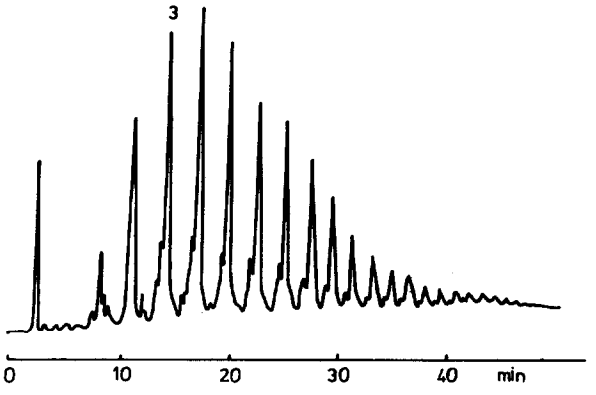

Fig. 3. Chromatogram of NPE_6 using gradient elution. Eluents and gradient as in Fig. 2B.

The method proposed by Vonk *et al.* [17] is very suitable for the analysis of non-ionic surfactants with a low ethoxylation degree. Our attempts to use it for surfactants having average ethoxylation numbers higher than 10 resulted in excessive band widths of the peaks at the end of

chromatogram. This effect denotes strong adsorption of the surfactant molecules on the silica, and makes the eluent less able to remove them from the column. Attempts to improve the polarity of eluent B led to the second elution system in Table 1. The chromatogram obtained with NPE_{10} is presented in Fig. 4. Although more polar, the eluent does not alter the resolution, but it shortens the duration of analysis and removes a larger number of oligomers from the column than the first eluent mixture. The chromatogram is complicated and shows for low ethoxylation degrees (up to 9) a small leading peak accompanying the main peak. On increasing the eluent strength, the large peak of the $(n+1)$th ethoxymer comes closer to the small peak of the nth ethoxymer, and overlaps it at $n=9$.

In normal-phase chromatography, *ortho*-, *meta*- and *para*-isomers elute from the column in the same elution order [16]. The sequence accounts for the strength of interaction between the solute molecules and the active sites on the stationary phase. The *p*-alkylphenol may result from synthesis with a certain amount of *ortho*-isomer. On ethoxylation this material will give a corresponding amount of *ortho*-derivative. The presence of a bulky alkyl group in the *ortho* position hinders the interaction between the hydroxyl active site of silica and the polyoxyethylene chains of the surfactant. Consequently, the *ortho*-isomer is less retained by the column than its *para* counterpart. When submitted to IR analysis, the NPE_{10} sample revealed as much as 30% of *o*-alkylate. Hence the leading peaks were assigned to the *ortho*-isomer.

Often, the formulation chemist needs nonionic surfactants with a certain value of the hydrophile–lipophile balance (HLB). If the respective surfactant is not commonly available, the desired product may be obtained by surfactant blending. As the HLB is an additive property, a range of intermediate HLBs can be obtained by blending appropriate amounts of surfactants with low and high HLB values. HPLC may assist in this search. Fig. 5 shows the chromatogram of the NPE_4 and NPE_{30} mixture and the gradient profile used. NPE_4 shows a good oligomer separation and suggests that the analysis of low-molecular-mass surfactants can be accomplished by suitable matching of the gradient in less than 20 min. At the same time,

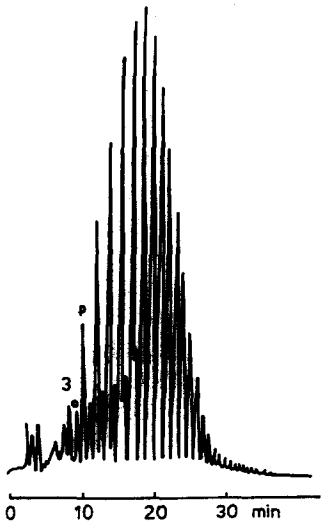

Fig. 4. Chromatogram of NPE_{10}. Eluent A, *n*-hexane–diethyl ether (80:20, v/v); eluent B, *n*-hexane–diethyl ether–dioxane–ethanol–2-propanol–water–acetic acid (10:15:50:20:5:1:0.25, v/v). Gradient: 10–95% B in 40 min.

