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Separation and determination of oligomers and homologues of aliphatic alcohol ethoxylates in textile lubricants and lubricant emulsion by high-performance liquid chromatography

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Abstract

Homologous mixtures of 3,5-dinitrobenzenoates of aliphatic alcohol ethoxylates (AEs) were separated by high-performance liquid chromatography (HPLC) with high resolution using an amino bonded silica column and gradient elution of ternary solvents (hexane–dichloromethane–methanol). When the method was combined with novel sample clean-up and extraction procedures, oligomers of AEs in textile lubricants and a lubricant emulsion were satisfactorily determined with recoveries >75% and good reproducibility. A reversed-phase HPLC method was also developed to characterise the alkyl groups of AEs.

Keywords: Textile lubricants; Aliphatic alcohol ethoxylates; Alcohol ethoxylates

1. Introduction

Aliphatic alcohol ethoxylates (AEs) are an increasingly important class of non-ionic surfactants used as emulsifiers and scouring, finishing and wetting agents in the textile industry [1], as well as an important component of textile lubricants.

Commercial AEs are a complex mixture [2] of varied alkyl groups (isomers and homologues) and with a range of ethylene oxide adducts (EO, oligomers). Commonly the alkyl groups in AEs consist of both linear and branched aliphatic chains. The alkyl groups and ethylene oxide units influence the application of AEs separately. Hence, two AEs having different alkyl groups (number of carbon atoms or structure) and identical average EO units might be found to have different surfactant character, and two identical alkyl chain AEs with different EO units might also have different surfactant character.

In textile lubricants, AEs play a significant role in the effectiveness of emulsions, as well as influencing physico-chemical properties such as stability and resistance to oxidation, while at the same time being more biodegradable than alkylphenol ethoxylates [3,4]. Quantitative characterisation of their oligomers and homologues, necessary for quality control and lubricant research, is complicated by the distribution of EO oligomers, alkyl homologues and isomers, and can be achieved only by instrumental methods.

Although thin-layer chromatography [5] and paper chromatography [6] have been successful in separat-

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ing various oligomers of alkyl ethoxylates, irreproducibility and difficult quantification of these techniques limit their applicability in this area. Gas chromatography (GC) with HBr cleavage was used to determine the alcohol ethoxylates in environmental samples [7], with the alkyl bromide cleavage products being determined by GC, but no significant information about EO distribution was provided. The analysis of ethylene oxide derivatives of secondary alcohols by GC has been carried out by Puschmann [8], using acetate derivatives. Conventional GC, however, is useful only in the determination of AEs with short EO units. Recently, high-temperature GC using aluminium-clad fused-silica capillary columns [9,10], has been demonstrated as a viable method for the quantitative characterisation of commercial alcohol ethoxylate samples, but the technique still discriminates against high-molecular-mass components.

Supercritical fluid chromatography (SFC) was proposed as an alternative analytical procedure for both qualitative and quantitative characterisation of AEs [9,11]. SFC has the advantage of time because derivatization is not required, but has a resolution limitation [9].

High-performance liquid chromatography (HPLC) has been used to determine both EO oligomers and alkyl homologues of AE derivatives by conventional UV detection [3,12,13], or without derivatization by using specific detectors such as mass spectrometry [4,14] and evaporative light scattering [3,15–17]. In general, reversed-phase HPLC has been employed to determine AEs according to their alkyl groups, i.e., homologues [18,19], whereas the analysis of AEs in terms of their EO distribution has been achieved by normal-phase HPLC using amino-, cyano- and diol-bonded silica [3,13,20,21]. However, Mengerink et al. [17]. reported that a complete analysis of oligomers of AE was achieved by reverse phase LC using two C_{18} columns. A combination of ion-exchange chromatography and complexation of metallic cations by alcohol ethoxylates has been successfully applied to determine various AEs [22,23]. The lack of UV chromophores in AEs requires a derivatization for HPLC methods using UV detection, with chromophore-bearing reagents having previously included phenylisocyanate [3,19], 1-naphthylisocyanate [18] and 3,5-dinitrobenzoyl chloride [13,20].

Mass spectrometry (MS) and HPLC–MS have emerged as powerful techniques for determination of AEs by both alkyl chains and EO oligomers [14,24,25], and ^{13}C nuclear magnetic resonance spectrometry has also offered detailed information for molecular structure analysis of AEs. However, neither of these are likely to be adopted as routine industrial monitoring techniques due to cost and complexity.

The application of the cited investigations has focused on the determination of AEs in environmental samples. Marcomini and Zanette [26] recently published a review of chromatographic determination of AEs in the environment. No literature has been found for analysis of AEs in textile lubricant formulations or textile samples.

