

Quantitative Analysis of Polyethylene Glycol Monododecyl Ethers by Gas Chromatography after Silylation *

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Oxyethylation mixtures obtained from the alkali-catalyzed reaction of dodecanol with ethylene oxide, have been analysed by gas chromatography after silylation. Small differences in composition were observed between adduct mixtures obtained from KOH- and NaOH-catalyzed oxyethylations. Comparison of the results with the Weibull-Nycander theory indicates that differences in reactivity exist, not only between dodecanol and oxyethylated components, but also between the oxyethylated components themselves.

The distribution of compounds formed in the reaction between ethylene oxide and long-chain alcohols has been widely studied.¹ It has been generally accepted that the distribution can be approximately described by the equations derived by Weibull and Nycander.² These are based on the assumption that in the series of consecutive reactions all steps except the first one proceed with the same rate.

Gas chromatography after silylation has proved to be a useful technique for the analysis of oxyethylation mixtures.^{3,4} Results obtained from the application of this method to the quantitative analysis of polyethylene glycol monododecyl ethers are now presented.

EXPERIMENTAL

Materials. Reference substances were obtained from Dr. S. Schüring.⁵ Their purity was estimated by gas chromatography after silylation, the lower members being 99 % pure, the higher ethers 94-95 % pure, contaminated by only small amounts of lower members. The purity of dodecanol-1 and hexadecanol-1 used in the investigation was >99 % and >98 %, respectively. Trimethylchlorosilane and hexamethyldisilazane were obtained from Dow Corning Corp. and distilled before use. Ethylene oxide from Mo och Domsjö Aktiebolag was used without further purification.

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Silylation technique and gas chromatography. The method has been described earlier.⁴ Column temperature was programmed with a gradient of 10°C/min from a starting temperature of 100°C. The relative retention data, given in Table 1, are based on 8–10 measurements for each compound, except for the pentadecaethylene glycol ether derivate, whose retention was determined by 5 measurements.

Table 1. Relative retention data.

Compound ^a <i>n</i>	Relative retention ^b	Standard deviation
0	0.43	0.011
1	0.81	0.004
2	1.18	0.004
3	1.51	0.007
4	1.80	0.010
5	2.06	0.013
6	2.30	0.017
7	2.53	0.018
8	2.74	0.022
9	2.93	0.025
10	3.12	0.028
11	3.29	0.032
12	3.45	0.030
13	3.60	0.040
14	3.76	0.038
15	3.91	0.033
Standard ^b	1.00	0.013

^a C₁₂H₂₅O(CH₂CH₂O)_{*n*}Si(CH₃)₃.

^b C₁₆H₃₃OSi(CH₃)₃; 6.32 min.

Quantitative analysis. Peak areas were calculated as before.⁴ Equations of linear regression for the substances to be analysed were determined using the method given by Salminen and Koivistoinen.⁶ The determinations were based on 9 measurements for each compound in mixtures of known composition which were corrected for any impurities

Table 2. Calibration lines.

Compound ^a <i>n</i>	Equation of calibration line ^b	Square of correlation coefficient	Std. error of estimate	Validity range
0	$y = 0.008 + 0.905 x$	0.998	0.034	0.3 < <i>x</i> < 2.5
1	$y = -0.005 + 0.839 x$	0.994	0.043	0.4 < <i>x</i> < 2.0
2	$y = -0.056 + 0.830 x$	0.994	0.025	0.5 < <i>x</i> < 1.5
3	$y = 0.009 + 0.740 x$	0.953	0.034	0.9 < <i>x</i> < 1.4
4	$(y = -0.019 + 0.720 x)$	—	—	—
5	$y = -0.047 + 0.700 x$	0.992	0.024	0.5 < <i>x</i> < 1.3
6	$y = -0.063 + 0.764 x$	0.992	0.030	0.3 < <i>x</i> < 1.5
7	$(y = -0.067 + 0.735 x)$	—	—	—
8	$y = -0.071 + 0.705 x$	0.978	0.043	0.2 < <i>x</i> < 1.3
9	$(y = -0.080 + 0.709 x)$	—	—	—
10	$y = -0.089 + 0.712 x$	0.994	0.018	0.1 < <i>x</i> < 0.7

^a C₁₂H₂₅O(CH₂CH₂O)_{*n*}Si(CH₃)₃.

