DEGRADATION AND ANALYSIS OF POLYOXYETHYLENE MONOALKYL ETHERS IN THE PRESENCE OF ACETYL CHLORIDE AND FERRIC CHLORIDE

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SUMMARY

Degradation of model and commercial polyoxyethylene glycol monoalkyl ethers in the presence of anhydrous ferric chloride and an excess of acetyl chloride was studied. It was found that 2-chloroethyl acetate is the main product of the polyoxyethylene chain degradation. Hydrophobic alkyls form mainly unidentified resins. 2,6-Dimethyl-γ-pyrone and its derivatives are by-products formed from acetyl chloride and acetic acid. Using an internal standard method, the composition of the products obtained by degradation of polyoxyethylene chains can be determined and used to calculate the average degree of ethoxylation. However, this method is limited to preparations for which the hydrophobes can be identified and their contents determined.

INTRODUCTION

In our previous papers[1,2] the degradation of polyoxyethylene glycols, block copolymers of ethylene oxide–butylene oxide and polyoxyethylene monoalkyl ethers in the presence of an excess of acetyl chloride was reported. The degradation is complete after 2 h at 250°C. 2-Chloroethyl acetate formed from the polyoxyethylene chain and alkyl chlorides obtained from the hydrophobic alkyls are the main products. However, other products are also formed during the degradation. As a result, several components must be identified and their contents determined by taking into account correction factors. This is troublesome even for model pure compounds or polydisperse polyoxyethylene glycol monoalkyl ethers obtained by ethoxylation of a single alcohol.

Commercial products are obtained from mixtures of different alcohols and their compositions are usually very complex. Therefore, the composition of the degradation products is also very complex and it is a very difficult task to separate and identify all

components formed during degradation. This complexity decreases the precision and accuracy of the qualitative analysis.

The aim of this work is to study the degradation of some model and commercial polyoxyethylene glycol monoalkyl ethers in the presence of acetyl chloride and ferric chloride and the application of this method, proposed for the first time by Waszeciak and Nadeau[3], for determining the average degree of alcohol ethoxylation and the composition of the hydrophobic constituent in some commercial products.

EXPERIMENTAL

The following reagents were used for degradation studies: model trioxyethylene glycol monoalkyl ether (E-3), $H(OCH_2CH_2)_3OC_{10}H_{21}$, of purity $>94\%$ as determined by gas chromatography (GC); commercial oleyl alcohol fraction treated with ethylene oxide (O-5); commercial Rokanol K-3 (NZPO Rokita, Brzeg Dolny, Poland), a product of the reaction of alcohols obtained from rape seed oil with ethylene oxide; commercial Rokanol K-20 (NZPO Rokita), a product of the reaction of alcohols obtained from rape seed oil with ethylene oxide; commercial Rokanol L-3 (NZPO Rokita), a product of the reaction of a mixture of saturated alcohols $C_{12}-C_{18}$ with ethylene oxide; acetyl chloride, pure for analysis (Fluka, Buchs, Switzerland); anhydrous ferric chloride (POCh Gliwice, Poland).

A sample (0.05 g) of polyoxyethylene glycol monoalkyl ethers, 0.005–0.02 g of hexadecane used as an internal standard and 0.05 g of anhydrous ferric chloride were weighed into a reaction vial of capacity $5 \, cm^3$ (Supelco, Bellefonte, PA, U.S.A.). Acetyl chloride (0.8 cm³) was added by means of a syringe and the reaction mixture was shaken to obtain a clear solution. It was heated at 150°C for 30 min. The cooled post-reaction mixture was diluted 1:1 in dichloromethane and analyzed by means of GC.

A gas chromatograph (Perkin-Elmer Model 900) with a flame ionization detector was used. The separation was carried out in stainless-steel columns: I, 0.9 m × 2.7 mm I.D. packed with 3% OV-101 on Chromosorb G AW DMCS, 60–80 mesh; II, 0.9 m × 2.7 mm I.D. packed with 3% OV-17 on Chromosorb G AW DMCS, 60–80 mesh; III, 1.6 m × 2.7 mm I.D. packed with 12% Carbowax 20 M-TPA on Chromosorb W AW DMCS, 80–100 mesh. Argon was used as the carrier gas and its flow-rate was 30 cm³ min⁻¹. The temperature of column I was 100°C for 1 min, and then raised to 300°C at 8°C min⁻¹. The temperatures of the injector and the detector were 300 and 320°C, respectively. The temperature of column II was 80°C for 1 min, and then raised to 290°C at 6°C min⁻¹. The temperatures of the injector and the detector were 300°C. The temperature of column III was 100°C for 1 min, and then raised to 220°C at 5°C min⁻¹. The temperatures of the injector and the detector were 250°C.

