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Note

Chromatographic separation of a wide range of ethoxylated non-ionic surfactants and their sulphonates using high-performance liquid chromatography

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Alkylphenol ethoxylates are formed by reacting alkylphenols with an excess of ethene oxide. The isomeric homogeneity of the oligomers will reflect the composition and purity of the parent phenol. Like many condensation reactions, the final product is a mixture of oligomers. The surfactant composition determines its physical and chemical properties; these often form a Poisson distribution.

Other chromatographic techniques [*e.g.* thin-layer chromatography (TLC) and gas chromatography (GC)] are of limited applicability in this area. Reproducibility and quantification are somewhat problematic with TLC[1]. With GC only a very limited number of oligomers is usually eluted from the column[2], even if the volatility of the sample is increased by derivatisation[3]. Liquid chromatography (LC) can however overcome the problems of long analysis times, limited application, lack of specifity and poor accuracy.

A multitude of LC methods exist for the separation of surfactants, many using buffers[4], salts[5] and derivatisation[6]. HPLC has been used recently for characterising surfactants and this work has generally been performed with reversed-phase columns. Nevertheless, satisfactory resolution has so far only been shown for adducts up to 9 or 10 ethene oxide (EO) units[7] or up to 16 EO units[8].

There have been only a few studies of the use of normal-phase chromatography. One[9] suggested that a bonded-phase CN column might be better suited to this type of separation. Isocratic elution has been shown to be unsatisfactory, so gradient elution is required; the complexity of surfactants results in their separations being very sensitive to gradient composition. Therefore the present work was undertaken to provide a new simple and rapid chromatographic analytical method equally applicable to nonionic surfactants containing an oligomer distribution from approximately 4 to 50 EO units and in the presence of sulphonate derivatives.

EXPERIMENTAL

The non-ionic ethoxylated surfactants and their sulphonate derivatives used were obtained from Hoechst (Frankfurt, F.R.G.) and have formulae shown in Table I. Sulphonation of the surfactants leads to mixtures of nonionic and anionic component, the ratio of which depends on the degree of conversion. All were used without further purification.

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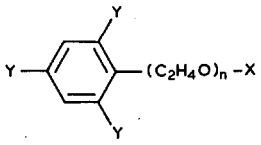
TABLE I

SURFACTANTS USED AND ANALYSED



n is the number of EO units (*i.e.* $4 \leqslant n \leqslant 50$) and C_4H_9 or $(CH_3)_3C$– is the alkyl group Y. X is H or SO_2 in the primary non-ionic surfactant and its sulphonate respectively.

n	*Name*
4	Sapogenat T040 (sulphonate) T040S
6	Sapogenat T060 T060S
8	Sapogenat T080 T080S
10	Sapogenat T100 T100S
13	Sapogenat T130
15	Sapogenat T150 T150S
18	Sapogenat T180
50	Sapogenat T500

The solvents used were HPLC-grade hexane, 2-methoxyethanol and isopropanol (Rathburn). Due to the attraction of the samples to the stationary phase, a strong solvent is needed for elution in reasonable times. 2-Methoxyethanol provides the necessary strength required for the rapid elution of oligomers, whilst isopropanol ensures homogeneity in the mobile phase. Isopropanol alone is insufficiently polar for elution.

Gradient elution HPLC was performed with a Gilson high performance liquid chromatograph equipped with a UV indochrome detector operating at 255 nm. This corresponds to the maximal absorption of the aromatic ring and it is assumed that all oligomers have the same molar absorptivities at this wavelength. The two pumps used were Gilson Model 302 and with a dynamic mixture, Model No. 811. Samples were injected directly onto the column via a 20-mm^3 loop using an auto-injector (Model 231) and a diluter (Model 401). The sampling system and pumps were controlled by an Apple IIe computer. The column (25 cm × 4.6 mm) was a Dupont Zorbax CN (particlke size 10 μm) which was located in an oven (Pye Unicam PU4031) maintained at 323 ± 0.5 K throughout analyses. In order to protect the analytical column from severe contamination a stainless-steel pre-column (50 × 4.6 mm) was used packed with Permaphase ETH (DuPont).

Sample preparation

One problem associated with gradient elution for oligomer analysis is sample solubility; shorter chain length oligomers may be more soluble in the solvent used than those of longer chain lengths or *vice versa*. Ideally, the sample should be dissolved in the solvent mixture which begins the gradient (solvent A). Injection of the sample dissolved in the final solvent (solvent B) may cause a temporary disturbance of the phase system leading to inferior chromatographic separation. In the case of present analyses, all surfactants dissolved well in solvent B. The specific conditions for the gradient analysis are described in the legend of Fig. 1. To reduce this "sample solvent effect" the gradient was initiated with 98% solvent A and 2% solvent B. Also a small amount of solvent A was added to the dissolved sample but this was limited by solubility. All samples were prepared as 10% (w/v) solutions in solvent B containing 2% solvent A. Solutions of sulphonated surfactants were centrifuged as they were found to contain some insoluble material. Analysis of this residue showed the basic shape of the surfactant chromatogram but with very poor resolution, and it is possibly an artefact of the catalyst used in preparation or some highly polymerised material. All samples were run under indentical conditions. All gradients were started at the injection point and any baseline drift must therefore have been due to the change in the mobile phase.