As in the previous work [27] on the determination of nonyl phenol ethoxylates (NPEO), this paper describes the determination of AEs by both normal-phase HPLC using an amino column and reversed-phase HPLC using a C_{18} column in an attempt to characterise both the EO oligomer and alkyl group compositions. The samples investigated included commercial AEs, textile lubricants and a lubricant emulsion.

2. Experimental

The aliphatic alcohol ethoxylates (Synperonic A) of average 2EO, 3EO, 7EO were supplied by Benjamin R. Vickers and Sons, UK, and those with 11EO, 20EO and 50EO were obtained from ICI, UK. Dodecanol (C_{12}-OH), tridecanol (C_{13}-OH) and tetradecanol (C_{14}-OH) were purchased from Aldrich, UK. Octaethylene glycol monodecyl ether (C_{12}-8EO) was supplied by Fluka, UK. The textile lubricant Blend 2, which consists of 70% mineral oil, 10% oleic acid, 5% methyl oleate, 5% groundnut oil and 10% AE-7EO, and the individual components of Blend 2 were also supplied by Benjamin R. Vickers and Sons. Blend 1 and Blend 3 were prepared based on the formulation of Blend 2 by using AE-2EO and AE-11EO, respectively, instead of AE-7EO. HPLC

grade solvents were used. All samples for HPLC analysis were prepared by dissolving the analytes in dichloromethane.

The HPLC system consisted of Model 510 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) and a 5 μm Lichrosorb RP18 (250×4.6 mm, Capital HPLC, UK) were used. Samples (5 μl) were injected into the HPLC column for the analysis of AE-2EO, 3EO, 7EO and 11EO, and 10 μl for AE-20EO and 50EO. All mobile phase solvents were ultrasonically degassed. The flow-rate was 1 ml min^{-1}.

A VG MS9 mass spectrometer (Fisons Instruments) was operated in the fast atom bombardment mode (FAB-MS) with upper mass limit of 1000 *m/z*. Argon was used as the atom gas; the source temperature was ambient and the detector chamber pressure was 10^{-7} Torr (1 Torr = 133.322 Pa). A DPX 400 nuclear magnetic resonance spectrometer (Bruker Instruments) was used in the ^{13}C mode (100 MHz with CD_2Cl_2 solvent).

The derivatization reaction was carried out by heating an intimate mixture of 3,5-dinitrobenzoyl chloride (DNBC, 28 mg) and AE (0.10 μ*M*) at 60°C (water bath) for 10 min. The product was cooled, dissolved in dichloromethane (10 ml) and then shaken with 2% sodium carbonate solution (10 ml). The organic phase was dried with anhydrous sodium sulphate (2 g) and was then transferred to a 10 ml volumetric flask.

A lubricant emulsion was prepared by adding water to the lubricant (4:1, v/v) and manually stirring or ultrasonically agitating the emulsion for 5 min. Before analysis, an emulsion sample containing about 0.1 μ*M* AE was diluted to 10 ml using 10% NaCl solution. The emulsion was extracted with dichloromethane (2×10 ml) and the combined organic phase, dried with anhydrous sodium sulphate (2 g), was evaporated under nitrogen. In order to remove any non-polar component, a sample of emulsion residue or lubricant was extracted with a mixture of acetonitrile (10 ml) and *n*-hexane (10 ml); the lower phase was separated, and further acetonitrile (10 ml) was added. The combined lower phases were evaporated under nitrogen, prior to derivatization as above.

3. Results and discussion

3.1. Determination of AEs using an amino column

The dinitrobenzoyl derivatives of the AEs were examined using normal-phase HPLC with an amino column. Since there is a wide range of polarity of oligomers present in AEs, it was difficult to optimise the mobile phase, even employing gradient elution. Taking into consideration solvent characteristics such as UV cut-off, viscosity, compatibility and elution strengths, *n*-hexane was selected as the base solvent, with methanol as the strong eluting solvent and dichloromethane as the co-solvent. The gradient elution conditions are listed in Table 1. By slightly adjusting the ternary solvents in the mobile phase, the HPLC system can separate all the oligomers in AEs from 2EO to 50EO (Fig. 1). The split peaks appearing for every oligomer in the chromatograms (AE-2EO–11EO, 4-5 peaks, AE-20EO, 2–3 peaks) were considered to be the homologues of alkyl chains in the aliphatic alcohol sub-units. Therefore, this normal-phase HPLC system, summarised in Table 1 and Fig. 1, can not only separate the AEs by oligomer, but can also give some indication of aliphatic chain structure. Fig. 1 also shows that the resolution of the aliphatic parts AEs decreases as the EO number increases (only one peak for each oligomer of AE-50EO). In other words, the ability of

Table 1
The solvent programmes for the separation of AEs by HPLC

AEs	*X*:*Y*:*Z*	Gradient duration (min)	Final isocratic continuation (min)
2EO	5:15:80	40	10
3EO	5:15:80	45	10
7EO	8:24:68	60	10
11EO	10:30:60	70	20
20EO	15:35:50	90	20
50EO	20:40:40	110	20

Solvent A: hexane; solvent B: methanol–dichloromethane–hexane in the volumetric ratio of *X*:*Y*:*Z*, from 10% B to 80% B in all gradients.

