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Separation of broadly distributed nonylphenol ethoxylates and determination of ethylene oxide oligomers in textile lubricants and emulsions by high-performance liquid chromatography

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Abstract

A simple and rapid high-performance liquid chromatography method is described for separation and determination of ethoxylated nonylphenols. By using an amino bonded silica column with an acetonitrile–water gradient, the oligomers of ethoxylated nonylphenols with an average of 6 EO (ethylene oxide number) up to 40 EO were separated with satisfactory resolution. It was found that the partition of solutes between the stationary and mobile phases, and hydrogen bonding between solutes, solid-phase amino groups, water and acetonitrile were the main factors governing separation. The recoveries of total oligomers of nonylphenol-8 EO from a mixed emulsion with mineral oil, methyl oleate, peanut oil and the textile lubricant Blend 1 were 90.0±10.2, 95.6±7.9, 90.0±9.5 and 107.2±11.4%, respectively. The application of this method can be extended to determine non-ionic surfactants in other matrices.

Keywords: Ethylene oxide; Nonylphenol ethoxylates; Surfactants

1. Introduction

Non-ionic surfactants such as nonylphenol ethoxylates (NPEO) are widely used as wetting agents, emulsifiers and cleaners in the textile industry [1], as well as being important components in textile lubricants.

Commercial NPEOs are often a mixture of oligomers of different ethylene oxide number (EO). The oligomer distribution depends on both the initial ratio of ethylene oxide to nonylphenol and the synthesis route [2]. Oligomers of different EO may have widely divergent properties, e.g. nonylphenol-3 EO is lipophilic, whereas nonylphenol-10 EO is hydrophilic. Therefore, the behaviour of an NPEO in a textile lubricant formulation is dictated by its oligomeric composition. In textile processing, the lubricant is always applied as an emulsion in which the non-ionic surfactants mainly serve as emulsifiers, so they determine the effectiveness of the emulsion, in addition to physico-chemical properties such as stability and resistance to oxidation. An accurate determination of the oligomers is therefore necessary to evaluate the efficiency of emulsifiers and ensure

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the reproducibility of textile lubricants and their emulsions.

Various chromatographic procedures have been applied to the separation of NPEO oligomers. Thin-layer and paper chromatography are of limited applicability in this area [3–6], being mainly used as qualitative techniques. Gas chromatography has been used only for the low-EO mixtures [7,8], due to the limited volatility and thermal instability of the larger oligomers (EO > 8). The application of high-performance liquid chromatography (HPLC) in the determination of NPEO has been reviewed [9,10] and appears to be the most suitable technique for the separation and characterisation of NPEO.

The determination of non-ionic surfactants has generally been performed by normal phase chromatography [11–16]. Normal-phase HPLC using a diol column and gradient elution with non-polar solvents has been claimed by Zhou et al. [17] to separate up to 18 units of the NPEO oligomers. Angel et al. [18] reported the use of a silica column with gradient elution for the baseline separation of the EO adducts of alkylphenols with average EO of up to 40. Amino columns have been used in the majority of reports [11,15,19–22], mainly due to their commercial availability and high separation efficiency for the surfactant oligomers. However, most of the solvents used in the elution gradients were very complex and inherently unstable, e.g. [18] solvent A: *n*-hexane–diethyl ether (80:20, v/v) and solvent B: *n*-hexane–diethyl ether–dioxane–propan-2-ol–water–acetic acid (20:30:40:10:1:0.5, v/v).

Many authors [20,23–27] have used HPLC for the determination of non-ionic surfactants in environmental samples, and several [9,17,28] have applied the technique to ore flotation, petroleum spillage, the pulp and paper industry, etc. Only Taylor et al. [29] used HPLC to separate NPEO in textile lubricant formulations, and few peaks were detected due to the use of reversed-phase chromatography.

This paper describes the detailed determination of NPEO having large oligomer distributions with average EO numbers ranging between 6 and 40, by normal-phase HPLC using an amino column with a simple stable solvent gradient, covering the analysis of surfactant products, textile lubricants and emulsions.

