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GAS–LIQUID CHROMATOGRAPHIC FRACTIONATION OF POLYOXYETHYLENE NON-IONIC SURFACTANTS

POLYOXYETHYLENE MONO-*n*-ALKYL ETHERS

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SUMMARY

The gas–liquid chromatographic fractionation of the commercial biodegradable surfactants $RO(CH_2CH_2O)_{\bar{n}}H$ (where R is an *n*-alkyl group and $\bar{n}$ is the number-average degree of polymerization) can be approached only for $\bar{n} \leqslant 4$, as the truncation of the molecular-weight distribution occurs at higher $\bar{n}$ values. Although conversion into trimethylsilyl (TMS) derivatives improves the volatility of the oligomers, there is only a slight advantage in using this conversion procedure: TMS derivatives have the same elution temperature as untreated compounds above *ca.* 330°. The use of an internal standard as a reference compound for comparison of peak areas is a useful procedure, which has been tentatively applied to the reconstruction of the distribution of the surfactant with R = *n*-dodecyl and $\bar{n} = 7.1$. The choice of the internal standard is discussed.

INTRODUCTION

Polyoxyethylene mono-*n*-alkyl ethers, $RO(CH_2CH_2O)_{\bar{n}}OH$ (where R is an *n*-alkyl group and $\bar{n}$ is the number-average degree of polymerization), are biodegradable non-ionic surfactants that are widely used in commercial products. As a consequence of the polydisperse nature of these surfactants, problems arise in high-temperature gas–liquid chromatographic (GLC) fractionation. Moreover, industrial surfactants are sometimes produced from mixtures of various *n*-alkanols, which are prepared either from fatty natural products or from synthetic materials[1].

The fractionation of polyoxyethylene mono-*n*-alkyl ethers by means of GLC has already been described by Gildenberg and Trowbridge[2], who improved the volatility of the high-boiling compounds by conversion into acetate esters. Törnquist[3,4] suggested the use of trimethylsilyl (TMS) ethers. Despite this, fractionation was successful only in resolving surfactants with $\bar{n} \leqslant 3$ (ref. 5).

In this paper, the GLC fractionation of these surfactants is reconsidered and discussed in the light of the improvements in the GLC systems already used for fractionating polyoxyethylene alkylphenyl ethers[6–8]. A tentative method for the evaluation of the absolute molecular-weight distribution up to $\bar{n} = 7.1$ by means of an internal standard is suggested.

EXPERIMENTAL

Apparatus

A Pye-Unicam 104 double-column chromatograph with flame-ionization detectors was used. Pyrex glass columns (40 cm × 1.7 mm I.D.) were packed with 80–100-mesh Gas-Chrom Q coated with 3% (w/w) GE SE-30, GC grade (Applied Science Labs., State College, Pa., U.S.A.). Fractionation was carried out with a linear temperature programmer from 80° to 370° at the rate of 10°/min, and with injector and detector temperatures of 375° and 400°, respectively. The flow-rates of the gases were nitrogen 45, hydrogen 45 and air 300 ml/min. The effective peak number was 0.7 for C_{22}/C_{23} *n*-alkanes[9]. Peak areas were determined by means of a Hewlett-Packard 3380A integrator.

The purification of monodisperse surfactants was carried out by preparative elution adsorption chromatography; 30–50-μm silica gel (AR grade, Mallinckrodt, St. Louis, Mo., U.S.A.) was used as an adsorbent, packed in a 20 × 2 cm I.D. column. Eluted fractions were collected with an LKB Ultrorac 7000 fraction collector at 20°. Mixtures of acetone in dichloromethane were used as the eluent, with the linear gradient $A = 0.030\ V$, where A (%, v/v, at 20° before mixing) is the concentration of acetone and V (ml) is the volume of eluent at the top of the column.

Monodisperse surfactants

Monodisperse polyoxyethylene mono-*n*-alkyl ethers (C_mE_n, where m is the number of carbon atoms in the alkyl chain and n is the degree of polymerization of the ethoxy group) were prepared according to Mulley[10] using Fluka (Buchs, Switzerland) reagents. Re-distilled compounds were further purified by column chromatography and fractions were systematically checked by means of GLC. Purities and physical data are shown in Table I. The values are in accordance with those given in the literature[11].

