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THE DETERMINATION OF ETHOXYLATE OLIGOMER DISTRIBUTION OF NON-IONIC AND ANIONIC SURFACTANTS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

The characterisation of alkylphenoxy ethoxylated surfactants has been carried out by normal-phase high-performance liquid chromatography. Non-ionic surfactants have been chromatographed on silica and cyano-propyl bonded-phase columns by gradient elution. The equivalent anionic materials have also been characterised by normal-phase chromatography with an ion-pairing agent. The surfactants investigated contain mixtures of oligomers with chain lengths of up to 20 ethoxylate units, and the methods described enable the ethoxylate oligomers to be separated and quantified to produce the ethoxylate distribution, the average ethoxylate number and the anionic–non-ionic mass ratio. The assignment of ethoxylate number to the oligomers has been made by comparison with standard reference materials, and the use of retention time–ethoxylate number relationships.

INTRODUCTION

The alkylphenoxy surfactants are complex mixtures, containing molecules of different ethoxy chain lengths (in the range 1 up to 20), and the anionic surfactants may also contain representatives of both anionic and non-ionic species. Materials of such complexity, molecular weight and polarity range are best characterised by high-performance liquid chromatography (HPLC). Liquid chromatography has previously been used to characterise non-ionic surfactants of this type[1–7], but the characterisation of the anionic equivalents has not been reported. The anionic materials of the type $R–PhO–(CH_2CH_2O)_nR'SO_3^-$ can be chromatographed by using an ion-pairing agent, such as tetramethylammonium chloride, on silica and cyanopropyl bonded-phase columns. The anionic ethoxylate oligomers can be separated to enable the ethoxylate distribution and average ethoxylate number to be determined in the same way as for the non-ionic materials.

The correct assignment of ethoxylate numbers is critical for the characterisation, and for this purpose a reference material, $R–PhO(CH_2CH_2O)_3H$, was used and the structure was confirmed by mass spectrometry. This material was used to spike the non-ionic surfactant solutions to show the elution positions of the oligomers. The equivalent anionic surfactant was used as a reference material in the same way.

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Anionic surfactants may contain small amounts of non-ionic components, and the two HPLC methods developed allow the distribution of both the anionic and non-ionic components to be determined, together with the anionic–non-ionic ratio.

EXPERIMENTAL

Apparatus

The HPLC equipment included two Applied Chromatography Systems (ACS) Model 750/04 pumps, an ACS Model 750/37 microprocessor-controlled solvent programmer and a Kontron 720LC variable-wavelength UV detector. The columns used were 250 mm × 4.6 mm Hypersil-5 and Hypersil-5-CPS which were packed in the laboratory. Solutions of the surfactants were injected into the columns by using a Rheodyne 7010 injection valve, fitted with a 50-μl sample loop. The peak areas were determined with a Trivector Trilab computing integrator, and a BASIC programme was incorporated to calculate and plot the ethoxylate distributions, together with the average ethoxylate number and anionic–non-ionic ratio.

Chemicals

Surfactant samples were obtained from commercial suppliers, and were dissolved in the mobile phase mixture appropriate for the analysis. HPLC-grade hexane, obtained from Rathburn Chemicals, and absolute, synthetic-grade ethanol were used for the mobile phase mixtures. The ion-pairing agent, tetramethylammonium chloride, was obtained from Fisons Chemicals.

Procedure

In order to identify the ethoxylate oligomers of the surfactant chromatograms, a standard reference material of $R\text{–}PhO\text{–}(CH_2CH_2O)_3H$ was used to spike solutions of non-ionic surfactants in order to fix the elution position of the triethoxylate oligomer. The equivalent anionic reference material was also used in the same way to identify the surfactant oligomers.