^b $y = A/A_s$ (relative area); $x = W/W_s$ (relative composition).

in the reference substances. The internal standard (10–15 % hexadecanol-1) was added to the mixtures before silylation. Table 2 shows the calibration equations obtained for the different polyethylene glycol ether derivatives. Equations within brackets were obtained by interpolation (due to lack of reference substance). The calibration equations were used in the analysis of unknown samples. The equation for $n=10$ was used also for components with more than 10 ethylenoxy groups. Two independent analyses were carried out for each oxyethylation sample investigated. The amount of internal standard was 5–10 %.

Oxyethylation of dodecanol. The preparation of ethylene oxide adducts with different average molecular weight was carried out in a 2 l steel autoclave at 130–140°C and 3 atm.⁴ Sodium hydroxide or potassium hydroxide was used as a catalyst. The catalyst was neutralized with acetic acid after the reaction and any polyethylene glycol formed as a by-product removed by extraction.⁷ The average molecular weight of the adducts was calculated from hydroxyl group determinations.⁸ Experimental details of the oxyethylations are given in Table 3.

Table 3. Preparation of polyethylene glycol ethers.

Expt. No.	Dodecanol <i>g</i>	Ethylene oxide <i>g</i>	Catalyst ^a	Molecular weight ^b
1	100	51.8	0.5 % KOH	295
2	100	99.0	0.5 % KOH	372
3	100	146.5	0.5 % KOH	446
4	102.5	69.5	0.1 % KOH	322
5	102.5	68.5	0.05 % KOH	319
6	102.5	75.5	0.05 % NaOH	348
7	102.5	72.4	0.1 % NaOH	326
8	102.5	71.0	0.5 % NaOH	334

^a Initial concentration in weight percent of dodecanol charged.

^b As found by hydroxyl group determinations.

*Calculation of the theoretical molecular weight distribution.** Theoretical compositions were calculated from the Weibull-Nycander equations using their notations.² Thus, n_{00} represents moles of dodecanol initially present, n_i is the number of moles in the reaction mixture of a component having i ethylenoxy units, and v is the average molar ratio of ethylene oxide to starting material. The value v was calculated from the average molecular weight as found by end group determinations. Usually the value of the distribution constant was chosen as $c=2.5$.

RESULTS AND DISCUSSION

Polyethylene glycol monododecyl ethers studied in this work have average molecular weights in the range of 300–500. As an example of the excellent separations obtained, the gas chromatogram in Fig. 1 shows the individual components present in an adduct with an average molecular weight of 450. The corresponding relative retentions are given in Table 1.

* The calculations were greatly facilitated by the use of a small desk computer (Olivetti Programma 101). The program was made by Dr. B. Weibull at Mo och Domsjö Aktiebolag and somewhat modified by Civ.-ing. J. Johansson in this laboratory.

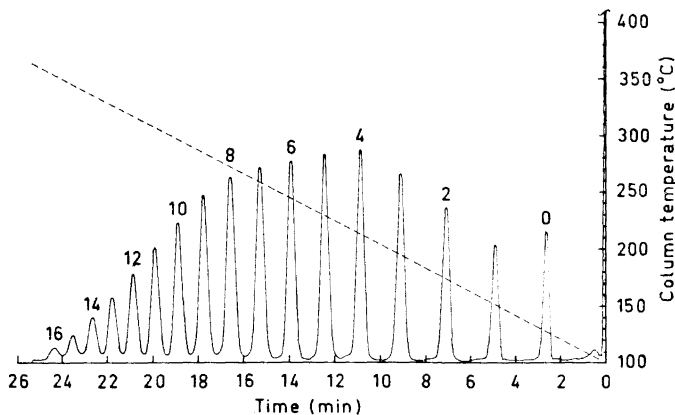


Fig. 1. Gas chromatogram of silylated polyethylene glycol monododecyl ether with an average molecular weight of 450 (Expt. No. 3). The figures represent the number of ethylenoxy units in the glycol ethers.

Calibration of the detector signal for the components present resulted in the calibration lines shown in Table 2. It is obvious that the relative area decreases somewhat with increasing polyether chain length, which was also the case in the series of silylated polyethylene glycols.⁴ It should be observed that the calibration lines given in Table 2 are strictly valid only within the relative concentration range indicated. Hence, the amount of internal standard used in the analysis of the oxyethylation mixtures had to be chosen within this range. Due to the presence of many components in a wide concentration range, the mixtures were generally analysed both with 5 % and 10 % internal standard present. Using this technique, the analytical figures obtained are believed to be correct within a few percent of the true value, except for components present in very small concentrations.