Polydisperse surfactants

The GLC fractionation was carried out on the following commercial poly-

TABLE I

GLC PURITY (PERCENTAGE OF PEAK AREA) AND PHYSICAL DATA FOR MONODISPERSE SURFACTANTS C_mE_n

C_mE_n	*Purity (%)*	*Oligomers present as impurities (%)*	*$n^{t°}_{589\ nm}$*		*M.p. (°C)*	*B.p. (°C/mmHg)*
			40°	*60°*		
$C_{12}E_6$	95.71	1.37 ($n = 4$) 2.51 ($n = 5$) 0.41 ($n = 7$)	1.4480	1.4408	21.0	190/0.055
$C_{14}E_4$	99.85	0.15 ($n = 3$)	1.4470	1.4393	26.5	187/0.015
$C_{16}E_4$	>99.99		1.4485	1.4410	34.5	195/0.020

disperse surfactants ($C_mE_{\bar{n}}$, where in this instance $\bar{n}$ is the number-average degree of polymerization determined by vapour-pressure osmometry): $C_{10}E_{\bar{4}}$, $C_{12}E_{\overline{3.8}}$, $C_{12}E_{\overline{7.1}}$, $C_{16}E_{\bar{8}}$, $C_{18}E_{\overline{12}}$, $C_{18:1}E_{\overline{12}}$ (Hüls, Marl, G.F.R.). An ethoxylated mixture of alcohols from hydrogenated coconut fat (Lutensol A8, BASF, Ludwigshafen am Rhein, G.F.R.) was also considered.

Silylation procedure

Surfactants dried at 40° and 0.1 mmHg over phosphorus pentoxide were treated 1:100 (w/w) in a sealed vial with Tri-Sil (Pierce, Rockford, Ill., U.S.A.) and the mixture was heated at 70° for 15 min.

RESULTS AND DISCUSSION

Analysis of polydisperse surfactants

Fig. 1 shows the elution temperatures observed in the fractionation of polydisperse surfactants. The data were obtained on untreated surfactants and also after silylation. The value of *n* was determined by using monodisperse compounds as internal standards. In comparison with steel columns, glass columns greatly improve the GLC performance. For a given *n* the elution temperature of the TMS derivative is systematically higher than of the untreated compound, but the difference tends to zero at *ca.* 330° for the C_{10}–C_{18} series. Blocking of hydroxyl groups by silylation gives the following advantages: (i) the interaction between the surfactant molecule and the support is reduced; the peaks of TMS derivatives are sharpened by reducing the tailing that appears when untreated surfactants are fractionated; (ii) the interaction among surfactant molecules is also reduced and the volatility is increased; (iii) pyrolysis fragments do not appear up to at least 440°. As the stationary phase has a very low polarity (McReynolds[12] constants: $X' = 15$, $Y' = 53$, $Z' = 44$, $U' = 64$, $S' = 41$), the elution temperatures of $C_{18}E_n$ and $C_{18:1}E_n$ are the same for a given *n*.

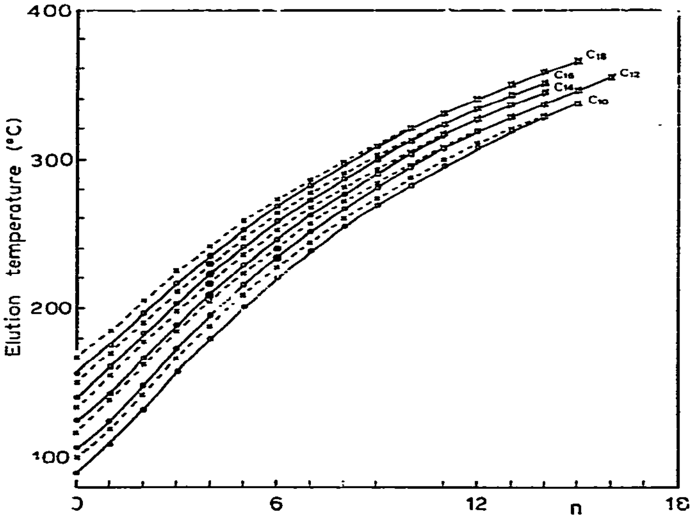

Fig. 1. Elution temperatures *versus n* observed for C_mE_n surfactants. ○, Untreated compounds (OH); ×, (TMS) derivatives; ●, internal standards.