The peak areas obtained from the chromatograms and their identified ethoxylate numbers were then entered into a BASIC programme to obtain both weight and molar ethoxylate distributions and average ethoxylate numbers. The calculation of the weight-average ethoxylate number involves multiplying the peak areas by the ratio of the molecular weights of the ethoxylate oligomer and the monoethoxy component. These values are then multiplied by the relevant ethoxylate number. The two sets of values are then summed: E_1 = sum of (peak area × mol. wt. ratio); E_2 = sum of (peak area × mol. wt. ratio × ethoxylate number). The weight-average ethoxylate number is then given by E_2/E_1 (see Fig. 2). The molar average ethoxylate number is obtained in a similar way, but omitting the molecular-weight ratio (see Fig. 2). The BASIC programme also enables the anionic/non-ionic ratio to be calculated for the anionic surfactants. The peak areas obtained from both HPLC methods were divided by the relevant concentration of the sample injected. These figures were then totalled, the percentages of each ethoxylated component calculated, and the mass ratio of the anionic–non-ionic components obtained. This ratio was also determined by the Iatroscan thin-layer chromatographic technique with silica rods and a solvent system of ethyl acetate–ethanol–ammonia (65:22.5:12.5). This sys-

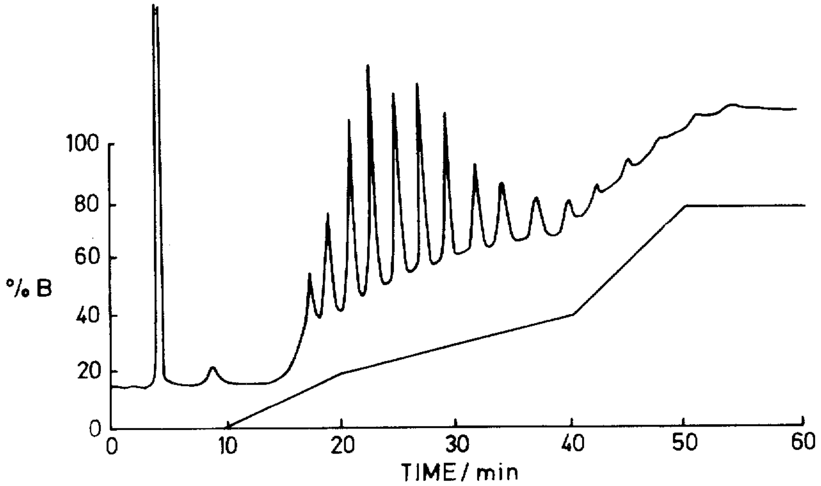

Fig. 1. Chromatogram of non-ionic surfactant R-PhO$(CH_2CH_2O)_{10}$H. Mobile phase: A, hexane; B, ethanol; flow-rate, 2.0 cm^3/min. Column: 250 × 4.6 mm, Hypersil 5. Detector: UV 220 nm.

tem separates the two types of surfactants into discrete peaks, and the ratio of the peak areas (corrected for the FID response) gives the anionic/non-ionic ratio.

RESULTS AND DISCUSSION

Non-ionic ethoxylate distribution

An example of the analysis of a non-ionic surfactant material is shown in Fig. 1, and the resultant computer printouts for the weight and molar ethoxylate distributions are given in Fig. 2. It has been shown by other workers[6] that the molar

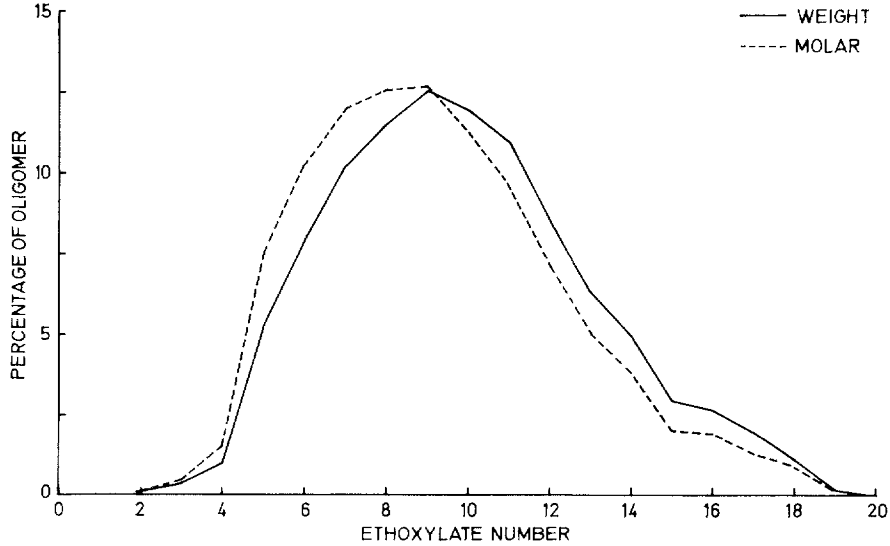

Fig. 2. Weight and molar distribution curves for R-PhO$(CH_2CH_2O)_{10}$H.

