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

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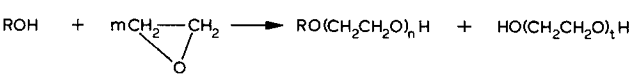
SUMMARY

Degradation of model polyoxyethylene glycol monoalkyl ethers in the presence of an excess of acetyl chloride was studied. The degradation products were identified by gas chromatography–mass spectrometry. It was found that degradation is complete at 250°C after 2 h, and this method of degradation can be used to determine the average degree of ethoxylation with high precision and accuracy. The degrees of ethoxylation determined were equal to the actual ones.

INTRODUCTION

Polyoxyethylene glycol monoalkyl ethers obtained in the reaction of different alcohols with ethylene oxide are complex polydisperse mixtures containing different homologues with increasing numbers of oxyethylene groups. Also present are polyoxyethylene glycols formed as by-products in the reaction:



The direct gas chromatographic (GC) analysis of such products is possible after converting them into trimethylsilyl, acetyl or other volatile derivatives, but only if they contain homologues having less than 16 or 17 oxyethylene groups[1].

Commercial products are obtained from mixtures of different alcohols and their compositions are usually very complex. It is usually impossible to separate all components of such commercial non-ionic surfactants. As they contain long polyoxyethylene chains or as they are obtained from commercial alcohols containing several components, the average degree of ethoxylation cannot be determined directly by GC. It is necessary to degrade the polyoxyethylene chain and to determine the contents of the different degradation products. Several methods for degradation have been employed but the results obtained were not completely satisfactory[2,3].

Fission of oxyethylene groups is usually carried out according to the procedure proposed by Siggia *et al.*[4] and adopted by the American Society for Testing and Materials and by the Commision International d'Analyse of the Comite' International des Derives Tensio-Actifs as standards D 2959-71, ANSI/ASTM D2959-74, ISO 2270-1972 (E). In this method hydroiodic acid is used and the overall reactions may be summarized as

$$R(OCH_2CH_2)_nOH \overset{HI}{\rightarrow} RI + n\, ICH_2CH_2I + (n + 1)H_2O$$

followed by

$$ICH_2CH_2I \overset{HI}{\rightarrow} I_2 + CH_3CH_2I$$

or

$$ICH_2CH_2I \rightarrow I_2 + CH_2{=}CH_2$$

The following reaction is also possible:

$$CH_2{=}CH_2 + HI \rightarrow CH_3CH_2I$$

Taking this into account, alkyl iodides and alkenes are not determined but the iodine content is estimated by titration with standard sodium thiosulphate solution. As a blank analysis is concurrently done, the content of ethylene oxide can be precisely determined with the reproducibility per individual analyst being within 1.5% of the average value.

However, as discussed by Cross[2], this method is not universal and cannot be used for the analysis of surfactants having polymeric chains of oxypropylene, either alone or as a copolymer with oxyethylene. Some problems also occur with the analysis of oxyethylated fatty amines and alkylphenols.

When an unknown product is analyzed the structure of the hydrophobe, which can be and usually is quite a complicated mixture, must also be determined. Hoyt *et al.*[5,6] proposed a complicated procedure, in which, after titration of the liberated iodine with sodium thiosulphate, the alkyl iodides were extracted from the resultant solution into hexane and separated by means of GC. Another portion of the same extract was trimethylsilanized and the overall composition of the mixture was deduced from the combined results.

However, the presence of free iodine can result in a free radical attack upon the alkyl iodide leading to its further conversion. Cross[2] suggests "to resist using the products of the oxyethylene estimation experiments for hydrophobe examination and to perform a second fission in which hypophosphorous acid has been added to reduce any iodine back to hydrogen iodide". In such a case the analysis must be done twice. We decided to look for a fission method which can be used to determine in one procedure both the content of the polyoxyethylene chain and the structure of the components forming the hydrophobic part of non-ionic surfactants.

The method of Waszeciak and Nadeau[7] was selected for further studies because it seemed to us that the reaction with acetyl chloride has potential for further development. Cross[2] came to the same conclusion: "Its simplicity, the lack of need for special glassware or lengthy heating periods, the quantitative nature, plus the fact that (in the case of oxyethylates) a single product is obtained which is amenable to flame ionization or electron capture detection all point to this technique being thoroughly worthy of further investigation".

The aim of this work is to study the degradation of some model polyoxyethylene glycol monoalkyl ethers in the presence of acetyl chloride and the application of this method to the determination of the average degree of alcohol ethoxylation.