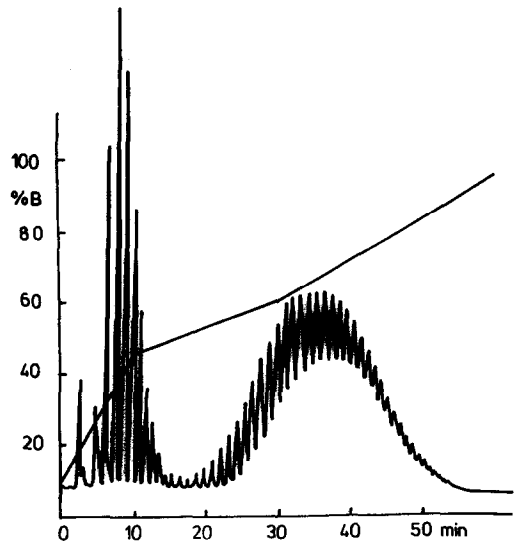

Fig. 5. Chromatographic behaviour of a low (NPE_4) and high (NPE_{30}) ethoxylate mixture. Conditions as in Fig. 4 except for the gradient profile.

lower molecular mass ethoxylates of known ethoxymer distribution such as NPE_4 are useful markers for higher molecular mass surfactants. The approach is very good when highly ethoxylated standards are not available. In the above chromatogram, as many as 50 oligomers are counted. By subtracting the NPE_4 oligomers, for NPE_{30} 39 oligomers result.

Because of poor resolution, the oligomer distribution for NPE_{30} cannot be obtained from the data in Fig. 5. To improve the resolution and obtain a baseline separation of NPE_{30} and higher ethoxylated surfactants, a more polar elution system is necessary. The chromatogram of NPE_{30} obtained with the third elution system in Table 1 is shown in Fig. 6. The sample has 41 ethoxymers, which agrees well with the previously reported number. Peak identification was made with the aid of an $NPEO_{15}$ ethoxymer standard, by using both internal and external standard methods. The most important achievement on elution with this system is the considerable improvement in resolution. Peak areas were used to determine the average ethoxymer numbers of NPE_{30} and NPE_{40} samples. They gave values of 29.00 and 37.20, respectively. For an NPE_{50} sample, poor resolution was obtained and it was not possible to obtain reliable data for calculating the oligomer distribution.

Fig. 7 shows the distribution of oligomers *versus* the ethoxymer number. The data were selected from a large number of examined samples and cover the range of commercially available NPEs with average ethoxymer numbers within the range 4–40. They illustrate the information that can be obtained about the oligomer distribution from ethoxylate samples by using HPLC. The method is currently applied to control the quality of industrially produced non-ionic surfactants. Table 3 presents some average ethoxymer numbers obtained by HPLC. The subscript on each sample abbreviation is the value stated by the producer. Generally, the agreement between the values is fairly good, but sometimes there are serious differences. This demonstrates the capability of HPLC of controlling both the synthesis and the end use of alkylphenol ethoxylates.

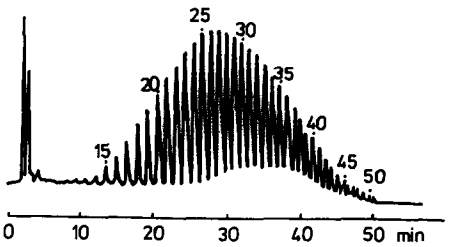

Fig. 6. Gradient elution of the oligomers from NPE_{30}. Eluent A, *n*-hexane–2-propanol (40:60, v/v); eluent B, ethanol–water (80:20, v/v). Gradient: 10–95% B in 45 min.

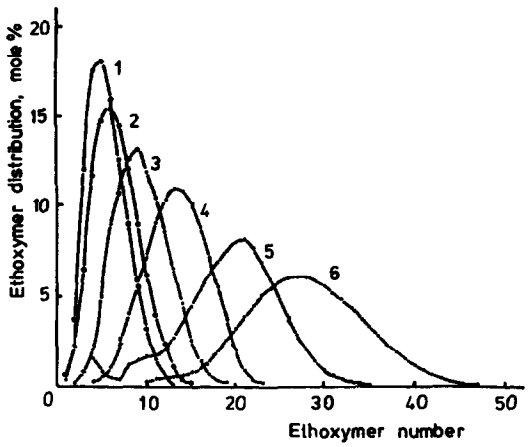

Fig. 7. Distribution of ethoxymers from various nonylphenol-based non-ionic surfactants: (1) NPE_4; (2) NPE_7; (3) NPE_{10}; (4) NPE_{15}; (5) NPE_{20}; (6) NPE_{30}.

Table 3
Average ethoxymer number of alkylphenol-based non-ionic surfactants determined by HPLC

Surfactant	Average ethoxymer No.	Surfactant	Average ethoxymer No.
NPE_3	2.96	NPE_{16}	18.13
NPE_4	4.44	NPE_{20}	19.38
NPE_6	6.09	NPE_{30}	29.00
NPE_7	6.64	NPE_{40}	37.20
NPE_8	8.68	OPE_2	1.79
NPE_{10}	10.22	OPE_3	2.75
NPE_{12}	12.23	OPE_6	6.17
NPE_{15}	13.11	OPE_8	8.05

3.2. Investigation of hydrophobic moiety

Reversed-phase HPLC can give information about the hydrophobic moiety of non-ionic surfactants [6–9,12]. It can be also used for the rapid identification and determination of non-ionic surfactants in technical samples [8,9,13,14], microemulsions for enhanced oil recovery [7], water and waste water samples [6,12–14] and during biodegradation tests [6,12].