The average degree of ethoxylation was calculated in a similar way as in our previous work[2]. Correction factors were calculated according to the method of Stenberg et al.[4] using the concept of the effective number of carbon atoms.

For comparison the ethoxylation degrees of polyoxyethylene monoalkyl ethers were also determined by the standard ISO 2270-1972(E) method.

In a direct analysis, polyoxyethylene glycol monoalkyl ethers were analyzed in the form of their acetates prepared in the standard way. Polyoxyethylene glycols were determined according to the Weibull method[5].

The identification of the separated components was carried out by means of a mass spectrometer coupled to a gas chromatograph (GC–MS 2091; LKB, Bromma, Sweden). The chromatographic columns and separation conditions were the same as in the GC analysis: columns II and III were used. An ionization energy of 70 eV and an ion-source temperature of 250°C were employed.

RESULTS AND DISCUSSION

In the previous paper[2] model E-3 and E-7 products were used only for degradation studies. E-3 contains mainly the homologue having three oxyethylene groups and its content is above 94%. E-7 is a polydisperse mixture obtained from pure dodecyl alcohol and contains succeeding homologues up to the compound having seventeen oxyethylene groups. O-5 contains homologues only up to compounds having six oxyethylene groups. However, in this case three different hydrophobic alkyls are present; the main components are appropriate derivatives of oleyl alcohol. L-3 contains homologues up to compounds having seven to eight oxyethylene groups and four different saturated alcohols (C_{12}–C_{18}) are present in this product (Fig. 1).

Chromatograms of these four products are relatively simple and all components can be separated. They can easily be identified by means of their retention indices[6] and their contents can be determined by the normalization method (Table I). These results can be further used to calculate the average degree of ethoxylation.

The chromatogram obtained for Rokanol K-3 is much more complex as a result of the presence of different saturated and unsaturated alcohols C_{12}–C_{22} present in this product (Fig. 2). Therefore, it is impossible to separate all the components present and
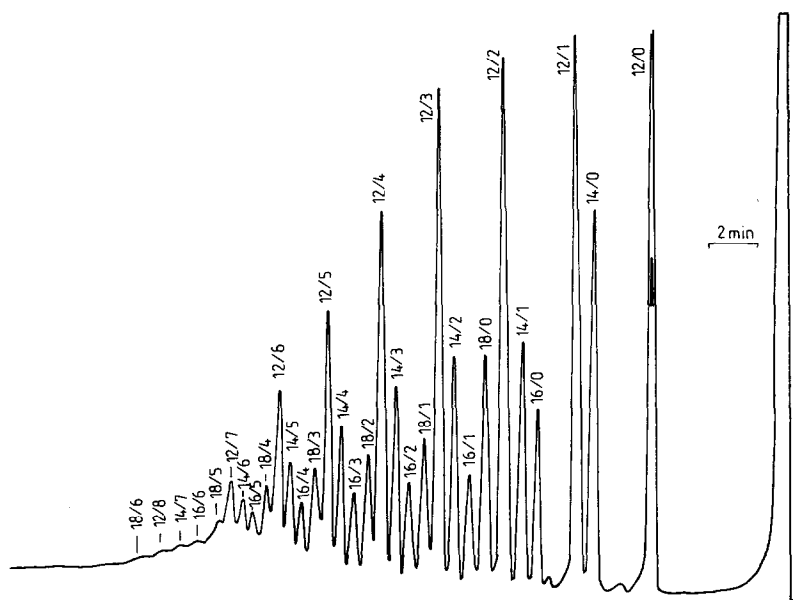

Fig. 1. Chromatogram of Rokanol L-3 on column I. Peak labelling: number of carbon atoms/degree of ethoxylation.

TABLE I

COMPOSITIONS OF THE POLYOXYETHYLENE GLYCOL MONOALKYL ETHERS

EO = Ethylene oxide.