EXPERIMENTAL

Model trioxyethylene glycol monodecyl ether (TGMDE), $C_{10}H_{21}O$-$(CH_2CH_2O)_3H$, of purity > 94% as determined by GC, and polyoxyethylene glycol monododecyl ethers (PGMDE), $C_{12}H_{25}O(CH_2CH_2O)_nH$, having an average degree of ethoxylation equal to 7, were used for degradation. Acetyl chloride, puriss. p.a. (Fluka, Buchs, Switzerland) was used as an acylation and degradation agent.

A sample (0.010–0.015 g) of polyoxyethylene glycol monoalkyl ethers was weighed into a reaction vial (Nimonic 80, Mettler Instr.) of capacity 0.5 cm^3. Acetyl chloride (200 μl) was then added and the reaction mixture was heated under pressure at 250°C for 2 h. The cooled post-reaction mixture was diluted in benzene or ethylene dichloride (1:1, v/v) and analyzed by 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, 0.4 m × 2.7 mm I.D. packed with 1% Dexsil 400 on Chromosorb G AW DMCS (80–100 mesh); II, 1.8 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 20M-TPA on Chromosorb W AW DMCS (80–100 mesh). Argon was used as the carrier gas at 30 cm^3/min. The temperature of column I was 130°C for 1 min and then raised to 360°C at 6°C/min. The temperatures of the injector and the detector were 380°C. The temperature of column II was 120°C for 4 min, and then raised to 300°C at 6°C/min. The temperatures of the injector and the detector were 300 and 320°C, respectively. The temperature of column III was 100°C for 1 min, and then raised to 220°C at 5°C/min. The temperatures of the injector and the detector were 250°C.

The average degree of ethoxylation, α in the direct analysis was calculated according to

$$\alpha = \frac{M_H \sum_{i=1}^{j} \frac{44\, n_i x_i}{M_i}}{44 \sum_{i=1}^{j} \frac{x_i M_H}{M_i}} \tag{1}$$

where M_H denotes the average molecular mass of the alcohols used to obtain the polyoxyethylene glycol monoalkyl ethers, M_i the molecular mass of the "i" homologue of the polyoxyethylene monoalkyl ethers, n_i the number of oxyethylene groups in this homologue and x_i the content of this homologue calculated from the surface areas of the separated peaks, assuming the correction factors to be 1. After degradation, α was calculated from

$$\alpha = \frac{\sum_{i=1}^{n} \frac{A_i K_i}{M_i}}{\sum_{j=1}^{m} \frac{A'_j K'_j}{M'_j}} \tag{2}$$

where M_i and M'_j denote the molecular masses of components "i" and "j" formed from the polyoxyethylene chain and hydrophobic alkyl, respectively, A_i and A'_j are the surface areas of the corresponding peaks and K_i and K'_j their correction factors, calculated according to the method of Sternberg *et al.*[8] using the concept of the effective number of carbon atoms.

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

Acetates of polyoxyethylene glycol monoalkyl ethers used in the direct analyses were obtained by esterification of their samples (0.1–0.2 g) with acetyl chloride (2 cm^3) at 50–60°C for 15 min. After cooling, hydrogen chloride, acetic acid and an excess of acetyl chloride were evaporated in a stream of dry nitrogen. Then, benzene (1 cm^3) was added and acetates were analyzed.

A thermoanalyzer TA-2 (Mettler Instr., Greifensee, Switzerland) was used. Samples (0.02–0.03 g) of polyoxyethylene glycol monododecyl ethers and of mixtures with acetyl chloride or trifluoroacetic anhydride (1:20, w/w) were placed in a platinum crucible with a perforated lid, capacity 0.5 cm^3, and heated to 500°C at a rate of 10°C/min. Argon was used as an inert gas.

RESULTS AND DISCUSSION

Fig. 1 shows the results of thermogravimetric–differential thermogravimetric analysis (TGA–DTG) of polyoxyethylene glycol monododecyl ethers (PGMDEs) and their acetates and trifluoroacetates in the presence of an excess of acetyl chloride or trifluoroacetic anhydride (1:20, w/w). Acetyl chloride promotes this degradation which commences below 200°C. At 250°C the degradation products do not contain initial homologues of PGMDE (Fig. 2). Before degradation, PGMDE contains homologues at least up to one having 17 oxyethylene units (12/17). Unreacted dodecyl alcohol (12/0) is also present. All 18 homologues of PGMDE are well separated but small peaks of polyglycols which should be eluted between the main peaks[1] are not