2. Experimental

The nonylphenol ethoxylates (Synperonic NP) of average 6 EO, 8 EO, 10 EO, 12 EO, 13 EO and 15 EO were supplied by Benjamin R. Vickers and Sons, UK, and those with 30 EO and 40 EO were obtained from ICI, UK. The textile lubricant Blend 1, solvent-refined mineral oil, methyl oleate and solvent-refined peanut oil were also supplied by Benjamin R. Vickers and Sons. HPLC-grade solvents were used. All samples for HPLC analysis were prepared by dissolving the analytes in acetonitrile.

The HPLC system consisted of Model 6000A pumps, a Model 660 solvent programmer, a U6K injector, a Model 455 UV absorbance detector operated at 276 nm and a Model 740 integrator (Waters, UK). A 5-μm Spherisorb NH_2 column (250×4.6 mm; Phenomonex, UK) was used. All mobile-phase solvents were ultrasonically degassed. The flow-rate was 1 ml min^{-1}.

A VG MS9 mass spectrometer was operated in the fast atom bombardment mode (FAB-MS) with upper mass limit of m/z 1000. Argon was used as the atom gas; the source temperature was ambient and the detector chamber pressure was 10^{-7} Torr.

A lubricant emulsion was prepared by adding an equal weight of water to the lubricant and manually stirring or ultrasonically agitating the emulsion for 5 min. In order to remove any non-polar components, a sample of emulsion or lubricant (containing ca. 50 mg NPEO) was extracted with a 1:1 mixture of acetonitrile and *n*-hexane (20 ml); the lower phase was separated, and a further 10 ml acetonitrile was added. The combined lower phases were dried over anhydrous sodium sulphate (AR, 5 g) and the filtered extract was then adjusted to a total volume of 25 ml.

3. Results and discussion

3.1. Isocratic separation of short-chain NPEO

Isocratic HPLC was performed using different ratios of water in acetonitrile, where it was found that Synperonic NP8 (i.e. average 8 EO) was satisfactorily resolved with 3.5% water in acetonitrile (Fig. 1). Isocratic conditions were initially consid-

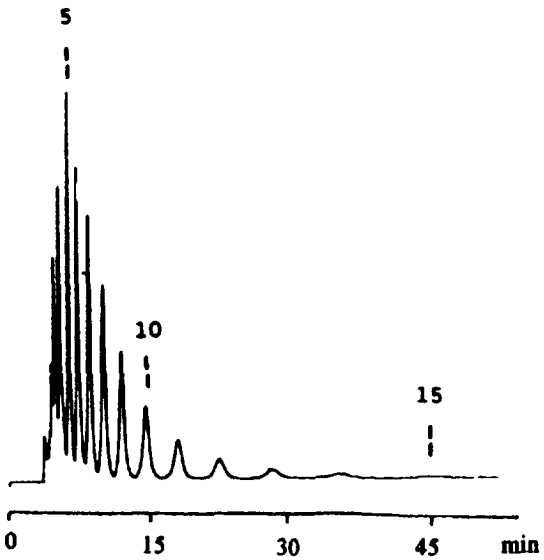

Fig. 1. HPLC chromatogram of Synperonic NP8 using isocratic elution. Conditions: mobile phase, acetonitrile–water (96.5:3.5); column, 5-μm Spherisorb NH_2 (250×4.6 mm I.D.).

ered because of their simplicity, reduced cost and rapidity, but the disadvantage was that short EO chains were eluted too rapidly while the larger oligomers were too difficult to elute, resulting in the early peaks being narrow and unresolved, while the last were broad and flat. Changing the eluant polarity gave a satisfactory resolution of NPEO from 0 to 16, and in general, these isocratic conditions were suitable for the determination of NPEO with average EO numbers <10.

A study of the influence of the polar component (water) on the capacity factors (k') or the retention times of the oligomers under isocratic conditions showed a linear relationship between the amount of water in the mobile phase and $\ln k'$ (Fig. 2), i.e. there was an exponential relationship between the water content and the retention times. The resolution and elution time for the surfactant oligomers could be easily adjusted by simply changing the water content. Aqueous mixtures of other organic solvents, including methanol, were also tested, but no satisfactory result was obtained.