E-7			O-5			Rokanol L-3		
Formula	n	Content (%, w/w)	Formula	n	Content (%, w/w)	Formula	n	Content (%, w/w)
$C_{12}H_{25}O(EO)_nH$	0	5.51	$C_{16}H_{33}O(EO)_nH$	0	0.00	$C_{12}H_{25}O(EO)_nH$	0	11.73
	1	3.15		1	0.00		1	10.85
	2	4.45		2	0.21		2	9.78
	3	5.95		3	0.83		3	8.77
	4	7.53		4	2.39		4	6.54
	5	8.69		5	1.68		5	4.10
	6	9.01		6	0.92		6	2.32
	7	9.56	$C_{18}H_{37}O(EO)_nH$	0	0.00		7	1.13
	8	9.35		1	0.46		8	0.11
	9	9.01		2	1.01	$C_{14}H_{29}O(EO)_nH$	0	6.84
	10	8.03		3	6.01		1	4.46
	11	6.75		4	5.17		2	3.73
	12	5.30		5	1.58		3	3.09
	13	3.64	$C_{18}H_{35}O(EO)_nH$	0	0.46		4	2.34
	14	2.33		1	0.97		5	1.34
	15	1.20		2	2.98		6	0.80
	16	0.46		3	26.62		7	0.28
	17	0.08		4	34.39	$C_{16}H_{33}O(EO)_nH$	0	3.30
				5	13.02		1	1.89
				6	1.32		2	1.57
							3	1.26
							4	0.67
							5	0.54
							6	0.34
						$C_{18}H_{37}O(EO)_nH$	0	4.00
							1	2.32
							2	2.15
							3	1.65
							4	1.07
							5	0.85
							6	0.19

some of them are coeluted (Table II). Thus, the contents of all components cannot be determined and the average degree of ethoxylation cannot be correctly calculated.

Rokanol K-20 contains much higher analogues having more oxyethylene groups and it cannot be analyzed by GC. As a result, its average degree of ethoxylation cannot be determined.

Polyoxyethylene glycols are also present in these products, but their contents, as determined by the Weibull method[5], are relatively low and equal to 0.0, 1.5, 0.96, 0.41, 1.17 and 2.19% for E-3, E-7, O-5, L-3, K-3 and K-20, respectively.

Degradation products were analyzed using columns containing silicone resins OV-101 and OV-17 and Carbowax 20 M-TPA as the liquid phases in columns I, II and III, respectively. Columns I and II were used to check the degree of degradation, while
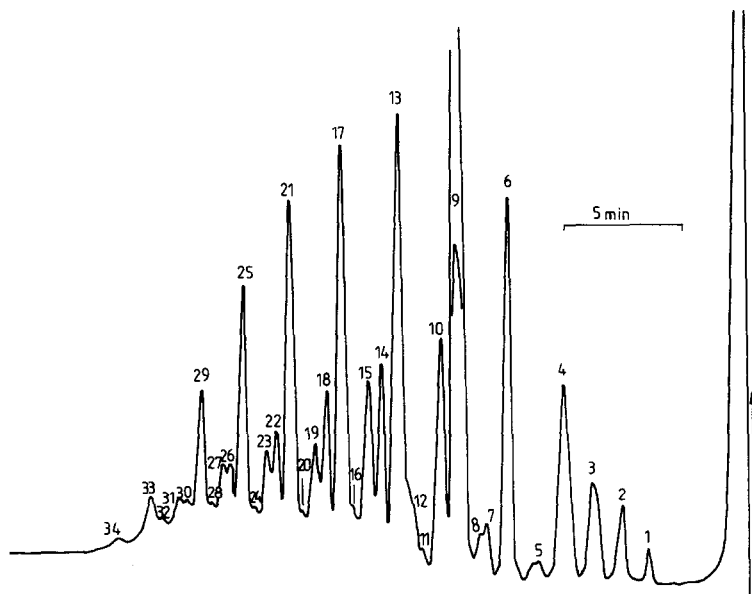
Fig. 2. Chromatogram of Rokanol K-3 on column I.

column III was used to separate all components after degradation and to determine their contents.

It was found that the degradation is complete at 150°C after 30 min (Fig. 3b). At 100°C, chromatograms are more complex and several peaks are observed (Fig. 3a). Most of these peaks are formed by the degradation of the hydrophobic alkyls (Table III). Their mass spectra have parent ions and show characteristic lines at m/z differing by 14 units, $i.e.$, the value characteristic for the methylene group. Thus, they are formed by splitting of methylene groups from the hydrophobic alkyls. These peaks largely disappear as the degradation is carried out at 150°C. Some high boiling resins are formed and they are not eluted from the column. However, small peaks of the products formed by degradation of the hydrophobic alkyls are still observed, and they can be used to identify hydrophobes in the initial polyoxyethylene glycol monoalkyl ethers.