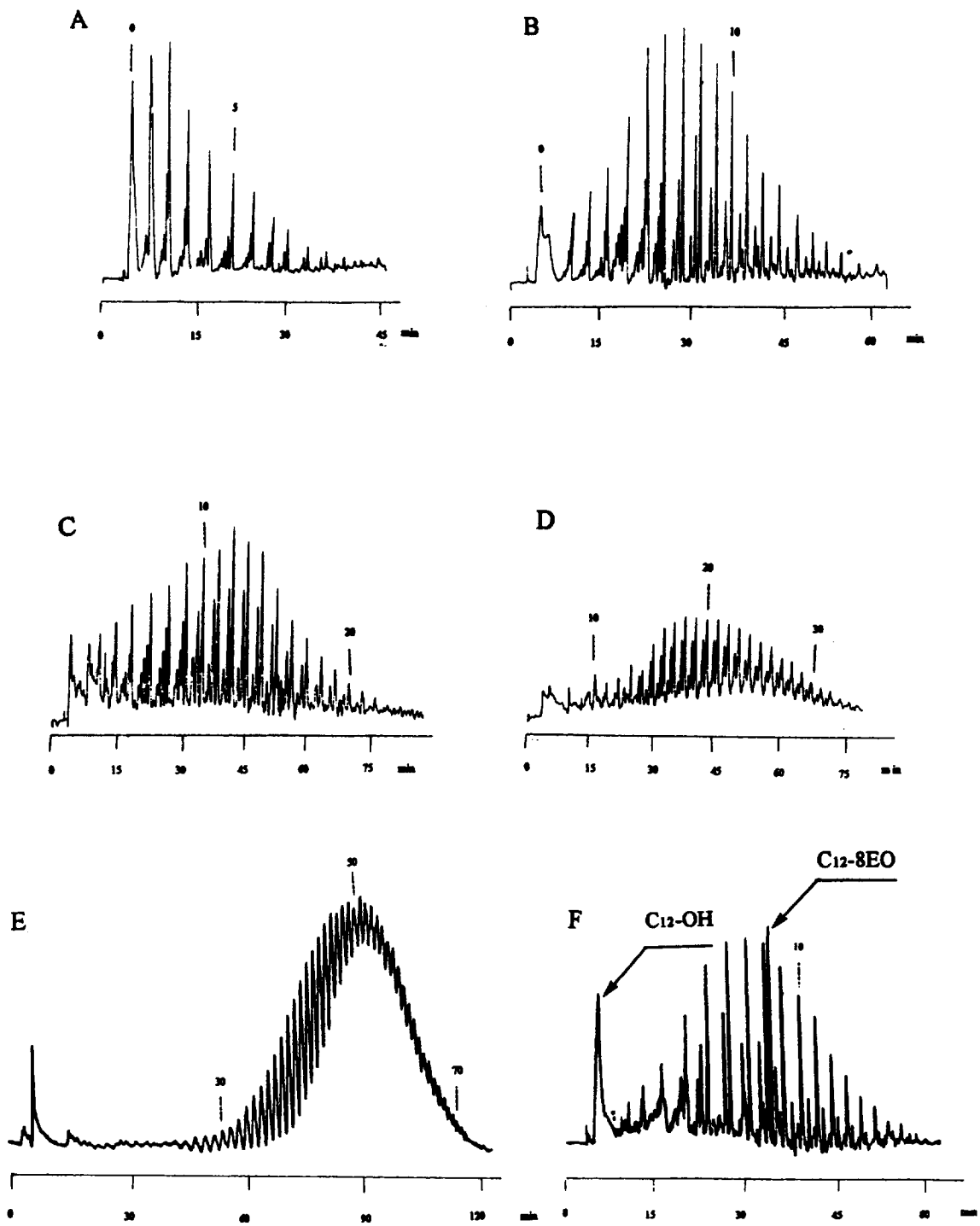

Fig. 1. Chromatograms of 3,5-dinitrobenzoyl derivatives of AEs by HPLC (UV at 276 nm, solvent gradient described in Table 1). (A) Synperonic A2; (B) Synperonic A7; (C) Synperonic A11; (D) Synperonic A20; (E) Synperonic A50 and (F) a mixture of Synperonic A7, C_{12}-8EO and C_{12}-OH. Column, 5 μm Spherisorb NH_2 (250×4.6 mm I.D.).

amino phase to distinguish between the aliphatic groups decreases as the polarity of mobile phase increases.

