

## Degradation and analysis of commercial polyoxyethylene glycol mono(4-alkylphenyl) ethers

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### ABSTRACT

Commercial polyoxyethylene glycol mono(4-alkylphenyl) ethers having different degrees of ethoxylation were degraded in the presence of acetyl chloride and anhydrous iron(III) chloride. Compounds formed from polyoxyethylene chains can be easily and precisely determined and their contents can be used to calculate the average degree of ethoxylation.

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### INTRODUCTION

In a previous study<sup>1</sup>, the degradation of model oligooxyethylene glycol mono(4-alkylphenyl) ethers was investigated and used to determine the average degree of alkylphenol ethoxylation. Good agreement between the average degrees of ethoxylation determined by means of degradation and by direct analysis was observed.

The composition of commercial products is usually much more complex than that studied previously<sup>1</sup>. In most instances nonylphenol is used as one reagent and contains several components, including different types of compounds and different isomers of the nonyl group. Up to now, their structures have not been determined. The average degree of ethoxylation is usually higher than that considered in our previous work<sup>1</sup>. Depending on the value of this average degree of ethoxylation, direct analysis gives results that more or less deviate from the actual values or it may even be impossible to analyse such products.

The aim of this work was to study the degradation of commercial polyoxyethylene glycol mono(4-alkylphenyl) ethers in the presence of an excess of acetyl chloride and anhydrous iron(III) chloride<sup>2</sup> and the application of this degradation to determine the average degree of alkylphenol ethoxylation.

## EXPERIMENTAL

The commercial polyoxyethylene glycol mono(4-alkylphenyl) ethers used were Rokafenol N-5 (NZPO "Rokita", Brzeg Dolny, Poland) and Lutensol AP-4, Lutensol AP-9 and Lutensol AP-14 (BASF, Ludwigshafen, F.R.G.). Analytical-reagent grade acetyl chloride (Fluka, Buchs, Switzerland) and anhydrous iron(III) chloride (POCh, Gliwice, Poland) were also used.

The degradation and chromatographic analyses were carried out according to the methods described previously<sup>1</sup>.

Chromatographic columns (0.9 m × 2.7 mm I.D.) filled with silicone resin OV-101 (3%) on Chromosorb G AW DMCS (60–80 mesh) were used for the direct analysis of commercial polyoxyethylene glycol mono(4-alkylphenyl) ethers. The temperature of these columns was 100°C for 1 min, then raised to 320°C at 8°C/min. Chromatographic columns (0.9 m × 2.7 mm I.D. and 1.6 m × 2.7 mm I.D.) filled with silicone resin OV-17 (3%) on Chromosorb G AW DMCS (60–80 mesh) and with Carbowax 20M-TPA (terminated with terephthalic acid) (12%) on Chromosorb W AW DMCS (80–100 mesh), were used for the analyses of degradation products. Their temperatures were 80°C and 100°C for 1 min, then raised to 290°C and 220°C at 6°C/min and 5°C/min, respectively.

The average degree of ethoxylation and the degree of degradation were calculated in the same way as for oligooxyethylene glycol mono(4-*tert*.-octylphenyl) ethers<sup>1</sup>.

## RESULTS AND DISCUSSION

Chromatograms of Lutensol AP-4, Rokafenol N-5 and Lutensol AP-9 are given in Figs. 1–3. They were separated as broad peaks according to the increased numbers of oxyethylene groups. Their compositions and retention indices are given in Table I. Separation was good but only up to the homologue containing ten oxyethylene units.

TABLE I

## RETENTION INDICES AND CONTENTS OF SUCCESSIVE HOMOLOGUES

Silicone resin OV-101.

No. of oxyethylene groups	Retention index, $I_p$	Content (wt.-%)		
		Lutensol AP-4	Rokafenol N-5	Lutensol AP-9
0	1668–1737	0.14	1.03	0.95
1	1929–2067	2.10	6.85	1.31
2	2170–2284	15.56	17.66	1.85
3	2416–2540	26.52	22.66	5.46
4	2680–2789	25.93	20.51	11.98
5	2909–3027	17.48	14.60	18.18
6	3153–3258	8.78	9.64	21.09
7	3371	2.68	5.13	19.68
8	3640	0.32	1.57	14.14
9	3881	—	0.20	4.78
10	4135	—	0.15	0.58

