

Note

Improvement in accuracy in the gas-liquid chromatographic determination of the molecular-weight distribution of polyoxyethylene non-ionic surfactants

L. FAVRETTO and B. STANCHER

Istituto di Merceologia, University of Trieste, Trieste (Italy)

(Received January 3rd, 1975)

Gas-liquid chromatography (GLC) is a valuable method for the determination of the molecular-weight distribution of polyoxyethylene non-ionic surfactants¹⁻⁷, but it is usually restricted to the fractionation of the lower, more volatile oligomers. Systematic errors arise from the truncation of the distribution at higher degrees of polymerization, as is demonstrated by the comparison of the number-average molecular weights obtained by osmometry and GLC⁸.

With particular reference to the compounds of general formula $RO(CH_2CH_2O)_nH$ (where R is the hydrophobic group of the surfactant molecule and n is the degree of polymerization), the limits of GLC have not yet been fully defined, as they depend on improvements to the instrumentation. The efficiency of silylation procedures⁹, generally claimed to increase the volatility of these compounds, is also not clear.

This paper is a contribution to the study of the actual limits of GLC. A simple data processing method is suggested for correcting the analysis by reconstructing the tail of the distribution. Polyoxyethylene *p*-tert.-nonylphenyl ethers ($R = p$ -tert.-nonylphenyl) are considered as test compounds.

EXPERIMENTAL

A Pye-Unicam 104 double-column chromatograph fitted with flame ionization detectors and a linear temperature programmer was used. Stainless-steel columns (30 cm length, 1/8 in. I.D.) were packed with 80-100 mesh Gas-Chrom Z (Applied Science Labs., State College, Pa., U.S.A.) coated with 5 wt.% silicone rubber UCW 98 (Hewlett-Packard, Avondale, Pa., U.S.A.). Fractionation of polyoxyethylene oligomers was carried out with a temperature programme from 125-350° (10°/min); the injector temperature was 400° and the detector temperature 375°. The flow-rates of gases were: nitrogen, 45; hydrogen, 40; and air, 300 ml/min. The effective peak number was 0.4 for n -C₂₂/ n -C₂₃ paraffins¹⁰.

Number-average molecular weights (\bar{M}) were determined by vapour pressure osmometry (VPO) in 1,2-dichloroethane at 37° (Hewlett-Packard Mechrolab osmometer). The number-average degree of polymerization (\bar{n}) was calculated from \bar{M} [$\bar{n} = (\bar{M} - 219.3)/44.05$].

Commercial polyoxyethylene *p*-tert.-nonylphenyl ethers with $\bar{n} = 3.3, 5.4, 6.5$.

TABLE I

GLC ANALYSIS OF POLYOXYETHYLENE *p*,*tert*-NONYLPHENYL ETHERS AS UNTREATED COMPOUNDS (OH) AND TRIMETHYLSILYL (TMS) DERIVATIVES

n is the degree of polymerization, ET is the elution temperature, \bar{n}_{VPO} is measured by VPO, \bar{n}_{GLC} is calculated from molar fractions, x_n (obs., observed from GLC data; corr., corrected for the truncation), n_T is the point of truncation and *h* is the degree of truncation.

<i>n</i>	ET (°C)	x_n	$\bar{n}_{VPO} = 3.3$			$\bar{n}_{VPO} = 5.4$			$\bar{n}_{VPO} = 6.5$		
			OH obs.	TMS obs.	OH obs.	TMS obs.	OH obs.	TMS obs.	OH obs.	TMS obs.	
1	138	142	0.0080	0.0085	0.0047	0.0030	0.0030	0.0080	0.0080	0.0053	0.0053
2	149	155	0.0906	0.0897	0.0123	0.0048	0.0048	0.0103	0.0103	0.0086	0.0086
3	163	170	0.3505	0.3437	0.1082	0.0948	0.0948	0.0479	0.0479	0.0386	0.0386
4	181	187	0.2948	0.3034	0.2155	0.2127	0.2127	0.1216	0.1216	0.1225	0.1225
5	199	204	0.1531	0.1537	0.2287	0.2374	0.2374	0.1688	0.1688	0.1728	0.1728
6	216	221	0.0652	0.0640	0.1707	0.1775	0.1775	0.1675	0.1675	0.1822	0.1822
7	231	235	0.0256	0.0245	0.1176	0.1210	0.1210	0.1444	0.1444	0.1450	0.1450
8	244	248	0.0077	0.0085	0.0721	0.0738	0.0738	0.1228	0.1228	0.1100	0.1100
9	258	261	0.0045	0.0040	0.0375	0.0393	0.0393	0.0918	0.0787	0.0801	0.0801
10	270	273	Traces	Traces	0.0191	0.0180	0.0167	0.0599	0.0440	0.0653	0.0459
11	282	284			0.0100	0.0100	0.0097	0.0291	0.0310	0.0361	0.0330
12	293	294			0.0036	0.0055	0.0040	0.0161	0.0200	0.0143	0.0210
13	303	303			Traces	0.0027	0.0025	0.0093	0.0120	0.0096	0.0130
14	312	312				0.0038*	Traces	0.0025	0.0080	0.0064	0.0080
15	320	320					Traces	Traces	0.0056	0.0032	0.0050
16	328	328						Traces	0.0034	Traces	0.0035
17									0.0020		0.0018
18									0.0040**		0.0037**
\bar{n}_{GLC}			3.86	3.86	5.46	5.50	5.54	5.58	6.59	6.74	6.68