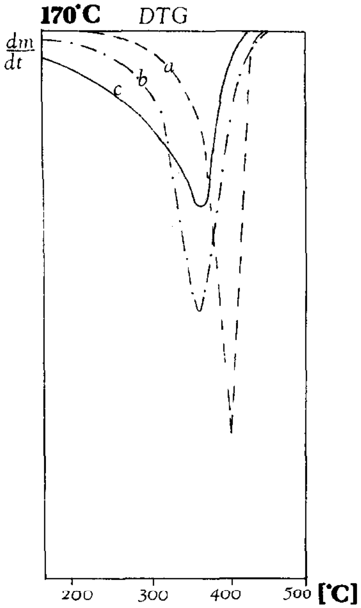


Fig. 1. Thermogravimetric analysis of the polyoxyethylene glycol monododecyl ethers: (a) PGME; (b) PGMDE–trifluoroacetic anhydride (1:20, w/w); (c) PGMDE–acetyl chloride (1:20, w/w).

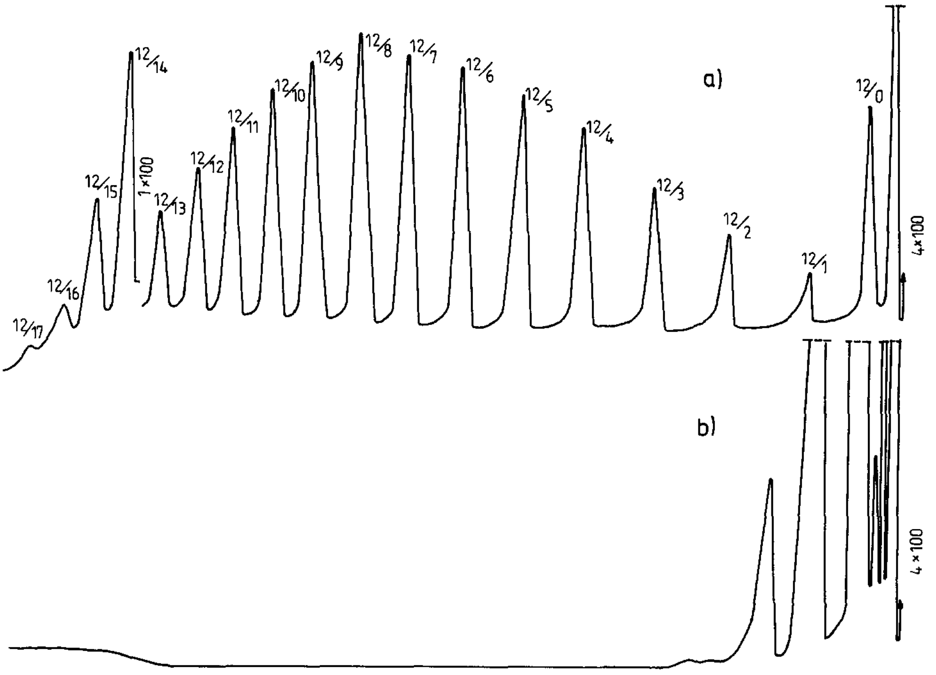


Fig. 2. Chromatogram of the polyoxyethylene glycol monododecyl ethers: (a) before degradation and (b) after degradation with acetyl chloride. Degradation conditions: 250°C; 2 h. Column I, analytical conditions as in Experimental.

observed under our chromatographic conditions. After degradation all these peaks disappear, and new ones at short retention times are observed. However these new components formed during degradation are not separated on column I in which Dexsil 400 was used as the liquid phase. A much better separation was obtained on column II packed with Chromosorb G AW DMCS impregnated with silicone resin OV-17 (sum of the first McReynolds constants, $\sum_{1}^{5} \Delta I = 884$), often used for the analysis of non-ionic surfactants having polyoxyethylene chains. However, this separation was also not complete. The best separation was achieved on column III packed with Chromosorb W AW DMCS impregnated with highly polar Carbowax 20M-TPA ($\sum_{1}^{5} \Delta I = 2318$). Thus column III was used to separate and identify degradation products by means of GC–mass spectrometry (MS).