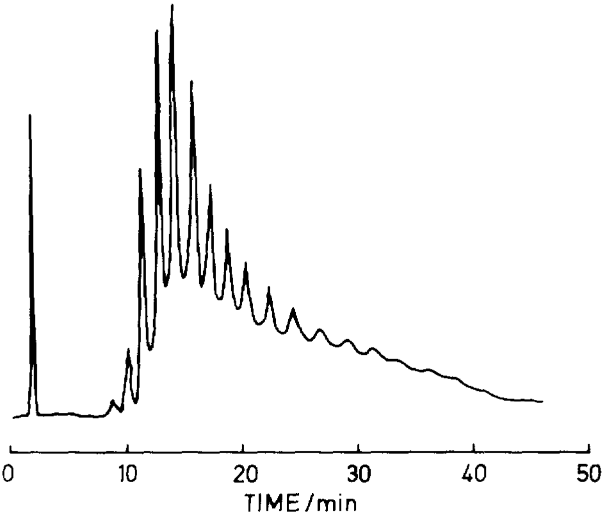

Fig. 3. Chromatogram of anionic surfactant R-PhO$(CH_2CH_2O)_6$R'SO_3^-. Mobile phase: hexane-ethanol (70:30), 0.01 *M* tetramethylammoniumchloride; flow-rate, 2.0 cm^3/min. Column: 250 × 4.6 mm, Hypersil 5-CPS. Detector: UV, 220 nm.

extinction coefficients of the ethoxylate oligomers are independent of the ethoxylate chain length and, therefore, the peak areas are directly proportional to the mole percent of the components. The weight distribution results give some additional information which is also useful for surfactant characterisation.

Anionic ethoxylate distribution

Surfactants themselves have been used as ion-pairing agents for chromatography[8], and therefore the addition of a cationic ion-pairing agent in this case provides an elegant chromatographic separation. The ion-pairing agent reduces the retention of the surfactant components as expected, but they are still well separated from the non-ionic components, which are eluted in the void, see Fig. 3. The same method of calculation for weight and molar ethoxylate distribution and average ethoxylate num-

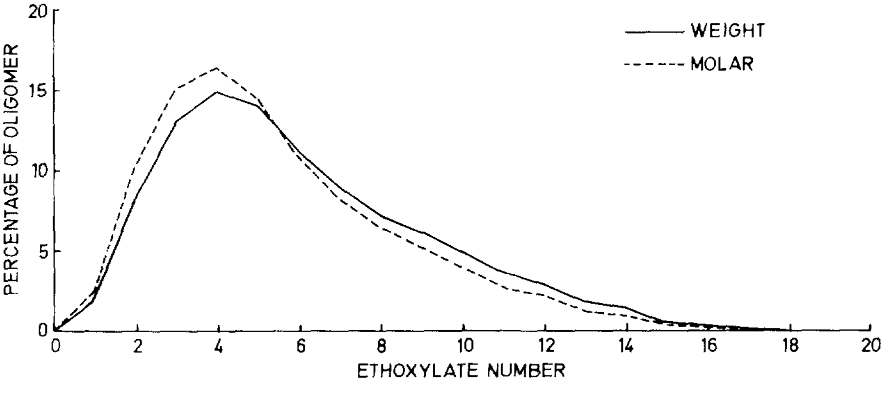

Fig. 4. Weight and molar distribution curves for R-PhO$(CH_2CH_2O)_6$R'SO_3^-.