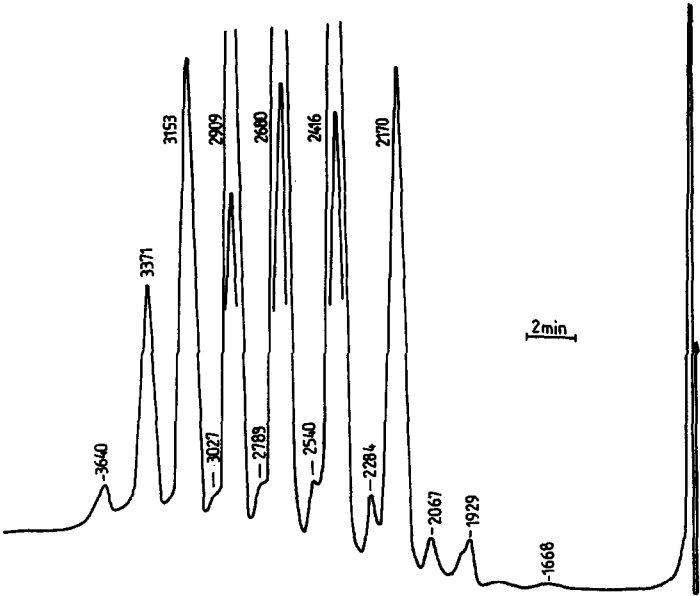


Fig. 1. Chromatogram of Lutensol AP-4 (acetate derivatives, OV-101). Numbers at peaks are retention indices.

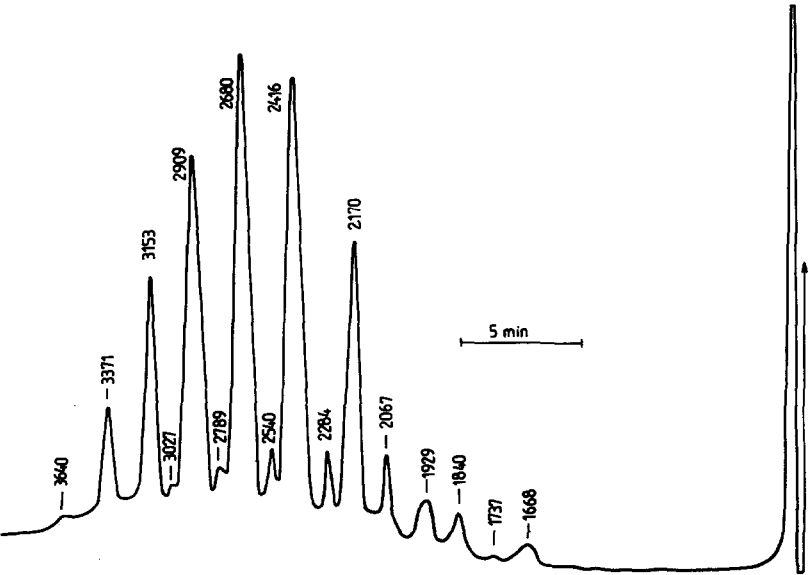


Fig. 2. Chromatogram of Rokafenol N-5 (acetate derivatives, OV-101).

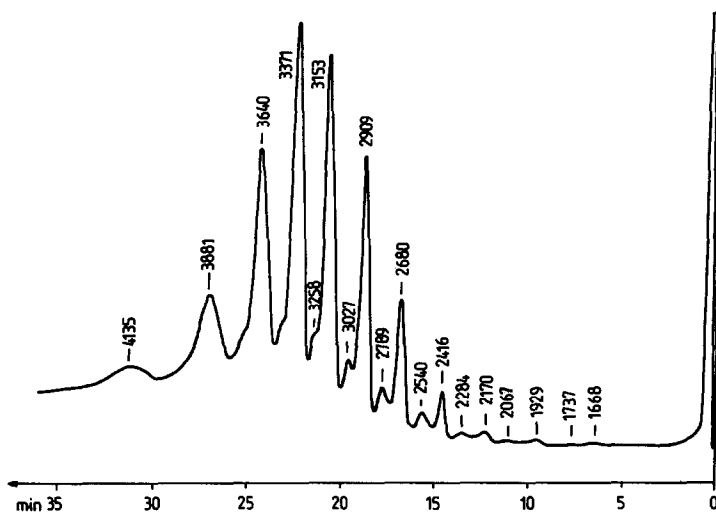


Fig. 3. Chromatogram of Lutensol AP-9 (acetate derivatives, OV-101).