3.2. Influence of the ratio between AE and dinitrobenzoyl chloride

Although several authors [3,13,19] have described the use of DNBC or phenylisocyanate for derivatization, most have not detailed how much of the reagent should be used. In order to accurately determine the AEs, the AE/reagent ratio was examined for Synperonic A7 (Table 2). From the chromatograms and peak areas it can be concluded that it is better for the reagent to be slightly in excess (~25%). However, an over-excess of reagent will interfere with the determination (Fig. 2), as reported by Nitschke and Huber [19].

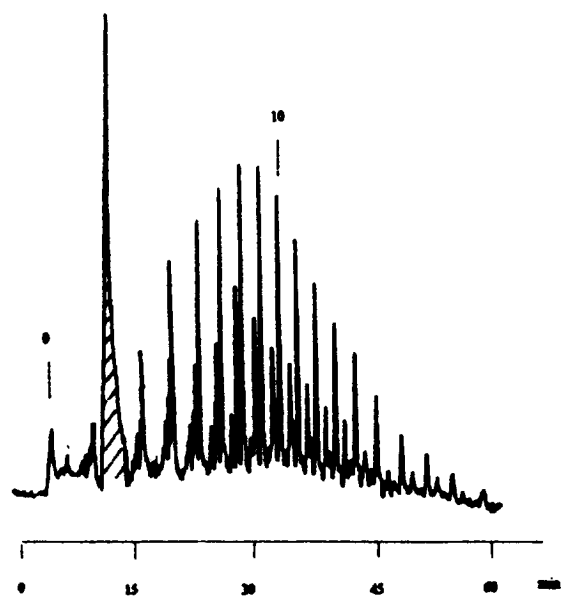

Fig. 2. Chromatogram of AE-7EO derivatized with excess DNBC. Conditions as in Fig. 1B. The hatched area indicates interference from excess derivatizing reagent.

3.3. Characterisation of the aliphatic chains of AEs by reversed-phase HPLC

The peaks in the derivatized AE chromatograms were compared to the peaks of derivatized aliphatic alcohols (n-$C_{12}H_{25}OH$, n-$C_{13}H_{27}OH$ and n-$C_{14}H_{29}OH$) under the same elution conditions. The main peak for AE-7EO appeared at the same t_R as n-$C_{13}H_{27}OH$ (Fig. 3); it is believed that tridecanol ethoxylate is the main component in this type of AE-7EO. The t_R values of n-$C_{12}H_{25}OH$ and n-$C_{14}H_{29}OH$ were 20.9 and 28.4 min, respectively, and no corresponding peak appeared in the chromatogram of AE-7EO, although there were some peaks nearby, which corresponded to some branched aliphatic alcohol ethoxylates. The second largest peak at t_R 30.3 min was considered to correspond to an AE with an alkyl chain $>C_{14}$. The small peaks with $t_R<20$ min were considered to be ethoxylates of alcohols with less than 12 carbons (either linear or branched).

There are more than 10 peaks in the derivatized AE-7EO sample, so it is apparent that the aliphatic parts of AE are correspondingly complex. In general, aliphatic differences in AEs have little influence on their separation by normal-phase HPLC, but may be seen in the chromatograms obtained using an amino column (Fig. 1), as approximately 4 peaks for each oligomer.

Table 2
The relationship of peak areas for AE-7EO and the mole ratio between the DNBC (3,5-dinitrobenzoyl chloride) and the AE

DNBC:AE	Total areas (10^5)	Area of 7EO oligomer (10^5)
1:2	16.8	1.2
1:1	27.8	2.3
1:0.75	45.9	3.7
1:0.5	49.6	3.5

3.4. Confirmation of the structure of AEs by mass spectroscopy and ^{13}C NMR spectroscopy

Characterisation of both oligomers and aliphatic chains of AE-7EO was also carried out using FAB-MS. The resultant spectrum not only demonstrates the oligomer series, but also shows the existence of aliphatic chains, in series A with m/z 201, 245, 289, 333, 377, 421, 465, 509, 553, 597, 641, 686, series B with m/z 317, 361, 405, 449, 493, 537, 581, 626, 670, and series C with m/z 283, 327, 415, 459, 503, 547, 591, 635, 679 (44 or 45 step, the mass of one EO unit). It is concluded that series A comprises the