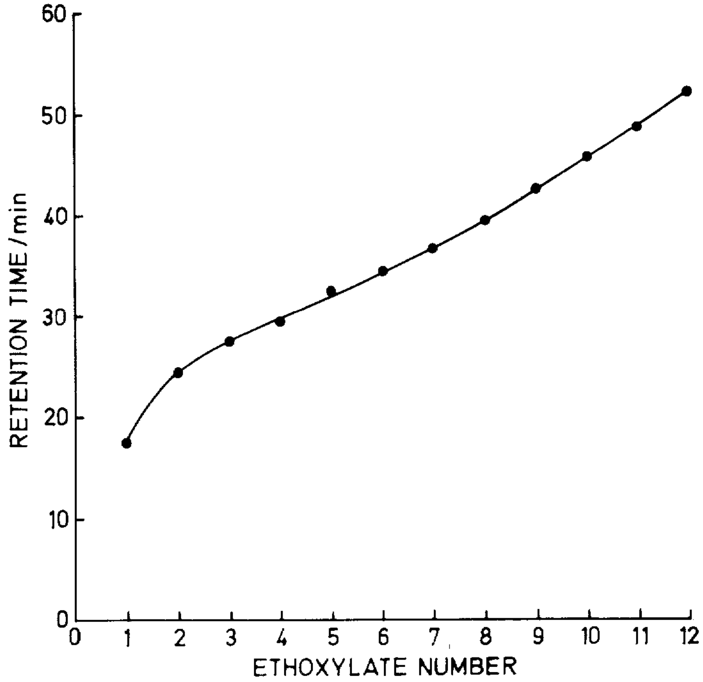

Fig. 5. Retention time *vs.* oligomer ethoxylate number relationship for ethoxylated anionic surfactants.

bers as that used for the non-ionic materials has been applied (see Fig. 4). Comparable separations have been obtained on both silica and cyanopropyl-bonded phase columns under identical chromatographic conditions.

Oligomer identification

The use of solutions spiked with the triethoxylate reference material allowed ethoxylate numbers to be assigned to successive peaks counted from the triethoxylate position.

It was also found that a simple relationship exists between the ethoxylate number and the retention time of the anionic oligomers (see Fig. 5), which is similar to that found for other homologous series of compounds. The regularity of this curve

TABLE I

A COMPARISON OF ANIONIC-NON-IONIC RATIOS DETERMINED FOR SURFACTANTS USING HPLC AND IATROSCAN TECHNIQUES

a and b are two different batches of the same material.

Surfactant		*HPLC*	*Iatroscan*
$RPhO(EO)_6R'SO_3^-$	a	88:12	93:7
$RPhO(EO)_6R'SO_3^-$	b	80:20	77:23
$RPhO(EO)_7R'SO_3^-$	a	92:8	91:9
$RPhO(EO)_7R'SO_3^-$	b	70:30	74:26

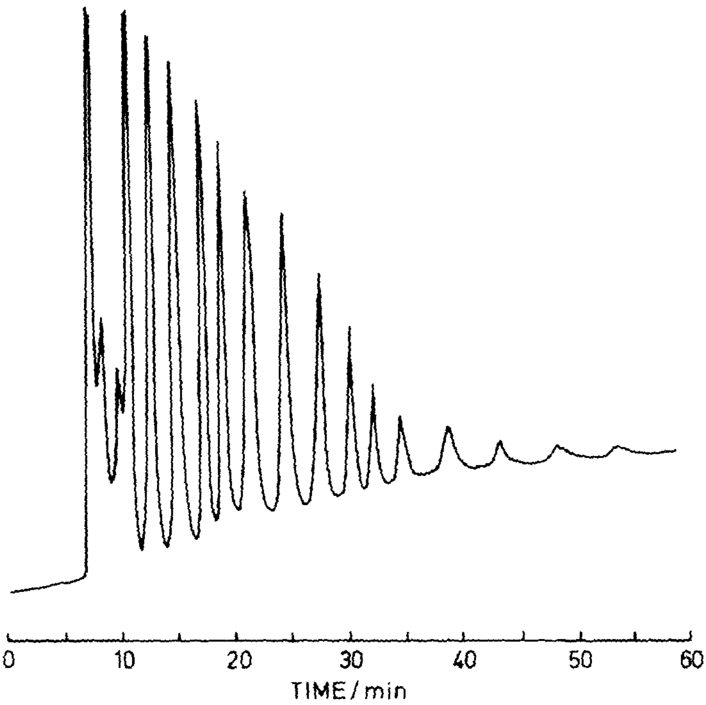

Fig. 6. Isocratic separation of non-ionic ethoxylate oligomers. Mobile phase: tetrahydrofuran–ethanol–water (94:5:1); flow-rate, 2.0 cm^3/min. Column: 250 × 4.6 mm Spherisorb S-5CN. Detector: UV 220 nm.