* $n \geq 14$.** $n \geq 18$.

and 7.5 were considered. The monodisperse compound with $n = 4$ was separated from a mixture ($\bar{n} = 3.3$) by preparative column chromatography¹¹. This oligomer had a GLC purity of 95.8% (as a peak area) and was used as an internal standard.

Trimethylsilyl (TMS) derivatives were prepared by standard procedures⁹. The reaction mixture was filtered through a Mitex 5 (Millipore) filter and injected directly.

RESULTS AND DISCUSSION

The chromatograms in Fig. 1 show an example of fractionation of the surfactant with $\bar{n} = 5.4$. All samples contain a few per cent (expressed as a peak area) of oligomers of another type, which have been not considered in this investigation.

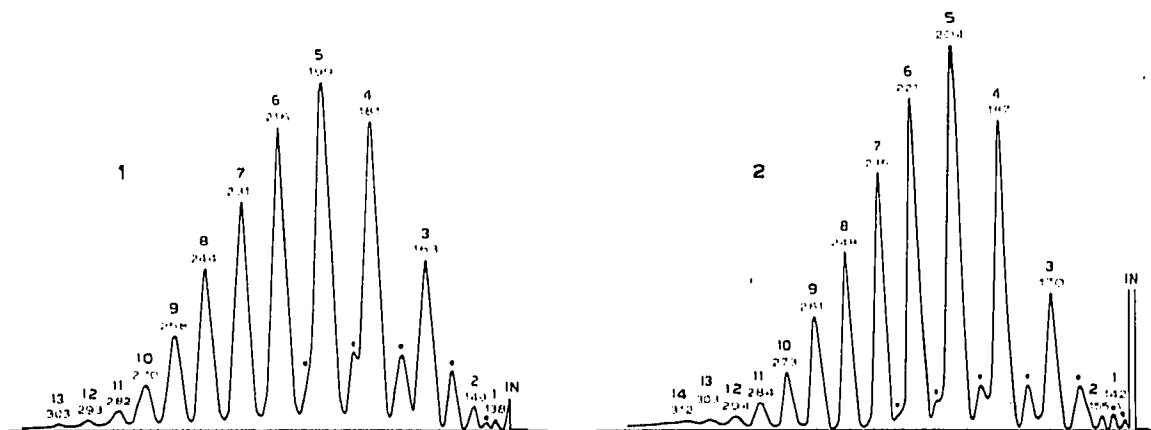


Fig. 1. Gas chromatograms of polyoxyethylene *p-tert.*-nonylphenyl ethers with $\bar{n}_{VPO} = 5.4$. 1, Untreated surfactant; 2, TMS derivative. Numbers over the peaks indicate the degree of polymerization (upper value) and the elution temperature (lower value). Peaks marked with spots are not considered in this study.

The elution temperature of the TMS derivatives is slightly higher than that of the untreated oligomers, but the difference tends to disappear with increase in n , so that elution temperatures are the same for $n \geq 13$ (see Table I). The TMS derivatives have the advantage of interacting more weakly than untreated compounds with the stationary phase, and the separation between peaks is thus improved.

Table I gives the results of the GLC analysis of the surfactants. The concordance of the molar fractions is observed only for the mixture with $\bar{n} = 3.3$, whereas the distribution appears truncated at higher \bar{n} .

In order to define the value of n at which cutting off occurs, a detailed analysis of the GLC data was performed. The cumulative percentage distribution largely fits a log-normal plot (see Fig. 2), so that the deviation from linearity indicates the value of n_T , at which truncation of the distribution begins (see Table I). The n_T value is 10 for TMS derivatives and 9 for untreated compounds. This plot is the basis for the further calculation of the degree of truncation (h) by the method of Fisher, reported by Hald¹². Table I shows that the degree of truncation is negligible for $\bar{n} = 5.4$ but is important for $\bar{n} = 6.5$.