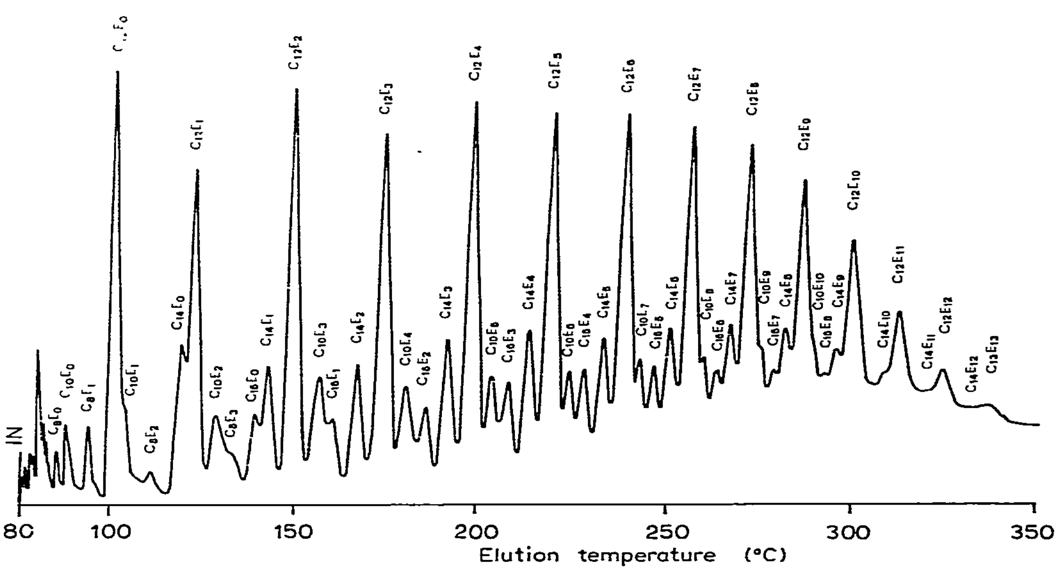

Fig. 2. Gas chromatogram of nonionic surfactant of the type C_mE_n (Lutensol A8).

As an example, Fig. 2 shows the chromatogram for the fractionation of a commercial non-ionic surfactant. With the suggested chromatographic system, TMS derivatives are resolved up to $n = 16$ with $C_{12}E_{\bar{n}}$ (elution temperature = 354°; see Table II), whereas the untreated surfactants are limited to $n = 15$ (elution temperature = 345°).

Analysis of the polydispersivity with an internal standard

The truncation of the distribution, which appears with increasing elution temperature, is a basic limitation of the GLC analysis of polydisperse surfactants. Various computing procedures[6] have been suggested for reconstructing the actual distribution, but their use is restricted to polyoxyethylene *p-tert.*-nonylphenyl ethers up to $\bar{n}_{VPO} = 6.5$. With polyoxyethylene mono-*n*-alkyl ethers, a further difficulty arises from the fact that these surfactants have a "dispersed" distribution[1]: for instance, the surfactant $C_{12}E_{\overline{3.8}}$ contains even $C_{12}E_{14}$ in a chromatographically dectectable percentage (see Table II).

The study was restricted to $C_{12}E_{\bar{n}}$ surfactants, with $\bar{n}_{VPO} = 3.8$ and 7.1. GLC analyses are quoted in Table II in which both untreated mixtures (OH) and (TMS) derivatives are considered. The chromatographic data are expressed as a percentage peak area (A_n, %) and as a molar fraction (x_n). Consistency of the analysis was tested by comparing $\bar{n}_{VPO}$ with $\bar{n}_{GLC}$ ($\bar{n} = \Sigma x_n n$).

With $\bar{n}_{VPO} = 3.8$ only the analysis of TMS derivatives approaches the osmometric value ($\bar{n}_{GLC} = 3.64$), wheras the untreated mixture is clearly truncated ($\bar{n}_{GLC} = 3.27$). With $\bar{n}_{VPO} = 7.1$, the comparison indicates that both distributions are truncated.

