

CHROM. 8367

Note

Analysis of polyoxyethylene non-ionic surfactants by coupling gas-liquid and thin-layer chromatography

B. STANCHER, L. FAVRETTO GABRIELLI and L. FAVRETTO

Istituto di Merceologia, Università di Trieste, Trieste (Italy)

(Received April 16th, 1975)

Gas-liquid chromatography (GLC) is a precise method for the control of the quality of industrial polyoxyethylene non-ionic surfactants, $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ (where R is a hydrophobic group and \bar{n} is the number average degree of polymerization), but the analysis is limited to the fractionation of polydispersions with low \bar{n} (for instance, up to 6.5 with R = *p-tert.*-nonylphenyl¹) by the restriction imposed by the volatility. Adsorption thin-layer chromatography (TLC) has also been claimed to improve substantially the accuracy in fractionating higher, slightly volatile oligomers²⁻⁴, although the lower terms are cut off by the limited peak capacity.

The combination of the advantages of the two techniques appears to be promising for establishing the actual distribution, although problems may arise in comparing two chromatographic techniques that have different analytical precisions. This paper deals with the analysis of typical surfactants such as polyoxyethylene *p-tert.*-nonylphenyl ethers [R = *p*-(1,1,3,3-tetramethylbutyl)phenyl].

EXPERIMENTAL

A Pyc-Unicam double-column chromatograph with flame ionization detectors was used. Stainless-steel columns (35 cm in length and 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 6% (w/w) UCW 98 silicone rubber (Hewlett-Packard, Avondale, Pa., U.S.A.). Fractionation was carried out with a linear temperature programme from 150 to 350° at the rate of 10°/min. The injector and detector temperatures were 400 and 375°, respectively. The flow-rates of the gases were nitrogen 40, hydrogen 40 and air 300 ml/min. The effective peak number was 0.5 for *n*-C₂₂/*n*-C₂₃ paraffins⁵.

TLC methods have been described previously²⁻⁴. The procedure is essentially based on a double development at 20° of not more than 20 μg of the surfactant on a 200-μm layer of Merck (Darmstadt, G.F.R.) activated silica gel G (10–40 μm) by the ascending (vertical) technique to a height of 22.5 cm in a stainless-steel sandwich chamber, in which the spacing between the thin layer and the covering was only 0.8 mm. Butan-2-one saturated with water (at 20°) was used as the eluent. After suitable conditioning of the layer, the spots were made visible with iodine vapour and then examined with a photometer (Joyce, Loebel & Co. Chromoscan), the absorbance (linear in the range 0–1) being measured at 465 nm. The integrated absorbance

of the peaks was determined planimetrically. In the range 0.1–2 μg of standards deposited on the layer, integrated absorbances varied linearly with the amounts spotted. The regression line passed through the origin of the coordinates and the observed integrated absorbances were scattered around the interpolating line with a root square deviation of 3–6% from the average value of the absorbances.

Commercial polyoxyethylene *p-tert.*-nonylphenyl ethers with $\bar{n} = 7.5, 8.6$ and 9.7 were analyzed by using as internal standard the following monodisperse compounds (GLC purity expressed as a percentage of the peak area is given in parentheses): $\bar{n} = 4$ (95.8), 5 (96.0) and 6 (98.5). They were prepared by column chromatography from the polydispersion with $\bar{n} = 5.4$ (ref. 6). The purity was also checked by infrared, ultraviolet and nuclear magnetic resonance spectroscopy. In 1,2-dichloroethane, the molecular weights determined by vapour pressure osmometry (VPO) at 37° (Hewlett-Packard Mechrolab), with theoretical values in parentheses, were 402 (396.6), 436 (440.6) and 479 (484.7), respectively.

Number-average molecular weights (\bar{M}) were determined by VPO in the same solvent. The number-average degree of polymerization (\bar{n}) was calculated from $\bar{M} [n = (\bar{M} - 219.3)/44.05]$.

The data were processed on an Olivetti 101 desk computer with a standard regression programme⁷.