Exemplary chromatograms of the degradation products are shown in Figs. 4 and 5. Hexane was used as an internal standard. The separated components were identified by gas chromatography–mass spectrometry (GC–MS) and by comparison of their retention indices with those determined for chromatographic standards (Tables IV and V). Also reported are the contents of the separated components as determined by the internal standard method.

Polyoxyethylene chains degrade in the same way as was reported previously for polyoxyethylene glycols[1]. Four different components were found with retention indices of 1065, 1318, 1536 and 1757 on Carbowax 20M-TPA, corresponding to 1,2-dichloroethane, 2-chloroethyl acetate, bis(2-chloroethyl) ether and 5-chloro-3-oxapentyl acetate. 2-Chloroethyl acetate is the main product of degradation. Acetic acid (I_p = 1427) is formed from an excess of acetyl chloride and can be neglected. Under the degradation conditions in the presence of ferric chloride, acetyl chloride and

TABLE II

COMPOSITION OF ROKANOL K-3

Peak No.	Component	Content (%, w/w)
1	Unknown	0.62
2	$C_{12}H_{25}OH$	1.57
3	Unknown	2.98
4	$C_{14}H_{29}OH + C_{12}H_{25}O(EO)H$	5.82
5	Unknown	0.54
6	$C_{16}H_{33}OH$	6.94
7	$C_{14}H_{29}O(EO)H$	0.85
8	$C_{12}H_{25}O(EO)_2H$	0.70
9	$C_{18}H_{37}OH + C_{18}H_{35}OH$	22.44
10	$C_{16}H_{33}(EO)H$	4.17
11	$C_{14}H_{29}O(EO)_2H$	0.22
12	$C_{12}H_{25}O(EO)_3H + C_{20}H_{41}OH$	1.31
13	$C_{18}H_{37}O(EO)H + C_{18}H_{35}O(EO)H$	11.80
14	$C_{16}H_{33}O(EO)_2H$	2.64
15	$C_{20}H_{41}O(EO)H + C_{22}H_{45}OH + C_{14}H_{29}O(EO)_3H$	3.27
16	$C_{12}H_{25}O(EO)_4H$	0.12
17	$C_{18}H_{37}(EO)_2H + C_{18}H_{35}(EO)_2H$	9.18
18	$C_{16}H_{33}O(EO)_3H$	2.00
19	$C_{20}H_{41}O(EO)_2H + C_{22}H_{45}O(EO)H + C_{14}H_{29}O(EO)_4H$	1.38
20	$C_{12}H_{25}O(EO)_5H$	0.15
21	$C_{18}H_{37}O(EO)_3H + C_{18}H_{35}O(EO)_3H$	6.96
22	$C_{16}H_{33}O(EO)_4H$	1.42
23	$C_{20}H_{41}O(EO)_3H + C_{22}H_{43}O(EO)_2H + C_{14}H_{29}O(EO)_5H$	1.16
24	$C_{12}H_{25}O(EO)_6H$	0.16
25	$C_{18}H_{37}O(EO)_4H + C_{18}H_{35}O(EO)_4H$	4.60
26	$C_{16}H_{33}O(EO)_5H$	1.17
27	$C_{20}H_{41}O(EO)_4H + C_{22}H_{43}O(EO)_3H + C_{14}H_{29}O(EO)_6H$	1.01
28	$C_{12}H_{25}O(EO)_7H$	0.18
29	$C_{18}H_{37}O(EO)_5H + C_{18}H_{35}O(EO)_5H$	2.66
30	$C_{16}H_{33}O(EO)_6H$	0.49
31	$C_{20}H_{41}O(EO)_5H + C_{22}H_{43}O(EO)_4H + C_{14}H_{29}O(EO)_7H$	0.31
32	$C_{12}H_{25}O(EO)_8H$	0.19
33	$C_{18}H_{37}O(EO)_6H + C_{18}H_{35}O(EO)_6H$	0.86
34	$C_{16}H_{33}O(EO)_7H$	0.13

acetic acid can form γ-pyrone derivatives which were identified in our previous work[1]. As they are not formed in the absence of ferric chloride, the appropriate peaks (I_p = 2035, 2107, 2227 and 2405) can also be ignored. Other small peaks having the retention indices 1470, 1684, 1873, 1893, 2078, 2241, 2288, 2480, 2692 and 2898 were the products formed by the degradation of hydrophobic alkyls. They can be used only to identify the alkyl structures in the initial polyoxyethylene glycol monoalkyl ethers because these alkyl groups formed mainly unidentified resins.