A tentative method for reconstructing the molecular-weight distribution of $C_{12}E_{\overline{7.1}}$ was suggested by observation that the cumulative distribution of the percentage peak area approximates to a straight line when it is plotted as a function of *n* on nor-

TABLE II

GLC ANALYSIS OF POLYDISPERSE SURFACTANTS, $RO(CH_2CH_2O)_{\bar{n}}H$, ($R = n$-DODECYL) AS UNTREATED COMPOUNDS (OH) AND TMS DERIVATIVES

n is the degree of polymerization; $\bar{n}$ is the number-average degree of polymerization ($\bar{n}_{VPO}$, measured by VPO; $\bar{n}_{GLC}$, calculated from the molar fractions); x_n is the molar fraction of the n-mer observed without the internal standard; A_n is the peak area (%) of the n-mer observed with the internal standard (extrapolated values are given in italics); X_n is the corresponding calculated molar fraction.

n	*Elution temp. (°C)*		$\bar{n}_{VPO} = 3.8$		$\bar{n}_{VPO} = 7.1$					
			x_n		*OH*			*TMS*		
	OH	*TMS*	*OH*	*TMS*	x_n	$A_n(\%)$	X_n	x_n	$A_n(\%)$	X_n
0	107	117	0.1660	0.1564	0.0712	2.00	0.0525	0.0611	2.40	0.0546
1	125	139	0.1603	0.1480	0.0740	2.65	0.0561	0.0598	2.65	0.0522
2	149	163	0.1414	0.1310	0.0809	3.45	0.0620	0.0786	4.15	0.0686
3	174	185	0.1308	0.1172	0.0789	3.90	0.0604	0.0724	4.30	0.0632
4	196	204	0.1082	0.1143	0.0941	5.30	0.0721	0.0774	5.12	0.0675
5	216	222	0.0858	0.0787	0.1060	6.70	0.0812	0.0877	6.38	0.0766
6	235	240	0.0667	0.0703	0.1129	7.90	0.0865	0.0893	7.10	0.0779
7	252	257	0.0503	0.0566	0.1084	8.40	0.0838	0.0940	8.10	0.0820
8	267	271	0.0368	0.0450	0.0833	*9.70*	0.0888	0.0921	9.02	0.0848
9	281	284	0.0248	0.0314	0.0660	*9.80*	0.0830	0.0768	*9.78*	0.0856
10	295	297	0.0153	0.0222	0.0466	*8.30*	0.0654	0.0596	*8.20*	0.0682
11	306	307	0.0084	0.0139	0.0332	*7.90*	0.0582	0.0498	*7.30*	0.0562
12	317	318	0.0038	0.0082	0.0225	*6.80*	0.0470	0.0392	*6.52*	0.0476
13	327	328	0.0014	0.0049	0.0139	*5.40*	0.0352	0.0297	*5.48*	0.0367
14	336	336		0.0019	0.0062	*4.70*	0.0289	0.0175	*4.10*	0.0253
15	345	345			0.0019	*2.10*	0.0123	0.0103	*3.20*	0.0200
16		354				*1.80*	0.0101	0.0047	*2.30*	0.0131
17						*1.40*	0.0074		*1.40*	0.0079
18						*0.79*	0.0041		*1.10*	0.0051
19						*0.46*	0.0023		*0.61*	0.0032
20						*0.27*	0.0013		*0.34*	0.0016
21						*0.15*	0.0008		*0.23*	0.0011
22						*0.13**	0.0006*		*0.11*	0.0005
23									*0.11***	0.0005**
$\bar{n}_{GLC}$			3.27	3.64	5.47		6.98	6.27		7.09

* $n \geqslant 22$.

** $n \geqslant 23$.

mal probability paper (see Fig. 3), at least up to $n = 11$ (OH) and $n = 12$ (TMS). Beyond these values curvature due to the truncation clearly appears.

By assuming that the GLC response is accurate up to $n_L = 7$ (OH) and $n_L = 8$ (TMS), an internal standard was mixed with the surfactant and the area of the peaks up to the above mentioned value was computed. As the internal standard the monodisperse compound $C_{16}\bar{E}_4$ was chosen: its peak is centered just between the peaks of $C_{12}\bar{E}_5$ and $C_{12}\bar{E}_6$. The analysis of 20:1 (w/w) mixtures (prepared by weighing on a Mettler microbalance) gives a peak of the internal standard with a height about the same as those of the contiguous peaks, near to the mode of the distribution. The limiting value of n (n_L) at which the GLC analysis gives accurate data was determined graphically by plotting on probability paper the percentage cumulative areas observed