RESULTS AND DISCUSSION

Fig. 1 shows an example of the fractionation of the surfactant with $\bar{n} = 8.6$. Comparison of the two chromatograms shows the cut-off of compounds with $n < 4$ in TLC and the truncation of those with $n > 10$ in GLC. These limitations appear more clearly when the cumulative percentage distribution of the molar fraction as a function of $\log n$ is considered (see Fig. 2). Therefore, the TLC distribution at lower n was corrected on the basis of the GLC data. In checking the correspondence between the data obtained by the two methods, regression analysis of the integrated TLC area (A_{TLC}) on the GLC peak area (A_{GLC}) always gave an interpolating line that passes

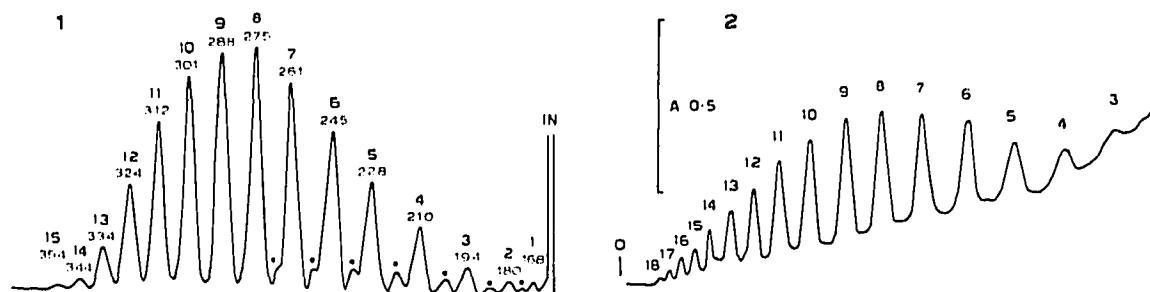


Fig. 1. Chromatograms obtained by GLC (1) and TLC (2) of polyoxyethylene *p-tert.*-nonylphenyl ethers with $n_{\text{VPO}} = 8.6$. Numbers over the peaks indicate the degree of polymerization. In the gas-liquid chromatogram the elution temperature is also indicated; peaks marked with spots are not considered in this study. In the thin-layer chromatogram, 0 is the starting point, F is the eluent front and A is the absorbance.

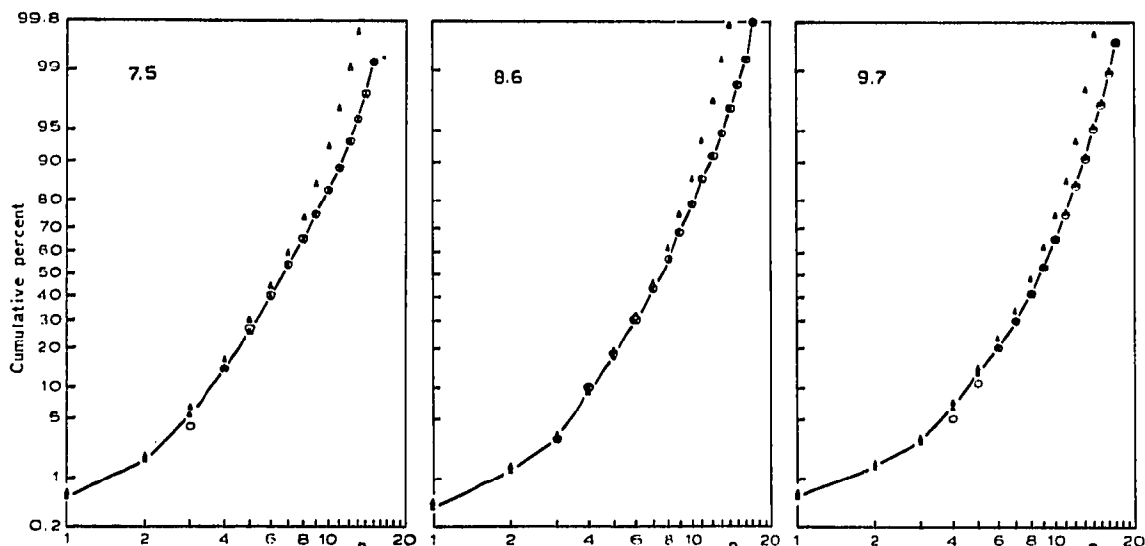


Fig. 2. Cumulative percentage distribution of the degree of polymerization (as log n) of polyoxyethylene *p*-*tert*-nonylphenyl ether non-ionic surfactants with $\bar{n} = 7.5, 8.6$ and 9.7 . Δ , GLC; \circ , TLC; \blacktriangle , GLC + TLC (points are joined by a solid line).