Due to this, the normalization method cannot be used to determine the composition of the degradation products. Thus, the internal standard method was
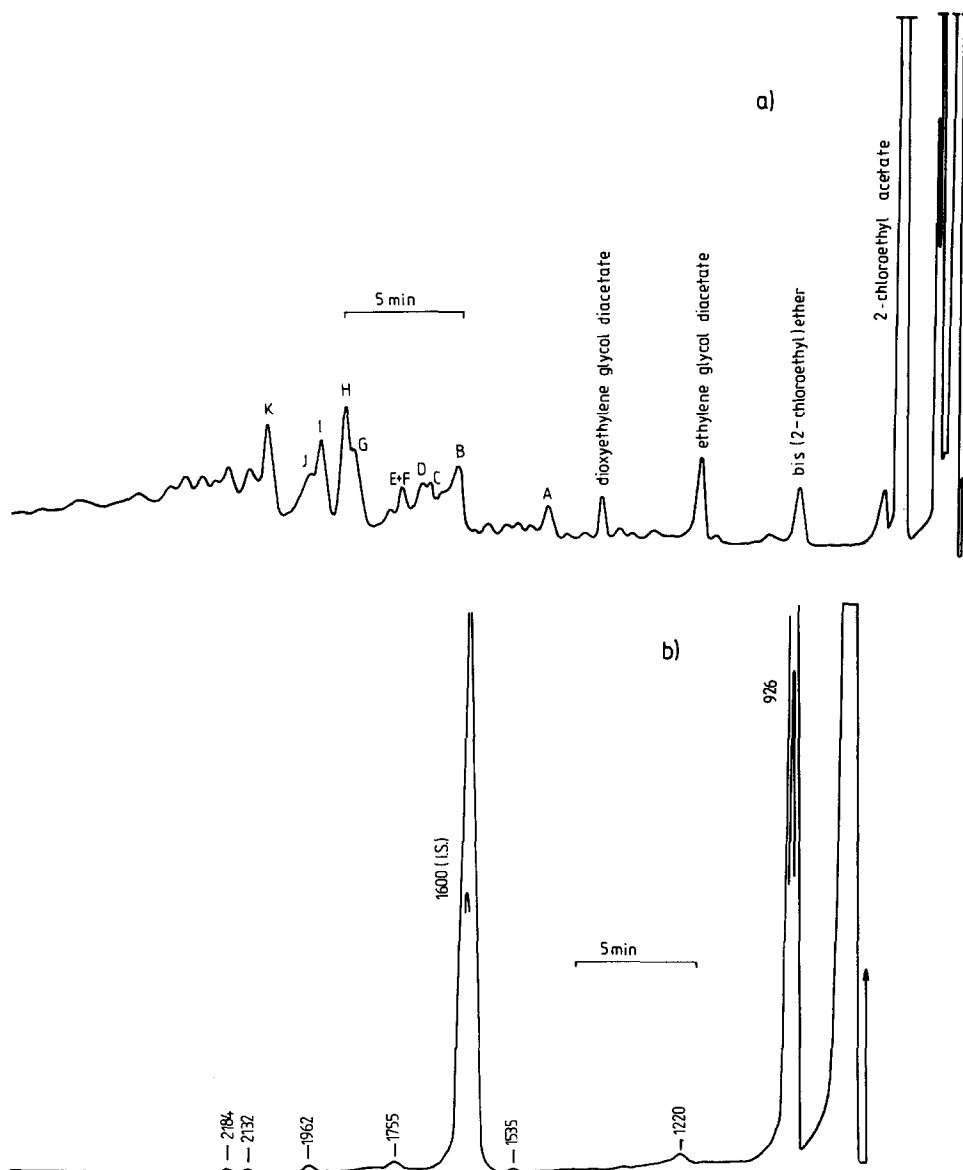
Fig. 3. Chromatograms of O-5 after degradation at (a) 100, (b) 150°C, on column II.

used. The small peaks of chlorohydrocarbons can be neglected and the average degrees of ethoxylation calculated from the masses of polyoxyethylene glycol monoalkyl ethers taken for analyses and from the contents of 1,2-dichloroethane, 2-chloroethyl acetate, bis(2-chloroethyl) ether and 5-chloro-3-oxapentyl acetate formed from the polyoxyethylene chains during their degradation.