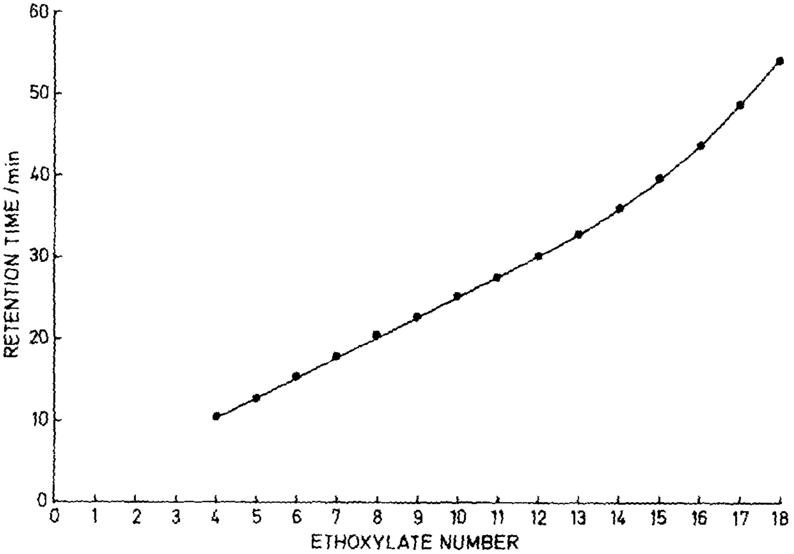

Fig. 7. Retention time *vs.* oligomer ethoxylate number for non-ionic ethoxylated surfactants.

has been used as an additional aid for ethoxylate number assignments when interpreting the chromatographic results. A similar relationship exists for the non-ionic oligomers which have been analysed under isocratic conditions (see Figs. 6 and 7). The polarity range covered by the non-ionic oligomers is too large to be covered by one isocratic system, and therefore the gradient method has been used for sample analysis. The relationship between oligomer number and retention time has only been established for the isocratic systems, but has been useful for identification purposes.

Anionic–non-ionic ratio

The two HPLC methods developed provide a means of assay for the ethoxylated components present in anionic surfactants. The distribution of both non-ionic and anionic ethoxylated material present can be obtained, and from these results the anionic–non-ionic ratio can be calculated. This ratio was also determined by the Iatroscan technique, as described in the procedure. A good correlation has been obtained between the results obtained by the two techniques (see Table I), which provides further confirmation of the component assignments made when interpreting the HPLC results.

CONCLUSIONS

The HPLC techniques described can provide the quantitative oligomer distribution information necessary for full characterisation of alkylphenoxy ethoxylated surfactants, both in non-ionic and anionic forms. The use of the relationships between retention time and ethoxylate number, and correlation with Iatroscan thin-layer chromatography, confirms the accuracy of ethoxylate number assignment.

The surfactant materials which have been analysed are commercial materials and have a wide range of applications. The methods described here may be used for quality control, and the results obtained can be used to assess the performance of these surfactants.

REFERENCES

1 K. J. Bombaugh, *J. Chromatogr.*, 53 (1970) 27–35.
2 J. F. K. Huber, F. F. M. Kolder and J. M. Miller, *Anal. Chem.*, 44 (1972) 105–1110.
3 C. F. Allen and L. I. Rice, *J. Chromatogr.*, 110 (1975) 151–155.
4 K. J. Bombaugh, R. F. Levangie, R. N. King and L. Abrahams, *J. Chromatogr. Sci.*, 8 (1970) 659.
5 HPLC of Surfactants, *Du Pont Liquid Chromatography Technical Report*, Du Pont, Wilmington, DE, 1980.
6 A. M. Rothman, *J. Chromatogr.*, 253 (1982) 283–288.
7 M. C. Allen and D. E. Linder, *J. Amer. Oil Chem. Soc.*, 58 (1981) 950.
8 J. H. Knox, and G. R. Laird, *J. Chromatogr.*, 122 (1976) 17–34.