Acetonitrile–water mixtures are relatively unusual as mobile phases in normal-phase HPLC and no study of non-ionic ethoxylated surfactants has been carried out using such solvents. Given the peak sequences of the oligomers in the chromatograms, reversed-phase conditions are not operational. Since 5% water (increasing to 20% in gradients, see below) was used in the mobile phase, any free silanol or silicon oxide groups in the stationary phase have little adsorptive function in the separation of the

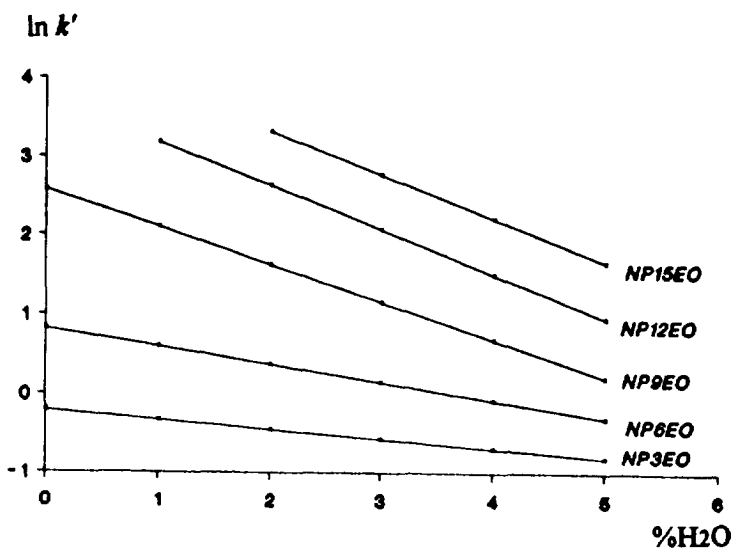

Fig. 2. Relationship between %water in mobile phase and $\ln k'$.

oligomers, which seems rather to depend upon other interactions, including partition, between the solutes, the mobile phase and the stationary phase. Hydrogen bonding can occur between the ethoxide groups of the solutes, the stationary phase amino groups, and water. Van der Waals interactions can occur between the ethoxide groups and acetonitrile, and the solutes can also compete with water in interacting with the amino groups. Consequently, the longer ethoxide chains require more water for hydrogen bonding, a situation which will concurrently reduce any hydrogen bonding between the ethoxide groups and the amino groups, leading to the shorter chains being eluted more readily.

3.2. Characterisation of oligomers in NPEOs

Due to a lack of discrete NPEOs, i.e. single EO-numbered components, identifications of the peaks in chromatograms were based on comparisons of the retention times with that of 4-*n*-nonylphenol (0 EO) and on the customary assumption that neighbouring peaks differ by 1 EO unit. The oligomers with large EO numbers were deduced by comparing their retention times with those of smaller EO numbers, e.g. the oligomer NP-13 EO in Synperonic NP15 was determined by comparison with that in Synperonic NP8, and NP-22 EO in Synperonic NP30 was correlated with that in Synperonic NP15, etc. The first peak in all chromatograms was initially suspected to belong to 4-*n*-nonylphenol, but was later found to belong either to an impurity or a catalyst from the ethoxylation stage of the synthesis.

Attempts to characterise the oligomers were also made by FAB-MS. The spectra typically contained ions derived by protonation of oligomers [30] to give pseudo-molecular ions, e.g. NP-8 EO gave: *m/z* 221 $[NP+H]^+$; 265 $[NP-1\ EO+H]^+$; 309 $[NP-2\ EO+H]^+$; 395.5 $[NP-4\ EO]^+$; 440.3 $[NP-5\ EO+H]^+$; 484.4 $[NP-6\ EO+H]^+$; 527.9 $[NP-7\ EO]^+$; 528.9 $[NP-7\ EO+H]^+$; 573.4 $[NP-8\ EO+H]^+$; and 617.8 $[NP-9\ EO+H]^+$.