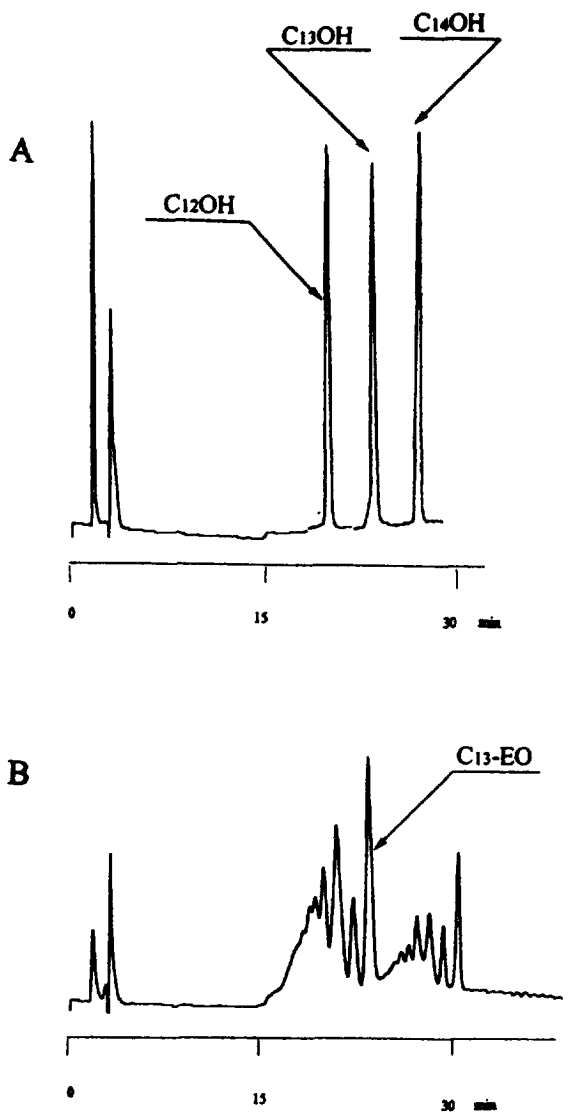

Fig. 3. Chromatograms of derivatives of (A) a mixture of dodecanol, tridecanol and tetradecanol and (B) AE-7EO. Conditions: column, 5 μm Lichrosorb RP18 (250×4.6 mm I.D.); solvent gradient from 20% B to 80% B in 35 min (solvent A methanol–water (80:20) and solvent B methanol); UV detection at 276 nm.

ions M+1 of $C_{13}H_{27}OH$ ethoxylated with different numbers of ethylene oxide. Series B is the contribution of the M−1 ions of dodecanol ethoxylates. Series C is the M−1 ions of $C_{19}H_{39}$-$(OCH_2CH_2)_n$-OH (n=0, 1, 2, 3...). The above deductions were confirmed by the FAB-MS spectra of $C_{12}H_{25}OH$, $C_{13}H_{27}OH$ and $C_{14}H_{29}OH$. Combined with the results of reversed-phase HPLC, it can be confirmed that tridecanol ethoxylates are the main components in AE-7EO.

Quantitative ^{13}C NMR of AE-7EO was also used to investigate both aliphatic and ethoxylate chains. The aggregate integral (equal to C numbers) at the low shift region (<35 ppm=aliphatic) was 10, and that at the high shift (>60 ppm=ethoxylate) was 13 (Fig. 4), both less than the theoretical (aliphatic=12 and ethoxylate=15). Quantification in ^{13}C NMR has problems with background noise, and tends to ignore small peaks. The chemical shift at 14.3 ppm (Fig. 4) is associated with the terminal-methyl alkyl chains, while that at 17.3 ppm (intensity 0.2) is believed to arise from branched methyl groups.

3.5. Oligomer distribution in AEs

C_{12}-8EO and C_{12}-OH (Fig. 1F) were used as internal standards, in addition the oligomers of AEs were deduced by comparing the retention times of oligomers having long EO chains with those whose short chain EO numbers were known. The response factors for C_{12}-OH, C_{12}-8EO and AE-7EO were examined, and are $4.06 \cdot 10^{-4}$ ppm (0.20 to 2.0 mg,

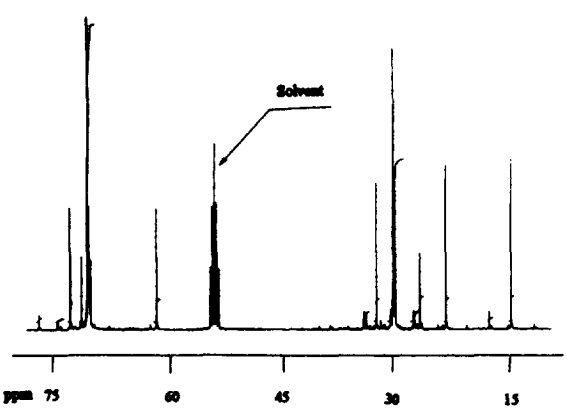

Fig. 4. Quantitative spectrum of ^{13}C NMR for AE-7EO. Chemical shifts (integral areas): 14.3 (1.00); 17.3 (0.14); 23.1 (0.93); 26.5–27.3 (1.01); 29.8–30.5 (6.43); 31.7–32.3 (0.90); 33.7–34.0 (0.38); 61.7 (0.98); 70.3–70.7 (13.93); 71.6 (0.79); 73.0 (0.98); 74.7 (0.14) and 77.1 (0.13).