We applied this method to the analysis of alkylphenol polyethoxylates. The surfactants under consideration were both homogeneously and polydisperse ethoxylates. The parent alkylphenols were also investigated.

Fig. 8 shows the chromatograms of (A) the parent nonylphenol and of (B) NPE_{30} and (C) NPE_7. The chromatogram of nonylphenol has a main peak that is preceded and succeeded by three and two smaller peaks, respectively. The chromatogram of NPE_{30} shows a similar "fingerprint" (see Fig. 8B). This "fingerprint" is typical of surfactants that show secondary peaks in normal-phase chromatography (see Figs. 3 and 4). The sample of NPE_7 is more homogeneous with respect to the nonylphenyl chain (see Fig. 8C). Here only minor impurities are associated with the main peak, which may be assigned to the *para*-isomer of nonylphenol. It is obvious that the surfactant was obtained from a carefully purified nonylphenol. Irrespective of the ethoxylation degree, all the NPE_n surfactants tested fell into these types of chromatograms.

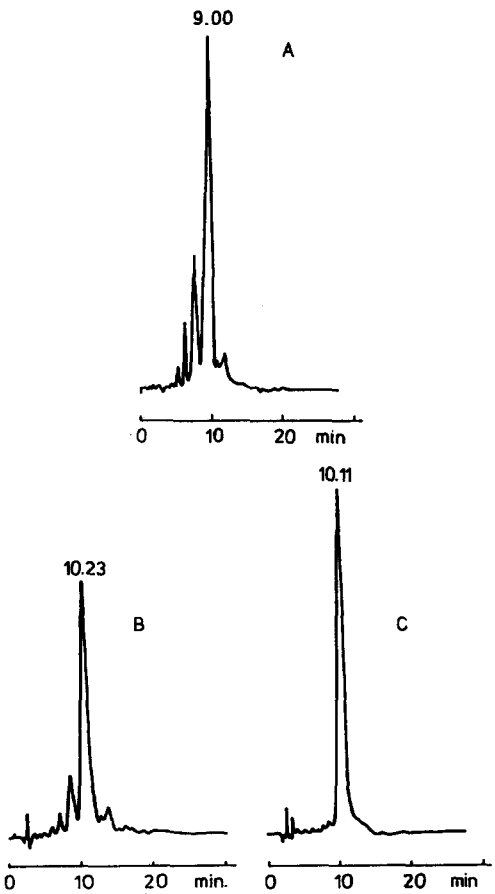

Fig. 8. Reversed-phase chromatogram of (A) nonylphenol, (B) NPE_{30} and (C) NPE_7 on an octadecylsilica column. Eluent: methanol–water (80:20, v/v).

Fig. 9 illustrates the chromatograms of (A) octylphenol and (B) OPE_6. They are simpler than those of nonylphenol and of ethoxylated nonylphenols. As only one peak is present in the sample it seems reasonable to assign it to *p*-octylphenol.

For both OPE_n and NPE_n surfactants the chromatograms show no influence of the ethoxylation degree on retention time. It is interesting that whatever the ethoxylation number, the surfactants are retained more tightly than their parent alkylphenols by the column. The phenomenon is equivalent to an increase in the

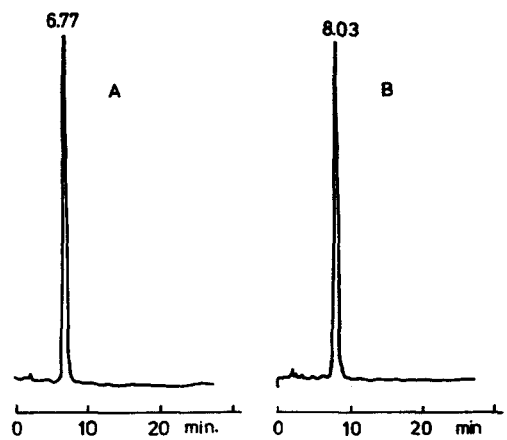

Fig. 9. Chromatogram of (A) octylphenol and (B) OPE_6. Column, octadecylsilica; eluent, methanol–water (80:20, v/v).

hydrophobic character of the alkylphenyl chains due to the presence of polyoxyethylene groups.

4. Conclusions

This work represents an attempt to use HPLC in the determination of ethoxylated octyl- and nonylphenols. The results confirm the power of this method to characterize the polyethoxylates and the possibility of detecting deficiencies appearing in synthesis.

Information about ethoxymer distribution was obtained by normal-phase chromatography on a silica column. The elution systems and the gradient programmes allow the baseline separation, identification and determination of oligomers. Surfactant samples having average ethoxylation numbers as high as 40 can be characterized in this way.

The hydrophobic moiety of the surfactants and the parent hydrophobe were investigated by reversed-phase chromatography. Differences between surfactants produced by alkylphenyl chains were found. The method can be used to distinguish non-ionic surfactants according to their alkylphenyl chains.

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