3.3. Gradient elution of NPEOs with large oligomer distributions

In order to separate the oligomers with a large EO number without sacrificing the resolution of smaller oligomers, a solvent gradient was required. Since acetonitrile can elute oligomers <8 EO, it was selected as solvent A in the gradient, and solvent B was formed from mixtures of acetonitrile and water appropriate to the average EO number to be determined. Table 1 shows the gradient programmes used in the determination of NPEOs with average EO 6–40; the commercial products were satisfactorily characterised and Fig. 3A–3E show the chromatograms belonging to Synperonics NP6–NP40. Increasing the column temperature reduced the retention times, but did not increase the oligomer resolution.

Table 1
The solvent programmes for the separation of NPEOs of different average EO

Analyte	%B in gradient at		Gradient duration (min)	Final isocratic continuation (min)
	Start	End		
Synperonic NP6	2.5	40	30	0
NP8	2.5	40	30	5
NP10	2.5	50	30	5
NP12	2.5	50	30	10
NP13	5.0	50	30	10
NP15	10.0	50	40	5
NP30	25.0	75	45	15
NP40	35.0	100	60	10
NP6+NP15	2.5	50	45	5

Solvent A: acetonitrile; solvent B: water–acetonitrile (20:80, v/v).

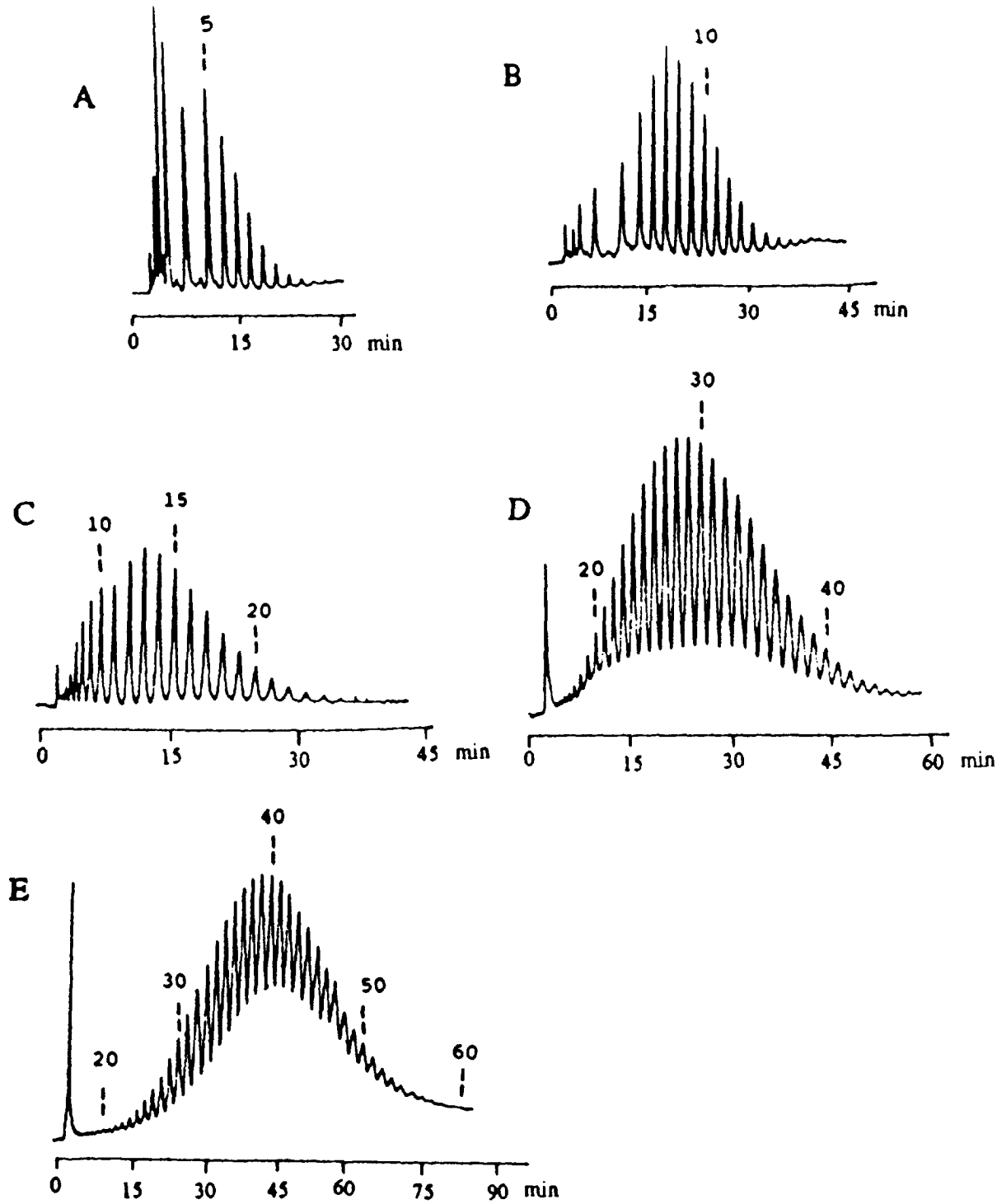

Fig. 3. HPLC chromatograms of Synperonic NPs using gradient programme: (A) Synperonic NP6; (B) Synperonic NP10; (C) Synperonic NP15; (D) Synperonic NP30; (E) Synperonic NP40. Conditions: column, 5-μm Spherisorb NH_2 (250×4.6 mm I.D.); solvent programme described in Table 1.