γ=0.999), $1.21 \cdot 10^{-3}$ ppm (0.50 to 5.0 mg, γ= 0.999) and $1.14 \cdot 10^{-3}$ ppm (10.0 to 50.0 mg, γ= 0.997), respectively. If the response factors are expressed in μM, they are $2.18 \cdot 10^{-9}$, $2.25 \cdot 10^{-9}$ and $2.24 \cdot 10^{-9}$ μM for C_{12}-OH, C_{12}-8EO and AE-7EO, respectively (on the assumption that average molar mass of AE-7EO is equal to 508, the molar mass of C_{13}-7EO). This demonstrates that dinitrobenzoyl is the only chromophore in the derivatives and alcohol alkyl chains have almost no influence on the UV absorption at 276 nm, i.e., the derivatized AEs have one chromophore per molecule and the response of the UV detector is independent of the polyoxyethylene and alcohol chain length. Since the molar absorption of AE derivatives is almost identical, the integrated peak area can be used directly to examine the mole ratio of each oligomer. The oligomer distributions of commercial AE-2EO, 3EO, 7EO, 11EO, 20EO and 50EO were thus determined by using the quantitative method in the literature [28] (see Fig. 5).

3.6. Determination of AE oligomers in textile lubricant blends and emulsions

Lubricant Blend 1 (300 mg), Blend 2 (400 mg) and Blend 3 (700 mg) were analysed for AEs. The solvent system hexane–acetonitrile was used for sample clean-up prior to derivatization and chromatography. In general, the clean-up procedure can reduce interference from matrices of textile lubricants, and more importantly protect the column from the detrimental effects of certain non-polar components.

Fig. 6 demonstrates some interference from co-extracted analytes, but the interference influences only AE-1EO, and the distribution of the ethylene oxides of AE-7EO is clearly demonstrated, while AE-11EO in Blend 3 can be determined more readily than AE-7EO in Blend 2. The recoveries of AE oligomers in the Blends were over 75%, and are reproducible (Table 3). AE-7EO in the Blend 2 emulsion was also determined by HPLC after extraction by dichloromethane and clean-up by hexane–acetonitrile (Table 3). The clean-up procedure was found to be unsuitable for Blend 1 due to the insolubility of AE-2EO in the acetonitrile phase; however, AE-2EO in Blend 1 was determined following the direct derivatization of Blend 1 at about

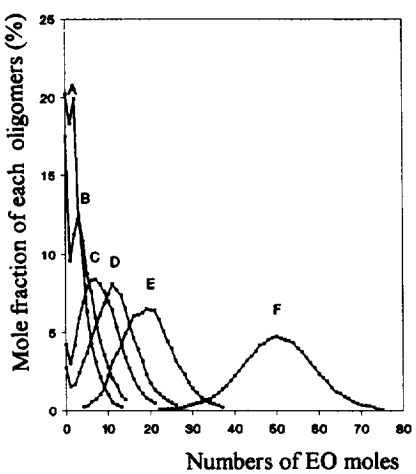

Fig. 5. Oligomer distributions of Synperonic As as determined by HPLC. (A) Synperonic A2; (B) Synperonic A3; (C) Synperonic A7; (D) Synperonic A11; (E) Synperonic A20; (F) Synperonic A50.

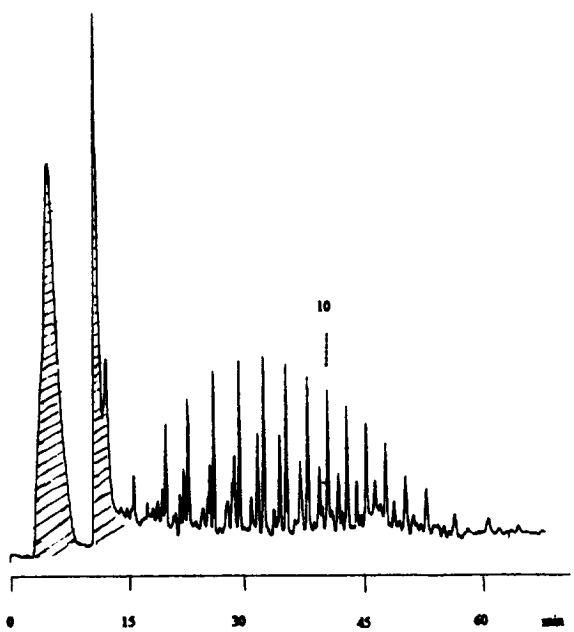

Fig. 6. Chromatogram of derivatized AE-7EO in a textile lubricant (Blend 2). Conditions same as in Fig. 1B. The hatched areas indicate background interference from the lubricant.