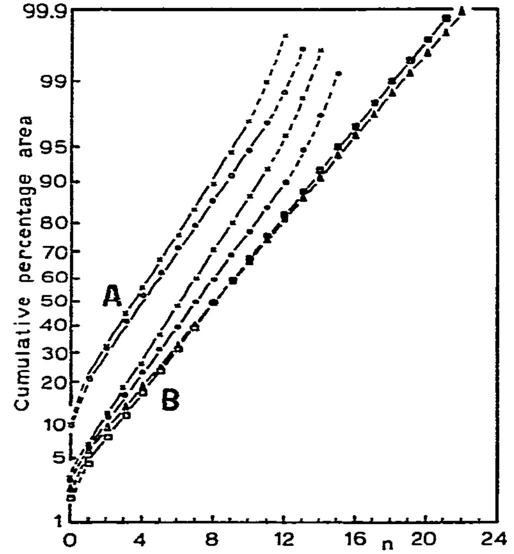

Fig. 3. Plot of cumulative percentage area *versus* n on probability paper for polydisperse surfactants $C_{12}E_{\bar{n}}$ (A, $\bar{n}_{VPO} = 2.8$; B, $\bar{n}_{VPO} = 7.1$). ×, Distribution of untreated (OH) compounds; ○, TMS derivatives. Reconstructed distributions by means of the internal standard: □, ■ OH; △, ▲, TMS. Open symbols are measured values by comparison with the internal standard; closed symbols are extrapolated values.

with the internal standard *versus* n; n_L was taken as the point at which deviation from linearity became appreciable.

The computational steps are as follows: (a) record total peak areas, including that of the internal standard; (b) calculate the theoretical total area of the distribution as 20 times the area of the standard; (c) determine the actual area percentages taking the internal standard as a reference area up to $n \leqslant 7$ for OH ($n \leqslant 8$ for TMS derivatives); (d) plot the actual cumulative percentage area on normal probability paper and check the linearity visually; (e) extend the straight line up to 99.9% and evaluate the theoretical area percentages for $n > 7$ for OH ($n > 8$ for TMS derivatives) by extrapolation to the point at which the line crosses with the n value (see Fig. 3); (f) compute the corrected molar fractions (X_n) from the area percentages (check that $\Sigma X_n = 1$); (g) compute $\bar{n}_{GLC} = \Sigma X_n n$.

The principal source of systematic errors is at stage (e). The accuracy of the graphical extrapolation obviously depends on the number of points needed for tracing the straight line up to n_L, that is, on the degree of truncation (h, %) of the normal distribution ($h = 100 - \sum_{0}^{n_L} A_n$). The commercial surfactant with $\bar{n} = 7.1$ is a limiting example for the application of this procedure as the h value is 59.7 (OH) or 50.7 (TMS). Moreover, inaccuracy can also arise from the assumption of the linearity of the cumulative percentage area *versus* n for higher n on probability paper.

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REFERENCES

1 W. B. Satkowski, S. K. Huang and R. L. Liss, in M. J. Schick (Editor), *Nonionic Surfactants*, Marcel Dekker, New York, 1967, p. 86.
2 L. Gildenberg and J. R. Trowbridge, *J. Amer. Oil Chem. Soc.*, 42 (1965) 69.
3 J. Törnquist, *Acta Chem. Scand.*, 20 (1966) 572.
4 J. Törnquist, *Acta Chem. Scand.*, 23 (1969) 1935.
5 R. Wickbold, *Fette, Seifen, Anstrichm.*, 9 (1968) 688.
6 L. Favretto and B. Stancher, *J. Chromatogr.*, 108 (1975) 183.
7 B. Stancher, L. Favretto Gabrielli and L. Favretto, *J. Chromatogr.*, 111 (1975) 459.
8 B. Stancher, F. Tunis and L. Favretto, *J. Chromatogr.*, 131 (1977) 309.
9 A. Murrel and S. G. Perry, *Nature (London)*, 196 (1962) 571.
10 B. A. Mulley, *J. Chem. Soc.*, (1958) 2065.
11 B. A. Mulley, in M. J. Schick (Editor), *Nonionic Surfactants*, Marcel Dekker, New York, 1967, p. 421.
12 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.