The method was also capable of determining a mixture of NPEOs, and Fig. 4 shows the results from a 1:1 mixture of Synperonic NP6 and NP15.

3.4. Distribution of NPEO oligomers

Replicate samples of several commercial NPEOs were determined by the appropriate gradients listed in Table 1. Since the phenyl ring is the sole chromophore (ϵ_{max} at 276 nm) in the oligomers, all oligomers were assumed to have the same molar absorption [31]. Mole fractions of the NPEO oligomers were calculated based on the respective peak areas for each oligomer in the chromatograms, and average EO numbers were obtained for the commercial products according to the mole fraction and the number of EO units in each oligomer. In general, the oligomer distributions for Synperonic NPs (Fig. 5) exhibited Gaussian distributions, where the EO number at the apex of the respective distributions was equal, or near to, the NPEO number listed by the manufacturer (Table 2). It can be seen that most of the EO averages determined by HPLC are smaller than the initial mole ratio of ethylene oxide and 4-*n*-nonylphenol in the synthesis. This may confirm the existence of UV-transparent free aliphatic polyethoxides [32] in the samples.

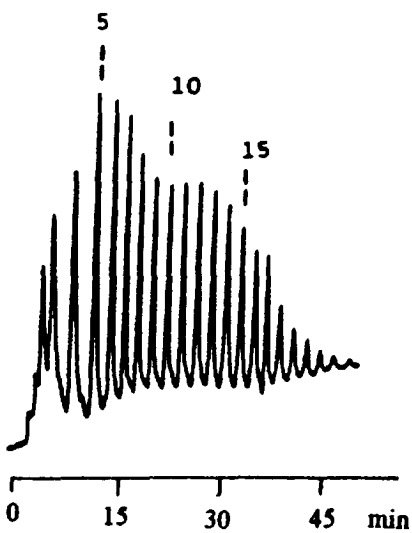

Fig. 4. Chromatogram of Synperonic NP6 and Synperonic NP15 mixture. Conditions: column, 5-μm Spherisorb NH_2 (250×4.6 mm I.D.); solvent programme described in Table 1.