Table 3
Recoveries of oligomers of Synperonic As in blends and Synperonic A7 in the emulsion as determined by HPLC using external standard method ($n=4$)

EO number	Synperonic A2 in Blend 1 $X\pm$S.D.%	Synperonic A7 in Blend 2 $X\pm$S.D.%	Synperonic A7 in emulsion $X\pm$S.D.%	Synperonic A11 in Blend 3 $X\pm$S.D.%
0	93.5±16.1	[a]	[a]	[a]
1	90.3±20.8	[a]	[a]	[a]
2	82.8±21.4	75.1±14.3	78.3±16.4	[a]
3	80.3±16.3	81.4±12.6	80.4±13.8	93.4±15.3
4	83.2±14.2	90.1±10.5	85.6±14.5	94.3±14.4
5	82.7±15.7	87.3±9.8	79.7±12.3	98.7±13.2
6	100.5±13.9	80.6±12.1	93.1±10.2	103.4±11.9
7	92.3±10.5	86.2±7.7	94.9±9.6	105.6±12.5
8	98.6±8.6	75.3±6.3	87.7±8.7	99.1±10.3
9	93.4±7.8	81.6±7.2	90.3±9.1	95.8±6.6
10	95.6±12.2	94.8±11.5	97.5±10.3	93.9±7.6
11	94.7±14.3	89.0±12.9	95.8±8.5	96.4±6.9
12	97.9±11.9	96.2±9.1	96.0±9.9	87.7±7.8
13		103.4±10.4	104.1±10.7	89.6±8.9
14		88.5±7.8	96.4±11.2	85.4±8.6
15		86.9±12.7	91.7±13.3	87.8±9.8
16		93.7±10.8	98.2±12.6	90.3±9.5
17		103.4±13.6	87.3±14.8	98.1±10.4
18				100.5±11.7
19				103.2±12.3
20				97.5±16.1
21				108.3±13.7
22				93.8±12.4
23				86.6±14.6
24				102.5±14.3
25				106.9±17.5

[a] Unable to determine due to background.

200°C, although some interference was present in the chromatogram.

In addition, two separate commercial batches of AE-2EO (Sample 1 and Sample 2), which showed different performance while used in textile lubricants, were examined by both normal-phase and reversed-phase HPLC. The normal-phase HPLC chromatograms (Fig. 7A,B) confirmed that the two samples were alkyl alcohol ethoxylated (2EO) with only slight differences in the peak shapes and the ratios of different aliphatic chains. However, the reversed-phase chromatograms (Fig. 7C,D), apparently suggested greater differences. The analyses show clearly that tridecanol ethoxylates and dodecanol ethoxylates are the main components in Sample 1 and Sample 2, respectively, and the components in Sample 1 have longer, or more branched, aliphatic chains than those in Sample 2.

4. Conclusion

Normal-phase HPLC using an amino column and gradient elution (hexane–dichloromethane–methanol) can be used to give an indication of the distribution of oligomers with different ethyl oxides, and also give an intimation of the existence of homologous aliphatic chains in derivatized AEs. Reverse phase HPLC was shown to be useful in tracing aliphatic chains or homologues in the alcohol parts of AEs.