RESULTS AND DISCUSSION

The chromatograms shown in Fig. 1a-h are of the non-ionic surfactants; their corresponding sulphonates are those in Fig. $1a_s$–f_s.

Non-ionics are eluted first and show the expected Poisson distribution of oligomers; the shorter chain lengths being eluted first. The smaller intermediate peaks are thought to arise from alkyl groups of differing lengths but the same number of EO units as the main adjacent peak.

The initial peaks in the chromatograms (labelled α and β in Fig. 1) are not part of the surfactant but are attributed to the parent tri-*tert.*-butylphenols remaining unconverted; this was especially so when the non-ionic containes only 4 EO units (see Fig. 1a). Interestingly α and β peaks are not attributable to phenol (see Fig. 1i).

It is noteworthy that as the value of n increases so the fraction of chromatograms $1a_s$–f_s represented by the non-sulphonated surfactants increases; this suggests that as the number of EO units increases so sulphonation becomes progressively more difficult. It is possible that steric hindrance (caused by the increasingly flexible EO chain) restricts the approaching sulphonate ion.

CONCLUSIONS

The analysis of the surfactants and their sulphonates reported here has shown them to contain a significant amount of residual alkylphenol, which distorts the shape of the first few emergent surfactant peaks. It is assumed, but not proven, that the order of elution of the different chain length oligomers is the same for the corresponding sulphonates. It is noted that all of the chromatograms appeared to have a Poisson distribution with differing EO chain lengths; this is in agreement with the predicted distribution of the products of the EO-phenol polymerisation[10].

Fig. 1a and h chromatograms of a surfactant with an average chain length of 4 and 50 EO units illustrate the good resolution of a wide range of surfactants. The resolution between successive oligomers decreases considerably as the EO chain increases beyond 18 units. It appears impossible to improve the separation even with an optimal gradient profile for this. This may be partly due the continuously decreasing relative differences between successive oligomers with increasing molecular weights. The main cause is thought to be due to the decreasing accessibility to the silica pores of the higher-molecular-weight oligomers (size exclusion), thereby decreasing the retention by the column. Mixtures of non-ionic ethoxylated and their sulphonate derivatives are also readily separated.

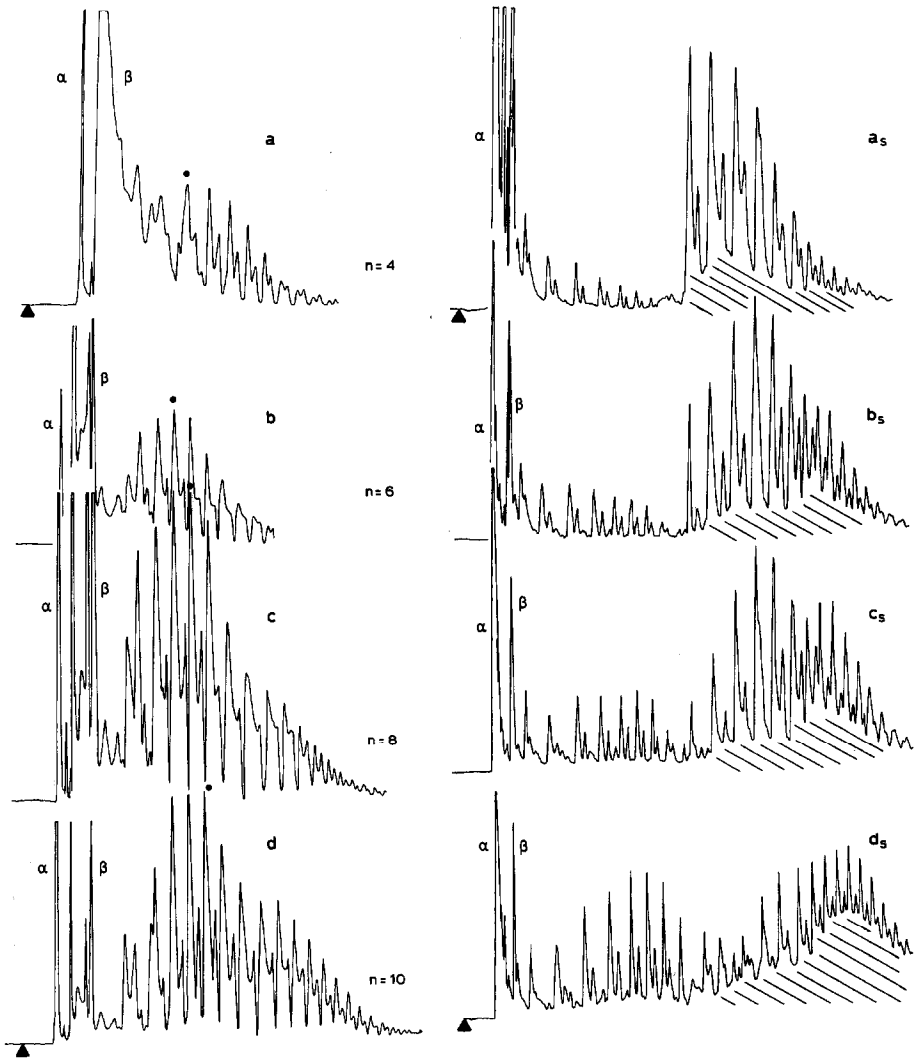


Fig. 1.