Lutensol AP-14 contains higher homologues than those present in previous preparations and it elutes from the column only to the extent of about 2%, hence it was impossible to analyse it directly). Its degradation was complete at 150°C after 30 min (Fig. 4). Under these conditions the degradation of other commercial preparations investigated was also complete and the peaks of the initial components were not observed on the chromatograms. The chromatograms of the degradation products of Lutensol AP-9 shown in Figs. 5 and 6 demonstrate the completeness of degradation and the similarity of the degradation products to those identified previously<sup>1</sup>.

2-Chloroethyl acetate ( $I_p = 1318$  on Carbowax 20M-TPA) is the main product formed by the degradation of the polyoxyethylene chains. 1,2-Dichloroethane ( $I_p =$

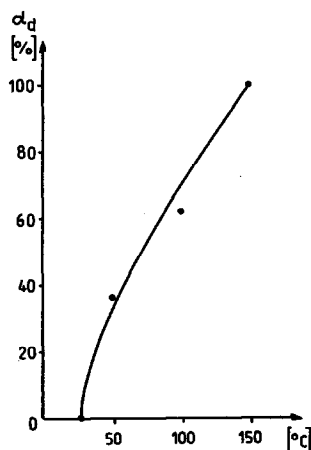


Fig. 4. Effect of temperature on degree of degradation ( $\alpha_d$ ) of Lutensol AP-14 (30 min).

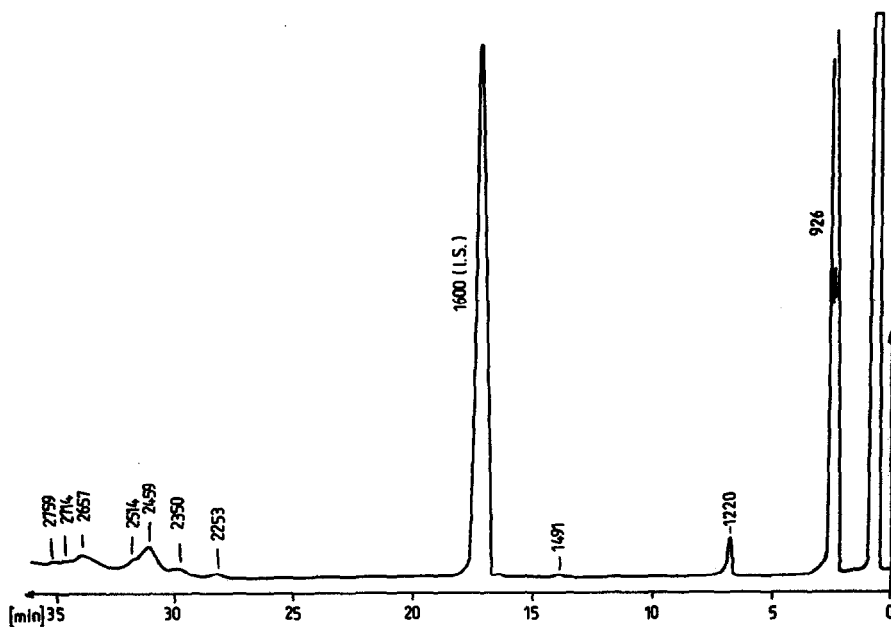


Fig. 5. Chromatogram of the degradation products formed from Lutensol AP-9 (silicone resin OV-17). I.S. = Internal standard.

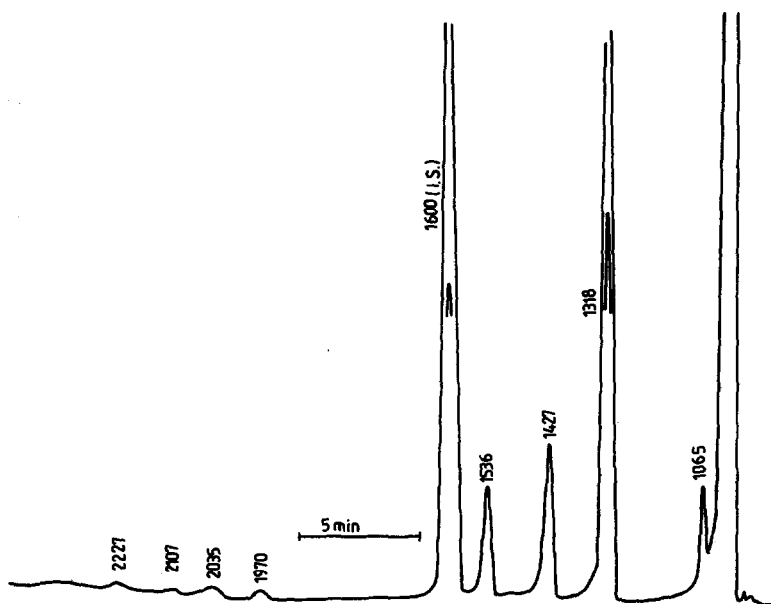


Fig. 6. Chromatogram of the degradation products formed from Lutensol AP-9 (Carbowax 20M-TPA).