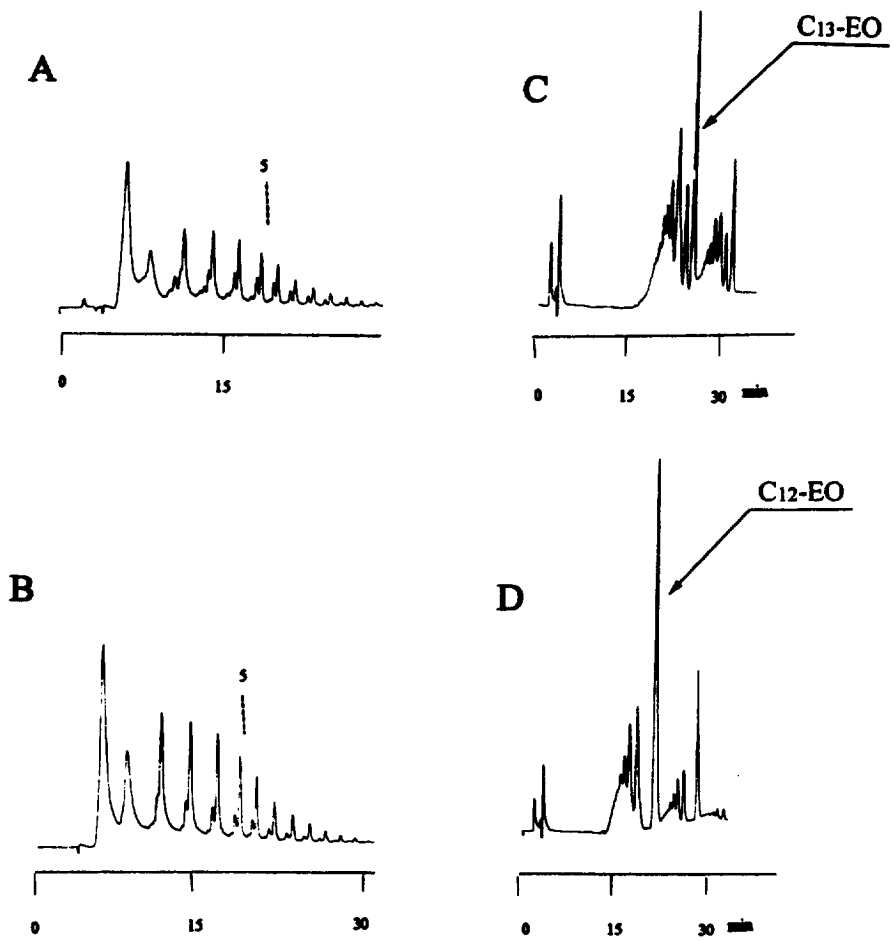

Fig. 7. Chromatograms of derivatized AE-2EO by both normal-phase and reversed-phase HPLC. (A) and (C) Vickers Sample 1; (B) and (D) Vickers Sample 2. Conditions: (A) and (B) same as in Fig. 1A and (C) and (D) as in Fig. 3.

HPLC using an amino bonded silica column can be used to determine AEs in textile lubricants as well as their emulsions. This HPLC method and extraction and clean-up procedures could also be applicable to other types of lubricants and possibly to environmental samples.

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References

[1] D.A. Mckenzie, J. Am. Oil Chem. Soc., 55 (1978) 93.
[2] M.J. Schick, Nonionic Surfactants, Marcel Dekker, New York, 1967.
[3] S.T. Dubey, L. Kravetz and J.P. Salanitro, J. Am. Oil Chem. Soc., 72 (1995) 23.
[4] L. Kravetz, J.P. Salanitro, P.B. Dorn and K.F. Guin, J. Am. Oil Chem. Soc., 68 (1991) 610.
[5] W. Gerhard and H.R. Holzbauer, Tenside Detergents, 12 (1975) 313.

[6] G.L. Selden and J.H. Benedict, J. Am. Oil Chem. Soc., 45 (1968) 652.
[7] I.I. Kaduji and J.B. Stead, Analyst, 101 (1976) 728.
[8] H. Puschman, Tenside Detergents, 5 (1968) 207.
[9] A.H. Silver and H.T. Kalinoski, J. Am. Oil Chem. Soc., 69 (1992) 599.
[10] S.R. Lipsky and M.L. Duffy, J. High Resolut. Chromatogr., Chromatogr. Commun., 9 (1986) 376.
[11] P.R. Geissler, J. Am. Oil Chem. Soc., 66 (1989) 685.
[12] M.C. Allen and D.E. Linder, J. Am. Oil Chem. Soc., 58 (1981) 950.
[13] P.L. Desbene, B. Desmazieres, V. Evan, J.J. Basselier and L. Minssieux, Chromatographia, 24 (1987) 857.
[14] K.A. Evans, S.T. Dubey, L. Kravetz, I. Dzidic, J. Gumulka, R. Mueller and J.R. Stork, Anal. Chem., 66 (1994) 699.
[15] G.R. Bear, J. Chromatogr., 459 (1988) 91.
[16] P.L. Desbene and B. Desmazieres, J. Chromatogr. A, 661 (1994) 207.
[17] Y. Mengerink, H.C.J. De Man and S. Van der Wal, J Chromatogr., 552 (1991) 593.
[18] K. Lemr, M. Zanette and A. Marcomini, J. Chromatogr. A, 686 (1994) 219.
[19] L. Nitschke and L. Huber, Fresenius J. Anal. Chem., 345 (1993) 585.
[20] P.L. Desbene, B. Desmazieres, J.J. Basselier and L. Minssieux, Chromatographia, 24 (1987) 588.
[21] I. Zeman, J. Silha and M. Bares, Tenside Detergents, 23 (1986) 181.
[22] B. Desmazieres, F. Portet and P.L. Desbene, Chromatographia, 36 (1993) 307.
[23] T. Okada, Anal. Chem., 63 (1991) 1043.
[24] M.P. Chiarelli, M.L. Gross and D.A. Peake, Anal. Chem. Acta, 228 (1990) 169.
[25] C. Crescenzi, A. D. Corcia, R. Samperi and A. Marcomini, Anal. Chem., 67 (1995) 1797.
[26] A. Marcomini and M. Zanette. J. Chromatogr. A, 733 (1996) 193.
[27] C. Sun, M. Baird, M.A. Anderson and D.L. Brydon, J. Chromatogr. A, 731 (1996) 161.
[28] Z. Wang and M. Fingas, J. Chromatogr. A, 673 (1993) 145.