The values of the degree of ethoxylation together with some statistical

TABLE III

COMPONENTS IDENTIFIED IN THE DEGRADATION OF HYDROPHOBIC ALKYLS

O-5, silicone resin OV-17, $T = 100°C$.

Peak	Molecular mass	Component
A	224	$C_{16}H_{32}$
B	250 + 252	$C_{18}H_{34} + C_{18}H_{36}$
C	250 + 224	$C_{18}H_{34} + C_{16}H_{32}$
D	250 + 224	$C_{18}H_{34} + C_{16}H_{32}$
E	260	$C_{16}H_{33}Cl$
F	238	$C_{17}H_{34}$
G	286 + 250	$C_{18}H_{35}Cl + C_{18}H_{34}$
H	286 + 250	$C_{18}H_{35}Cl + C_{18}H_{34}$
I	286 + 250	$C_{18}H_{35}Cl + C_{18}H_{34}$
J	250	$C_{18}H_{34}$
K	316	$C_{20}H_{41}Cl$

assessment are presented in Table VI. Much higher values were obtained after degradation as a result of incomplete elution in the direct analysis of homologues containing long polyoxyethylene chains. Similar results were obtained from both methods for the model trioxyethylene glycol monodecyl ether.

Thus, the direct analysis cannot be used to determine the average degree of ethoxylation for commercial non-ionic surfactants. In this case the surfactants must first be degraded and the average degrees of ethoxylation can be calculated from the contents of components formed by degradation of the polyoxyethylene chains.

The contents of the oxyethylene groups present in the surfactants studied and/or the average degrees of ethoxylation obtained by means of the method discussed are

TABLE IV

CONTENTS OF THE COMPONENTS FORMED BY DEGRADATION OF HYDROPHOBIC ALKYLS

Compound	Retention index		Content (%, w/w)					
	Carbowax 20M-TPA	OV-17	E-3	E-7	O-5	L-3	K-3	K-20
1-Chlorodecane	1470	1335	5.50	—	—	—	—	—
1-Chlorododecane	1684	1535	—	8.42	0.18	7.29	0.25	0.10
Dodecyl acetate	1893	a	—	0.30	—	—	—	—
1-Chlorotetradecane	1873	1755	—	—	0.20	5.52	0.20	0.15
1-Chlorohexadecane	2078	1962	—	—	0.74	3.13	1.99	0.56
1-Chloro-9-octadecene	2241	2132	—	—	0.96	—	—	—
1-Chlorooctadecane	2288	2184	—	—	0.37	1.17	6.22	0.50
1-Chloroeicosane	2480	2398	—	—	—	0.62	6.09	0.28
1-Chlorodocosane	2692	2610	—	—	—	—	0.50	—
1-Chlorotetracosane	2898	2818	—	—	—	—	0.50	—
High-boiling resins	b	b	51.42	29.70	52.56	52.06	50.65	26.07