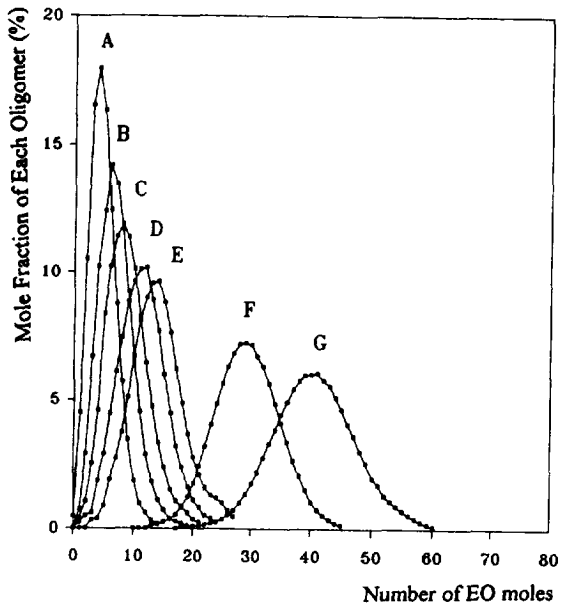

Fig. 5. Oligomer distributions of Synperonic NPs as determined by HPLC. (A) Synperonic NP6; (B) Synperonic NP8; (C) Synperonic NP10; (D) Synperonic NP13; (E) Synperonic NP15; (F) Synperonic NP30; (G) Synperonic NP40.

3.5. Determination of NPEO oligomers in emulsions and textile lubricants

NPEOs are used as emulsifiers in textile lubricants which may have to be multi-component systems. The major component, usually >50% of a textile lubricant, is the base oil, which can be a natural product such as mineral or vegetable oil, or a semi- or fully-synthetic organic compound. In the present study, mineral oil, peanut oil and methyl oleate were selected as base oils for emulsions comprised of 90% base oil and 10% NPEO emulsifier mixed with an equal weight of water. Mineral oil, peanut oil and methyl oleate are all technical-grade materials which are a mixture of many components, some of which are non-polar and may be insoluble in the mobile phase and can thus be removed by the acetonitrile–hexane phase separation procedure.

Since mineral oil is the main component in Blend 1, the separation procedure was also used for non-emulsified Blend 1 and its emulsion, resulting in oil-derived background interference affecting only the 4-*n*-nonylphenol and NP-1 EO peaks in the chromatograms (Fig. 6A, B), a similar situation

Table 2
Average ethylene oxide number of Synperonic NPs determined by HPLC

Synperonic surfactant	Average EO number	Synperonic surfactant	Average EO number
NP6	4.8	NP13	11.3
NP8	7.0	NP15	14.3
NP10	8.6	NP30	29.1
NP12	9.4	NP40	40.4

$n = 6$.

occurring with alternative base oils (Fig. 6C). Recoveries of Synperonic NP8 oligomers were calculated from the known initial concentration of 10% (w/w). The recoveries of the NPEOs in the emulsions and Blend 1 (Table 3), confirm that the HPLC procedure used is suitable for NPEO-type emulsifiers in both emulsions and lubricants.

4. Conclusion

Using an NH_2 column with an acetonitrile–water isocratic mixture or gradient as mobile phase provides information on the quantitative oligomer distribution of nonylphenol ethoxylate (NPEO) mixtures. In the gradient mode, oligomers of up to 60 ethoxide (EO) units can be characterised. The separation is not dominated by a simple adsorption mechanism, with partition and hydrogen bonding between the analytes, the amino groups in the stationary phase, water and acetonitrile being considered as playing important roles. The method can be applied to mixtures of surfactants, and textile lubricants and their emulsions, and should be applicable to similar determinations in the wider environment.