TABLE II  
COMPOSITION OF DEGRADATION PRODUCTS

Type of compound <sup>a</sup>	Component	Retention index		Content (wt.-%)			
		Carbowax 20M-TPA	OV-17	Lutensol AP-4	Rokafenol N-5	Lutensol AP-9	Lutensol AP-14
I	1,2-Dichloroethane	1065	745	2.33	1.08	7.05	2.83
	2-Chloroethyl acetate	1318	926	34.69	33.61	43.32	64.30
	Bis(2-chloroethyl) ether	1536	1220	4.96	4.48	7.83	1.41
	Dioxyethylene glycol diacetate	1970	1491	0.21	2.67	—	2.12
II	Volatile components	—	2253–2759	4.38	2.98	2.43	2.46
	High-boiling resins	—	—	53.43	55.18	42.97	26.88

<sup>a</sup> I and II denote components obtained from polyoxyethylene chains and alkylphenyl groups, respectively.

1065), bis(2-chloroethyl) ether ( $I_p = 1536$ ) and dioxyethylene ( $I_p = 1970$ ) are formed in small amounts. Acetic acid ( $I_p = 1427$ ) is formed from acetyl chloride and  $\gamma$ -pyrone derivatives ( $I_p = 2035, 2107$  and  $2227$ ) are formed from acetic acid, as discussed previously<sup>3</sup>.

Alkylphenyl groups form mainly unidentified high-molecular-mass resins and only small amounts of low-molecular-mass compounds are formed which elute from the chromatographic column ( $I_p = 2253, 2350, 2459, 2514, 2657, 2714$  and  $2759$  on silicone resin OV-17). Their mass spectra are not specific enough to identify them, as a result of their different and branched alkyl groups. Their contents cannot be determined and the average degree of ethoxylation can be calculated only from the contents of products formed by the degradation of the polyoxyethylene chains and the mass of the starting sample, assuming the appropriate average molar mass for a hydrophobic alkylphenyl group.

The contents of the separated components are given in Table II and the average degrees of alkylphenol ethoxylation obtained are presented in Table III. The values obtained by direct analysis are significantly lower than those obtained by degradation. These differences depend on the average degree of ethoxylation, and increase as the latter increases. They are not caused by the presence of polyoxyethylene glycols, the content of which is below 1%. For Rokafenol N-5 and Lutensol AP-9 these differences are about 10 and 24%, respectively. For Lutensol AP-14 the average degree of ethoxylation could be only determined by means of degradation.

## CONCLUSIONS

Commercial polyoxyethylene glycol mono(4-alkylphenyl) ethers containing several different components can be easily degraded in the presence of an excess of acetyl chloride and anhydrous iron(III) chloride. Compounds obtained by the degradation of the polyoxyethylene chains can be easily identified and their contents can be precisely determined. These values can be further used to calculate the average degree of alkylphenol ethoxylation.

TABLE III  
AVERAGE DEGREE OF ALKYLPHENOL ETHOXYLATION

*A* and *B* denote values obtained by direct analysis and by means of degradation, respectively.

Parameter	Lutensol AP-4		Rokafenol N-5		Lutensol AP-9		Lutensol AP-14	
	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>	<i>A</i> <sup>a</sup>	<i>B</i>
Degree of ethoxylation (individual results)	3.73 3.48 3.65 3.41 3.41 3.54	3.96 3.47 3.50 3.47 3.89 3.65	3.37 3.33 3.18 3.33 3.18 3.28	3.53 3.37 3.44 3.67 3.99 3.60	6.25 5.41 5.32 5.41 5.34 5.55	7.45 6.70 6.79 6.90 6.59 6.88		12.12 11.87 11.90 12.16 12.25 12.05
Average								
Standard deviation	0.14622	0.24530	0.09094	0.24515	0.3564	0.33531		0.16288
Confidence limits ( $\alpha = 0.05$ )	$\pm 0.20$	$\pm 0.34$	$\pm 0.13$	$\pm 0.34$	$\pm 0.55$	$\pm 0.47$		$\pm 0.23$
Average differences:								
$B - A$	0.11		0.32		1.33			—
$\frac{B - A}{A} \cdot 100(\%)$	3.10		9.76		23.96			—

<sup>a</sup> Determination impossible.

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