Some degradation products are the same as those identified previously in degradation products of polyoxyethylene glycols. Their mass spectra are quite similar

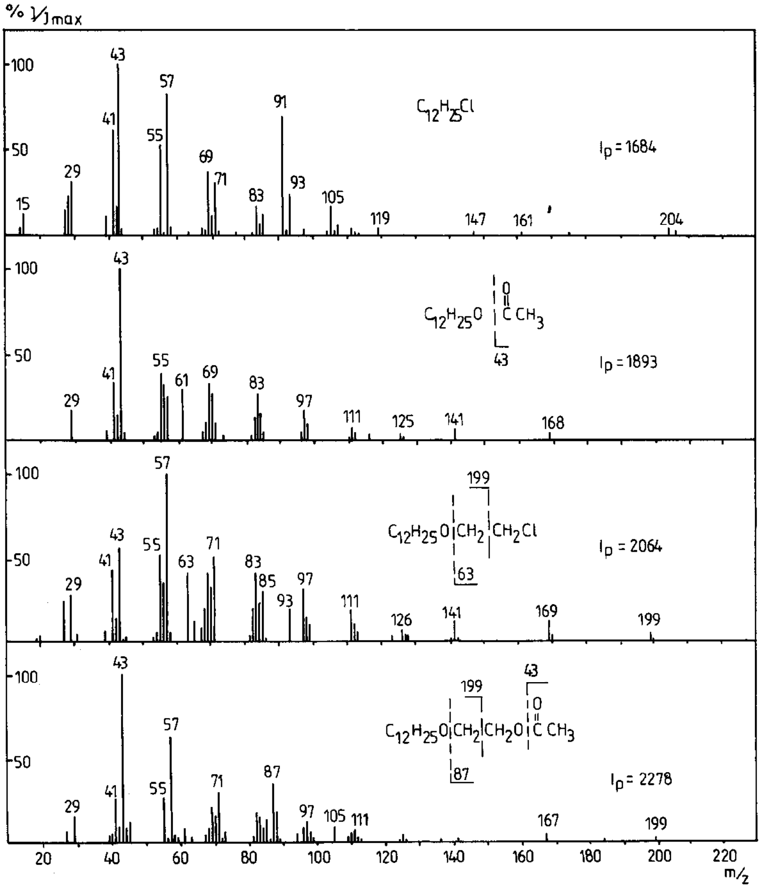


Fig. 3. Mass spectra of the separated components of the degradation products.

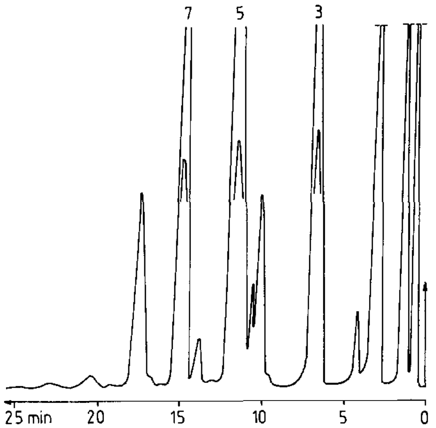


Fig. 4. Chromatogram of the polyoxyethylene glycol monododecyl ethers after degadation with acetyl chloride. Column II, analytical conditions as in Experimental. Peak identification as in Table I.

to those reported previously[9]. The highest intensity is observed at $m/z = 43$, characteristic for $[CH_3CO]^+$, formed by loss of an acetyl group. Other much lower intensity lines are observed as a result of the intramolecular splitting of the polyoxyethylene chain. Thus, the degradation of the polyoxyethylene chain in polyoxyethylene glycol monoalkyl ethers is similar to that of polyoxyethylene glycols[9]. Dodecyl chloride, cyclododecane, dodecyl acetate, 1-dodecyl-2-chloroethyl ether and 3-oxapentadecyl acetate are formed from the hydrophobic dodecyl group. The dodecyl group splits in a typical way between successive methylene groups, giving ions with molecular masses differing by 14.

The presence of chlorine atoms in some compounds is demonstrated by the characteristic ratio of isotopic line intensities. The presence of 1-chlorododecane, dodecyl acetate, cyclododecane, 1,2-dichloroethane and dioxy- and trioxyethylene

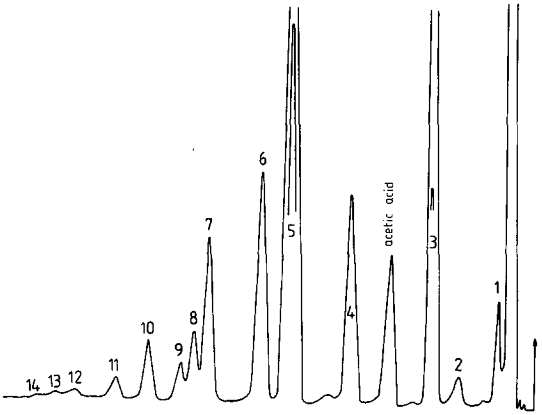


Fig. 5. Chromatogram of the polyoxyethylene glycol monododecyl ethers after degradation with acetyl chloride. Column III, analytical conditions as in Experimental. For peak identification see Table I.