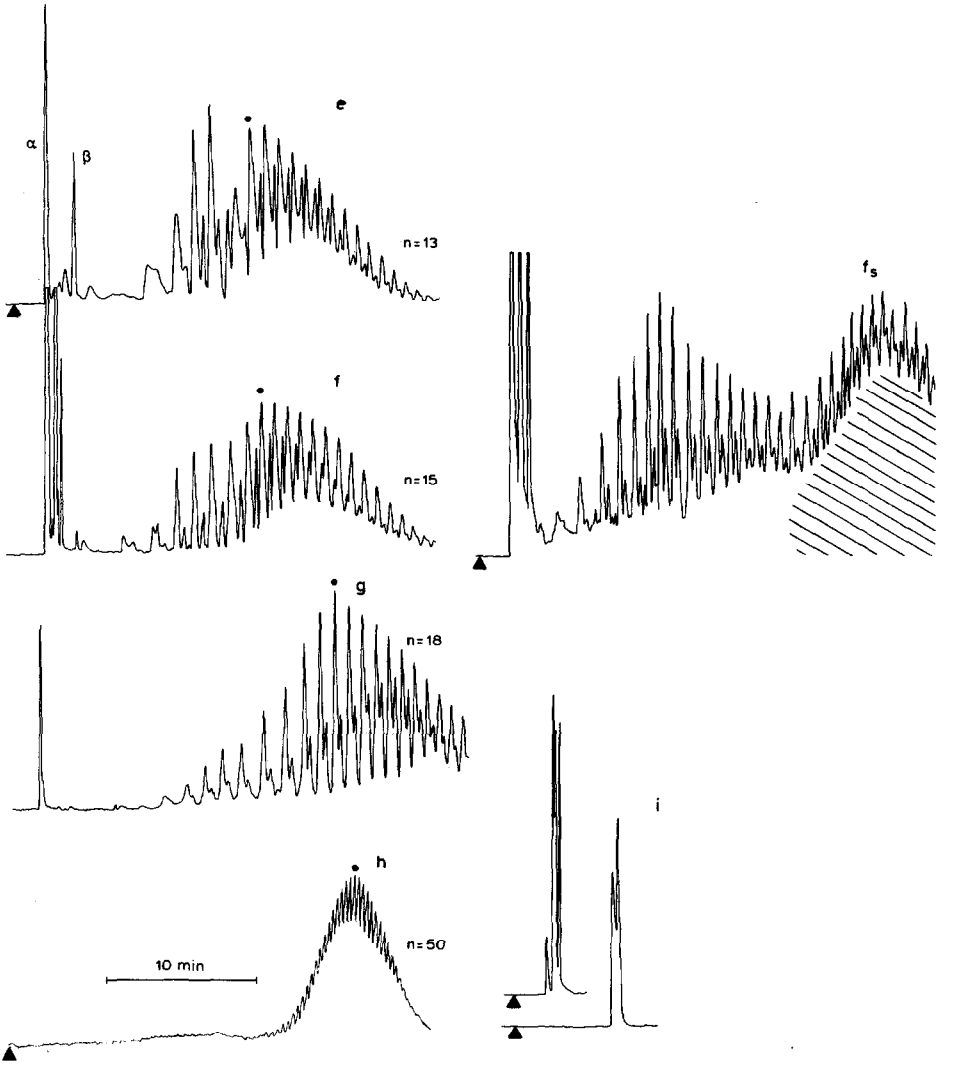


Fig. 1. HPLC traces for non-ionic ethoxylated surfactants (a, b, c, d, e, f, g and h correspond to molecules with an average 4, 6, 8, 10, 13, 15, 18 and 50 ethoxylate units) and their corresponding sulphonates (a_s, b_s, c_s, d_s and f_s). These were obtained under the following conditions: Zorbax CN column; temperature, 323 ± 1 K; flow, 1.5 cm^3 min^{-1}; mobile phase A, 100% hexane; mobile phase B, 2-methoxyethanol–isopropanol (75:25); chart speed, 10 mm min^{-1}; gradient profile, 2% B at 0 min, 50% B at 50 min. All were reproducible and repeatable. It is not yet possible to say that all components are entirely separated by the present approach, but this seems quite likely. The shaded area indicates the range of times of sulphonate elution. i shows the HPLC trace of the parent tri-*tert.*-butylphenol and phenol; the former appears to be the same as that denoted α and β in traces 1a–h.

Thus, the present method allows a chromatographic analysis of a wider range of non-ionic ethoxylated phenol surfactants, their sulphonates, and their mixtures than has previously been reported. This should be of value to the many workers studying enhanced oil recovery, surfactant and cosmetic chemistry.

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