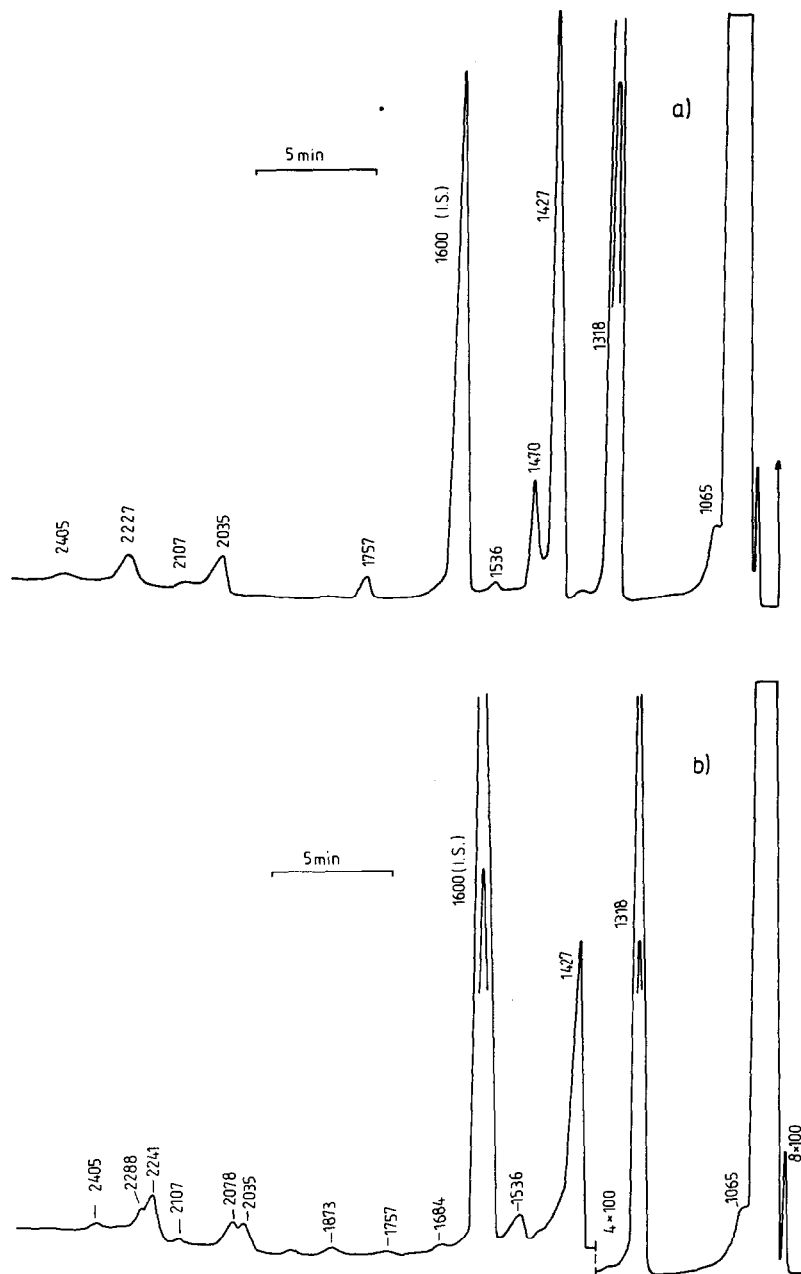[a] Not determined.

[b] Not eluted.

Fig. 4. Chromatograms of the degradation products of (a) E-3, (b) O-5 at 150°C, on column III.

somewhat lower than the values obtained according to the standard method ISO 2270-1972(E). The ratios of the contents determined by the standard method to those determined by GC after degradation are equal to 1.06, 1.04, 1.11, 1.10, 1.16 and 1.17 for E-3, E-7, O-5, L-3, K-3 and K-20, respectively. Thus, for surfactants having well
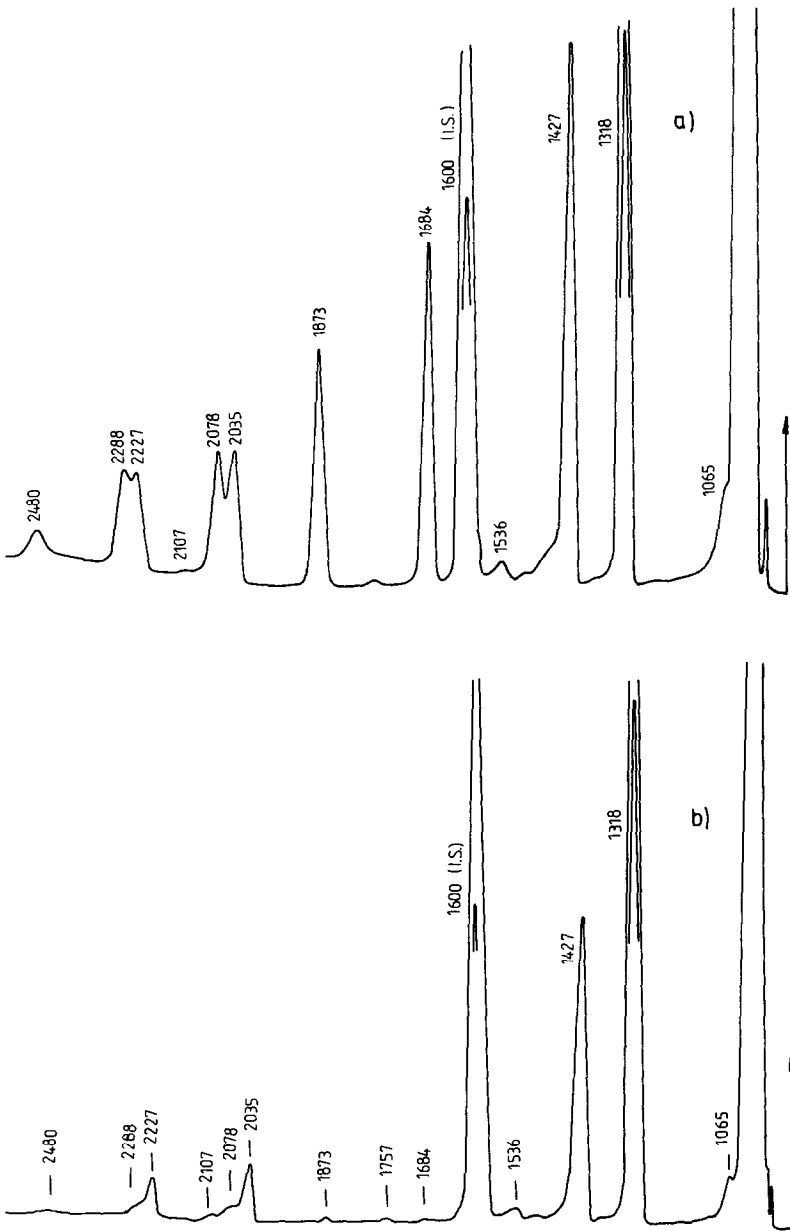
Fig. 5. Chromatograms of the degradation products of (a) Rokanol L-3, (b) Rokanol K-20 at 150°C, on column III.