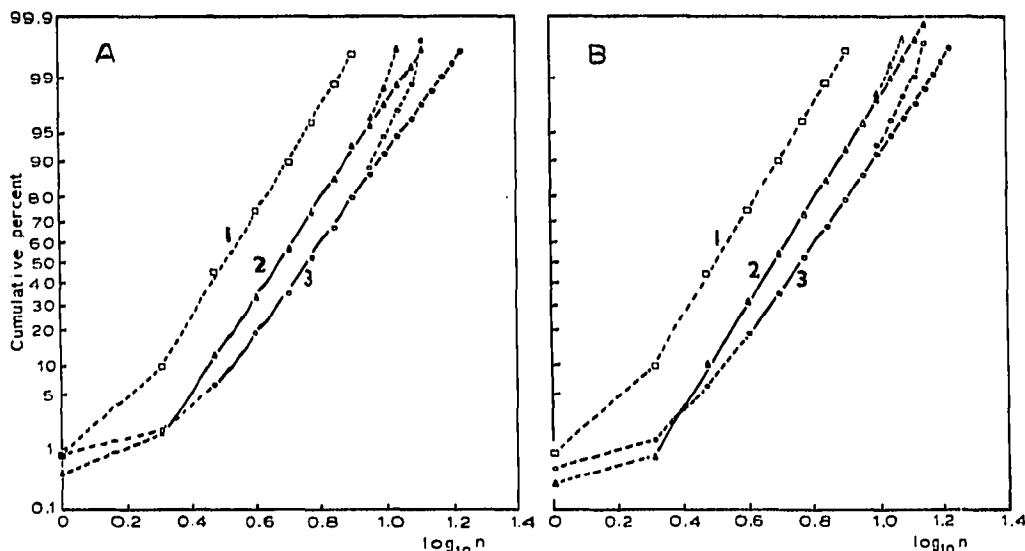


Fig. 2. Cumulative percentage distribution of the degree of polymerization (as $\log_{10} n$) of polyoxyethylene *p*-*tert*-nonylphenyl ether non-ionic surfactants. A, Untreated compounds; B, TMS derivatives. 1, $\bar{n}_{VPO} = 3.3$; 2, $\bar{n}_{VPO} = 5.4$; 3, $\bar{n}_{VPO} = 6.5$. Broken lines, observed points; solid lines, calculated points.

The corrected distribution can be approximated by graphical extrapolation of the linear interval of the observed distribution, although it can be also obtained by statistical procedures. The limits of application of this extrapolation procedure are imposed mainly by the linearity of the plot. With increase in n , the truncation also increases and linearity is no longer observed (as in the case of $\bar{n} = 7.5$).

In conclusion, GLC analysis may give an accurate picture of the distribution of polyoxyethylene *p*-*tert*-nonylphenyl ethers up to $\bar{n} = 6.5$. Values of $\bar{n}_{GLC} = \sum x_n n$, calculated from the corrected molar fraction (x_n), are in fact slightly higher than those determined by osmometry, which is influenced by the presence of unidentified low-molecular-weight oligomers.

ACKNOWLEDGEMENT

The authors thank Chemische Werke Hüls (Marl, Kreis Recklinghausen, G.F.R.) for supplying the surfactant samples.

REFERENCES

- 1 H. G. Nadeau, D. M. Oaks, Jr., A. W. Nichols and L. P. Carr, *Anal. Chem.*, 36 (1964) 1915.
- 2 L. Gildenberg and J. R. Trowbridge, *J. Amer. Oil Chem. Soc.*, 42 (1965) 69.
- 3 H. G. Nadeau and P. H. Waszeciak, in M. J. Schick (Editor), *Nonionic Surfactants*, Marcel Dekker, New York, 1967, p. 893.
- 4 J. Törnquist, *Acta Chem. Scand.*, 20 (1966) 572.
- 5 J. Törnquist, *Acta Chem. Scand.*, 21 (1967) 2095.
- 6 J. Törnquist, *Acta Chem. Scand.*, 23 (1969) 1935.

- 7 F. J. Ludwig, Sr., *Anal. Chem.*, 40 (1968) 1620.
- 8 C. Calzolari, L. Favretto and B. Stancher, *J. Chromatogr.*, 39 (1969) 318.
- 9 C. C. Sweeley, R. Bentley, M. Makita and W. W. Wells, *J. Amer. Chem. Soc.*, 85 (1963) 2497.
- 10 R. A. Murrel and S. G. Perry, *Nature (London)*, 196 (1962) 571.
- 11 T. Ishiwata, M. Nagayama and H. Isa, *Bull. Chem. Soc. Jap.*, 36 (1963) 129.
- 12 A. Hald, *Statistical Theory with Engineering Applications*, Wiley, New York, 1962, p. 144.