TABLE I

PRODUCTS OF DEGRADATION OF THE POLYOXYETHYLENE GLYCOL MONODODECYL ETHERS ON CARBOWAX 20M-TPA

Peak	*Compound*	*Formula*	*Retention index, I*	*Correction factor*	*Content (%, w/w)*
1	1,2-Dichloroethane	$ClCH_2CH_2Cl$	1065	1.21	4.76
2	Cyclododecane	$\overline{CH_2(CH_2)_{10}CH_2}$	1236	0.35	0.82
3	2-Chloroethyl acetate	$CH_3COOCH_2CH_2Cl$	1318	1.00	38.51
4	Bis(2-chloroethyl) ether	$ClCH_2CH_2OCH_2CH_2Cl$	1536	1.11	14.70
5	1-Chlorododecane	$CH_3(CH_2)_{10}CH_2Cl$	1684	0.37	14.90
6	5-Chloro-3-oxapentyl acetate	$CH_3COOCH_2CH_2OCH_2CH_2Cl$	1757	0.98	12.11
7	Dodecyl acetate	$CH_3COOC_{12}H_{25}$	1893	0.38	3.67
8	1,8-Dichloro-3,6-dioxaoctane	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	1935	1.07	4.80
9	Dioxyethylene glycol diacetate	$CH_3COOCH_2CH_2OCH_2CH_2OOCCH_3$	1970	0.91	1.79
10	1-Dodecyl-2-chloroethyl ether	$ClCH_2CH_2OC_{12}H_{25}$	2064	0.41	1.54
11	8-Chloro-3,6-dioxaoctyl acetate	$CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	2157	0.98	1.40
12	3-Oxapentadecyl acetate	$CH_3COOCH_2CH_2OC_{12}H_{25}$	2278	0.42	0.30
13	1,12-Dichloro-3,6,9-trioxaundecane	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	2330	1.04	0.54
14	Trioxyethylene glycol diacetate	$CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2OOCCH_3$	2375	0.92	0.16

TABLE II

PRODUCTS OF DEGRADATION OF TRIOXYETHYLENE GLYCOL MONODECYL ETHER ON CARBOWAX 20M-TPA

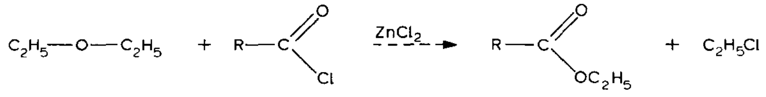
Compound	*Formula*	*Retention index, I*	*Correction factor*	*Content (%, w/w)*
Cyclodecane	$\overline{CH_2(CH_2)_8CH_2}$	1076	0.30	5.81
2-Chloroethyl acetate	$CH_3COOCH_2CH_2Cl$	1318	1.00	51.03
1-Chlorodecane	$CH_3(CH_2)_8CH_2Cl$	1470	0.38	19.24
Bis(2-chloroethyl) ether	$ClCH_2CH_2OCH_2CH_2Cl$	1536	1.11	6.53
Decyl acetate	$CH_3COOC_{10}H_{21}$	1684	0.40	6.40
5-Chloro-3-oxapentyl acetate	$CH_3COOCH_2CH_2OCH_2CH_2Cl$	1757	0.98	6.61
1-Decyl-2-chloroethyl ether	$ClCH_2CH_2OC_{10}H_{21}$	1838	0.44	2.78
1,8-Dichloro-3,6-dioxaoctane	$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	1935	1.07	0.42
Dioxaethylene glycol diacetate	$CH_3COOCH_2CH_2OCH_2CH_2OOCCH_3$	1970	0.91	0.38
3-Oxatridecyl acetate	$CH_3COOCH_2CH_2OC_{10}H_{21}$	2068	0.45	0.38
8-Chloro-3,6-dioxaoctyl acetate	$CH_3COOCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$	2157	0.98	0.42

glycol diacetates was also supported by comparison with the retention times of these compounds.

The mass spectra of the components separated are presented in Fig. 3. Those reported in our previous work[9] and obtained from the polyoxyethylene chain are omitted. Their formulae, retention indices, correction factors and contents are given in Table I. The numbers of the compounds given are the same as in the chromatograms in Figs. 4 and 5.