defined hydrophobic constituents the differences are small but statistically significant; they are equal to 5–10%. Lower deviations are expected when the experimentally determined correlation coefficients are used.

However, in the case of preparations K-3 and K-20 having more complex

TABLE V

CONTENTS OF THE COMPONENTS FORMED BY DEGRADATION OF POLYOXYETHYLENE CHAINS

Compound	Retention index		Content (%, w/w)					
	Carbowax 20M-TPA	OV-17	E-3	E-7	O-5	L-3	K-3	K-20
1,2-Dichloroethane	1065	a	2.45	5.08	2.12	2.43	2.68	10.35
2-Chloroethyl acetate	1318	926	38.57	54.33	42.02	26.10	29.37	60.44
Bis(2-chloroethyl) ether	1536	1220	0.74	1.34	0.85	0.95	0.56	0.88
5-Chloro-3-oxapentyl acetate	1757	b	1.32	0.84	0.00	0.73	0.99	0.67

^{a} Eluted with the solvent.
^{b} Not determined.

TABLE VI

AVERAGE DEGREE OF ETHOXYLATION OF ALIPHATIC ALCOHOLS

Polyoxyethylene glycol monoalkyl ethers	Direct analysis	Analysis after degradation	Relative difference (%)
E-3	2.70 ± 0.11	2.72 ± 0.18	0.7
E-7	5.43 ± 0.23	6.78 ± 0.29	24.9
O-5	3.46 ± 0.29	4.95 ± 0.19	43.1
Rokanol L-3	1.67 ± 0.08	2.06 ± 0.20	23.3
Rokanol K-3	1.39 ± 0.02	3.00 ± 0.04	115.8
Rokanol K-20	a	15.50 ± 0.46	—

^{a} Direct analysis is impossible.

compositions of the hydrophobic part, these differences are near 20%. This is caused by the errors in the average molecular mass determination of the hydrophobic part. Thus, the use of the chromatographic technique proposed is limited to products having well defined hydrophobic constituents or to those for which the hydrophobic constituents can be identified and their contents precisely determined. The positive feature of this method is the possibility of identifying the composition, of alcohols used to prepare non-ionic surfactants. This parameter must be always taken into consideration when non-ionic surfactants are analyzed, and it cannot be determined by the traditional standard method ISO 2270-1972 (E).

CONCLUSIONS

Degradation of polyoxyethylene glycol monoalkyl ethers in the presence of anhydrous ferric chloride and an excess of acetyl chloride is complete at 150°C after 30 min. 2-Chloroethyl acetate is the main product of the polyoxyethylene chain degradation. 1,2-Dichloroethane, bis(2-chloroethyl) ether and 5-chloro-3-oxapentyl acetate are also formed but only in small amounts. 2,6-Dimethyl-γ-pyrone and its

derivatives are by-products formed from acetyl chloride and acetic acid. Hydrophobic alkyls form mainly unidentified resins.

This method of degradation can be used for commercial products, even with quite an high degree of ethoxylation. Using an internal standard method, the composition of the products obtained by degradation of polyoxyethylene chains can be determined and used to calculate the average degree of ethoxylation. The components of the hydrophobic constituents in commercial products can also be identified. However, in the case of surfactants having very complex compositions of the hydrophobic part, some significant deviation of the polyoxyethylene chain content and/or of the degree of ethoxylation can be observed.

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