TABLE I

GLC AND TLC ANALYSIS OF POLYOXYETHYLENE *p*-*tert*-NONYLPHENYL ETHERS

n is the degree of polymerization; ET is the elution temperature; x_n is the molar fraction of the n oligomer determined by GLC, TLC and coupled GLC-TLC; \bar{n}_{VPO} is the number-average degree of polymerization evaluated by VPO; \bar{n} is calculated from molar fractions.

n	ET (°C)	x_n								
		$\bar{n}_{VPO} = 7.5$			$\bar{n}_{VPO} = 8.6$			$\bar{n}_{VPO} = 9.7$		
		GLC	TLC	GLC-TLC	GLC	TLC	GLC-TLC	GLC	TLC	GLC-TLC
1	168	0.0069		0.006	0.0047		0.004	0.0065		0.006
2	180	0.0122		0.011	0.0100		0.009	0.0100		0.009
3	194	0.0465	0.041	0.041	0.0218	0.032	0.020	0.0156		0.014
4	210	0.0990	0.100	0.087	0.0665	0.072	0.060	0.0436	0.050	0.038
5	228	0.1389	0.130	0.123	0.0965	0.085	0.087	0.0731	0.061	0.064
6	245	0.1463	0.133	0.129	0.1251	0.115	0.112	0.0900	0.095	0.079
7	261	0.1494	0.136	0.132	0.1447	0.133	0.130	0.1079	0.103	0.094
8	275	0.1394	0.116	0.123	0.1540	0.136	0.138	0.1413	0.112	0.123
9	288	0.1112	0.093	0.098	0.1328	0.111	0.119	0.1397	0.122	0.122
10	301	0.0772	0.081	0.081	0.1087	0.105	0.106	0.1251	0.117	0.116
11	312	0.0431	0.056	0.056	0.0724	0.073	0.074	0.1088	0.104	0.103
12	324	0.0201	0.048	0.047	0.0401	0.049	0.050	0.0750	0.084	0.083
13	334	0.0069	0.027	0.027	0.0159	0.037	0.038	0.0465	0.060	0.060
14	344	0.0029	0.019	0.019	0.0047	0.023	0.024	0.0141	0.044	0.044
15	354		0.012	0.012	0.0021	0.014	0.014	0.0028	0.022	0.021
16			0.008	0.008		0.008	0.008		0.015	0.014
17						0.005	0.005		0.007	0.006
18						0.002	0.002		0.004	0.004
\bar{n}		6.9	7.6	7.6	7.7	8.2	8.3	8.5	9.3	9.2

through the origin of the coordinates. The empirical relationships obtained ($A_{TLC} = bA_{GLC}$) were always valid in the range of n from 5 to 9, whereas at higher n , a systematic positive deviation from the interpolating line occurred. The coefficient of variation of A_{TLC} around the interpolating line ranged between 3 and 10% of the average of the A_{TLC} value ($5 \leq n \leq 9$).

The above relationship was used to correct A_{GLC} at $n > 9$ by assuming A_{TLC} to be accurate, so that $A_{GLC} = (1/b)A_{TLC}$ ($n > 9$), where b is the slope of the empirical relationship calculated by the method of least squares.

Table I summarizes the analytical results for various samples. The comparison of \bar{n}_{VPO} with \bar{n} calculated from the chromatographic data ($\bar{n} = \sum x_n n$) indicates that the proposed method is valid for the analysis of compounds with $\bar{n} = 7.5$ and 8.6. For $\bar{n}_{VPO} = 9.7$, the results are systematically lower ($\bar{n} = 9.2$). This fact probably reflects the cut-off in TLC at higher n , where the resolution between oligomers decreases progressively.

To conclude, coupling GLC with TLC analysis gives a more accurate picture of the distribution of the degree of polymerization of these polyoxyethylene non-ionic surfactants. As the method is centred on the accuracy of TLC, the results are accurate only up to $\bar{n} = 8.6$, while at higher \bar{n} systematic truncation occurs.

ACKNOWLEDGEMENTS

The authors thank Prof. Claudio Calzolari for his assistance. They also thank Chemische Werke Hüls (Marl, Kreis Recklinghausen, G.F.R.) for supplying the surfactant samples.

REFERENCES

- 1 L. Favretto and B. Stancher, *J. Chromatogr.*, 108 (1975) 183.
- 2 L. Favretto, G. Pertoldi Marletta and L. Favretto Gabrielli, *J. Chromatogr.*, 46 (1970) 255.
- 3 G. Pertoldi Marletta and L. Favretto Gabrielli, *Tec. Ital.*, 34 (1969) 649.
- 4 L. Favretto, *Riv. Ital. Sostanze Grasse*, 47 (1970) 187.
- 5 R. A. Murrel and S. G. Perry, *Nature (London)*, 196 (1962) 571.
- 6 T. Ishiwata, M. Nagayama and H. Isa, *Bull. Chem. Soc. Jap.*, 36 (1963) 129.
- 7 N. R. Draper and H. Smith, *Applied Regression Analysis*, Wiley, New York, 1966, pp. 1-43.