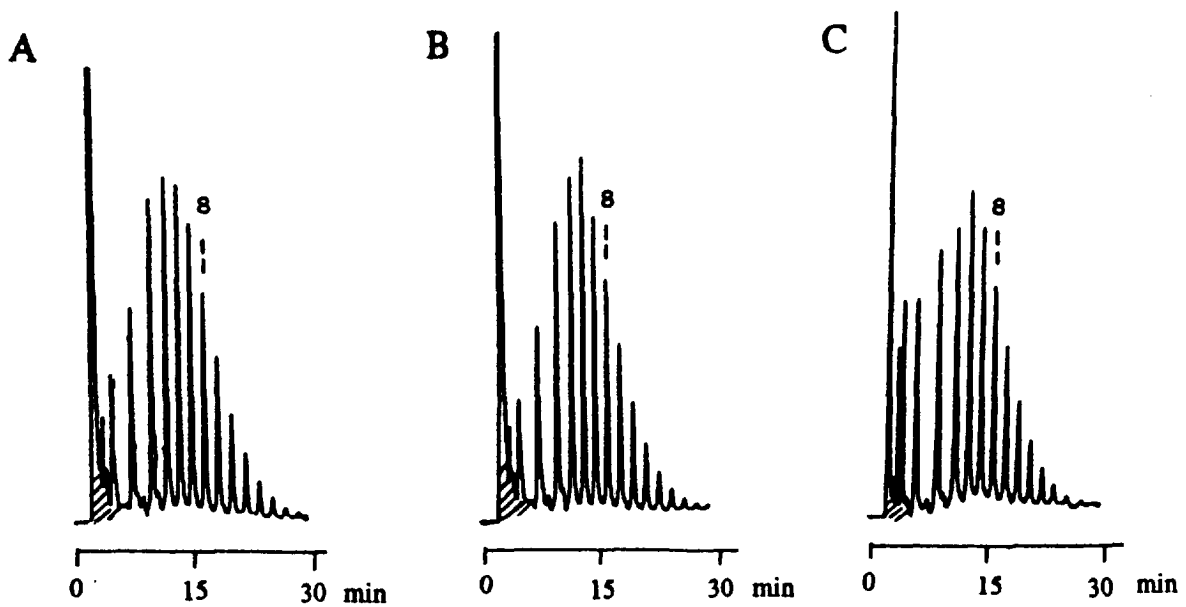

Fig. 6. HPLC chromatograms of Synperonic NP8 extracted from the lubricant Blend 1 and emulsions: (A) Synperonic NP8 in Blend 1; (B) Synperonic NP8 in Blend 1 emulsion; (C) Synperonic NP8 in peanut oil emulsion. Conditions: column, 5-μm Spherisorb NH_2 (250×4.6 mm I.D.); solvent programme described in Table 1. The hatched area indicates background interference from the base oil.

Table 3
Recoveries of oligomers of Synperonic NP8 used in the emulsions and Blend 1 as determined by HPLC

EO number	X±S.D.% of sample[a]				
	1	2	3	4	5
1	100.6±11.3	86.1±13.2	81.9±14.6	97.2±8.5	91.1±12.2
2	82.3±15.6	102.4±6.7	92.3±11.7	99.0±4.9	100.4±8.7
3	83.8±12.1	92.8±10.4	89.7±9.2	99.7±6.5	86.2±11.4
4	87.9±11.2	102.8±7.7	93.8±12.8	107.2±12.6	93.4±6.6
5	102.9±7.0	91.3±12.6	91.5±5.6	99.3±5.1	92.9±7.3
6	100.5±8.9	98.9±2.7	87.8±13.0	108.4±10.5	90.6±10.1
7	85.9±9.1	95.6±4.8	86.6±11.4	114.1±15.6	90.3±9.8
8	85.0±13.3	95.2±5.1	89.1±9.2	112.3±12.2	92.1±8.5
9	85.1±15.7	96.1±7.9	92.0±7.8	110.0±13.4	93.0±7.1
10	85.0±14.4	92.5±8.2	90.5±10.6	105.3±9.9	91.6±9.0
11	83.1±15.8	93.4±10.1	91.5±6.3	108.2±11.4	92.3±10.9
12	83.3±8.9	95.4±6.5	93.5±4.7	110.0±11.7	94.9±6.3
13	86.7±9.5	93.6±7.8	93.2±8.1	92.4±8.6	93.0±7.7
14	95.5±6.3	85.2±12.4	84.8±10.6	117.6±13.9	85.6±13.3
15	105.5±8.8	90.4±10.1	92.4±9.7	94.8±8.0	96.2±9.5
16	101.4±12.5	94.5±13.2	92.2±14	85.1±10.9	89.6±11.4
Total	90.0±10.2	95.6±7.9	90.0±9.5	107.2±11.4	91.9±9.2

$n = 3$ from four replicate emulsions or blend samples.
[a] Samples 1, 2, 3 and 4 are Synperonic NP8 in the emulsions of mineral oil, methyl oleate, peanut oil and lubricant Blend 1, respectively. Sample 5 is Synperonic NP8 in the lubricant Blend 1.

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