Quite similar degradation was observed when the model trioxyethylene glycol monodecyl ether (TGMDE), $H(OCH_2CH_2)_3OC_{10}H_{21}$, was used. Similar components were identified in the degradation products and their formulae and contents are given in Table II.

The results obtained demonstrate that the degradation of polyoxyethylene glycol monoalkyl ethers in the presence of an excess of acetyl chloride is complete at 250°C after 2 h. 2-Chloroethyl acetate formed from the polyoxyethylene chain and alkyl chloride obtained from the hydrophobic alkyl are the main products. Thus, the degradation proceeds in agreement with the Underwood reaction[10]:



Acetic acid is formed from acetyl chloride and can be neglected.

The most significant drawback of this degradation is the number of compounds formed. Several components must be identified and their contents determined taking

TABLE III

AVERAGE DEGREE OF ETHOXYLATION OF POLYOXYETHYLENE GLYCOL MONOALKYL ETHERS

Ether	*Parameter*	*Direct analysis*	*After degradation*	
			Internal standardization method eqn. 2	*Internal standard method*
TGMED	Ethoxylation	2.69	3.06	2.89
	degree	2.75	2.91	2.88
	(individual results)	2.58	2.96	3.00
		2.69	3.13	2.79
		2.78	3.16	2.87
	Average	2.70	3.04	2.89
	Standard deviation, s_r	0.0284	0.0353	0.0260
	Confidence limits ($\alpha = 0.05$)	±0.10	±0.15	±0.10
PGMDE	Ethoxylation degree	5.70	7.20	6.30
	(individual results)	5.32	6.90	6.54
		5.28	7.07	6.30
		5.45	6.80	6.53
		5.41	7.05	6.76
	Average	5.43	7.00	6.49
	Standard deviation, s_r	0.0303	0.0223	0.0298
	Confidence limits ($\alpha = 0.05$)	±0.23	±0.22	±0.27

into account their correction factors, which can influence the precision and accuracy of the qualitative analysis.

Average degrees of ethoxylation determined by the direct analysis of polyoxyethylene glycol monoalkyl ethers and after their degradation, together with a statistical assessment of the results obtained, are given in Table III. The precision of the measurements is good and similar for both products considered and for both methods of analysis. However, the accuracy of the two methods is different. Higher ethoxylation degrees were obtained after degradation, even for trioxyethylene glycol monodecyl ether. In the case of polyoxyethylene glycol monododecyl ethers having an average degree of ethoxylation of 7, calculated from the amount of ethylene oxide used for the synthesis, the direct analysis gives a value of 5.43, about 22% lower than the actual one. This means that some homologues of PGDME having long polyoxyethylene chains are not completely eluted from the column during chromatographic analysis. For products having average ethoxylation degrees higher than 7 this diifference would be even more significant.

A very good agreement is observed between the ethoxylation degree determined after degradation by the method of internal standardization using eqn. 2 and the actual ones calculated from the masses of reagents used during the syntheses of polyoxyethylene glycol monoalkyl ethers, *i.e.*, 3.04 and 3.0 for TGMDE and 7.00 and 7.0 for PGMDE, respectively. This demonstates the complete degradation of polyoxyethylene glycol monoalkyl ethers and complete elution of all degradation products from the chromatographic column. Thus, the degradation of polyoxyethylene glycol monoalkyl ethers in the presence of an excess of acetyl choride can be used to determine the average degree of ethoxylation with high precision and accuracy. The values determined using an internal standard (last column of Table III) are somewhat lower, *i.e.*, *ca.* 3.7 and 7.3% for TGMDE and PGMDE, respectively.

CONCLUSIONS

Degradation of polyoxyethylene glycol monoalkyl ethers in the presence of an excess of acetyl chloride is complete at 250°C after 2 h. 2-Chloroethyl acetate formed from the polyoxyethylene chain and alkyl chloride obtained from the hydrophobic alkyl are the main products. This degradation can be used to determine the average degree of ethoxylation with high precision and accuracy. The values obtained by means of the internal standardization are strictly the same as the actual ones. This confirms the complete degradation of polyoxyethylene glycol monoalkyl ethers and complete elution of all degradation products from the chromatographic column.

The most significant drawback of the degradation of polyoxyethylene glycol monoalkyl ethers in the presence of acetyl chloride is the number of compounds formed. They must all be identified and their contents quantitated. However, GC–MS need not be used because the polyoxyethelene chains are degraded to the same products which can be identified from their retention indices.

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