The various monododecyl ethers of polyethylene glycols were prepared from dodecanol and ethylene oxide, using potassium hydroxide or sodium hydroxide as a catalyst (Table 3). Their compositions were determined by duplicate analyses and compared with what could be expected from the Weibull-Nycander theory.

Table 4 shows that the average molecular weight of the adducts — as calculated from the observed compositions — agrees very well with the value found by end-group determinations (*cf.* Table 3). Comparison of the results from Expt. Nos. 4 and 5 and from Expt. Nos. 7 and 8 shows that the composition is independent of the catalyst concentration in the range investigated.

However, there is a small but significant difference in composition between adducts prepared with potassium hydroxide and sodium hydroxide as a catalyst. Fig. 2 shows the compositions of two ethylene oxide adducts with practically the same average molecular weight. The figure confirms Tischbirek's observation,⁹ that the amount of unreacted alcohol is lower when potassium hydroxide is used rather than sodium hydroxide. (For reason of clarity,

Table 4. Comparison of the observed molecular weight distribution (n_i/n_{00}) with the Weibull-Nylander theory ($c=2.5$).

Expt. No.	1 $v=2.46$		2 $v=4.22$		3 $v=5.90$		4 $v=3.08$		5 $v=3.00$		6 $v=3.67$		7 $v=3.17$		8 $v=3.34$	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
0	0.236	0.280	0.108	0.157	0.054	0.072	0.178	0.199	0.185	0.225	0.137	0.204	0.171	0.229	0.159	0.222
1	0.140	0.185	0.070	0.129	0.035	0.067	0.110	0.151	0.113	0.157	0.087	0.136	0.106	0.151	0.099	0.147
2	0.167	0.160	0.102	0.148	0.056	0.086	0.145	0.155	0.148	0.155	0.122	0.128	0.141	0.142	0.134	0.141
3	0.161	0.116	0.130	0.140	0.081	0.106	0.158	0.133	0.159	0.132	0.145	0.109	0.156	0.119	0.153	0.126
4	0.127	0.077	0.143	0.121	0.106	0.111	0.144	0.103	0.142	0.102	0.147	0.089	0.145	0.096	0.147	0.106
5	0.083	0.054	0.136	0.096	0.123	0.109	0.111	0.076	0.108	0.074	0.128	0.071	0.114	0.073	0.120	0.083
6	0.047	0.032	0.113	0.069	0.128	0.089	0.074	0.049	0.070	0.045	0.096	0.052	0.077	0.052	0.084	0.060
7	0.023	0.022	0.082	0.051	0.119	0.079	0.043	0.036	0.040	0.034	0.064	0.042	0.046	0.040	0.052	0.048
8	0.010	0.017	0.054	0.039	0.099	0.068	0.022	0.026	0.020	0.025	0.037	0.034	0.024	0.031	0.028	0.036
9	0.004	0.012	0.032	0.026	0.075	0.053	0.010	0.019	0.009	0.018	0.020	0.026	0.011	0.022	0.014	0.026
10	0.001	0.010	0.017	0.018	0.052	0.040	0.004	0.014	0.004	0.014	0.010	0.019	0.005	0.016	0.006	0.018
11	0.000	0.008	0.008	0.013	0.033	0.029	0.002	0.011	0.001	0.011	0.004	0.014	0.002	0.012	0.003	0.013
12		0.007	0.004	0.009	0.020	0.020	0.001	0.008	0.001	0.008	0.002	0.011	0.001	0.009	0.001	0.009
13		0.006	0.002	0.007	0.011	0.013	0.000	0.007	0.000	0.006	0.001	0.008	0.000	0.007	0.000	0.007
14		0.003	0.001	0.006	0.005	0.010	0.005	0.005	0.005	0.005	0.000	0.006	0.000	0.005	0.000	0.005
15			0.000	0.002	0.003	0.007	0.001	0.006	0.001	0.004	0.000	0.005	0.000	0.002	0.000	0.005
16					0.001	0.006	0.001	0.006	0.001	0.004		0.002		0.002		0.002
17					0.001											
18					0.000											
$\sum n_i/n_{00}$	0.999	0.989	1.002	1.031	1.002	0.965	1.002	0.997	1.000	1.015	1.000	0.956	0.999	1.006	1.000	1.047
Mol. weight		298		361		461		323		314		365		324		321

the distributions in this and the following figure are represented as continuous curves rather than block diagrams).

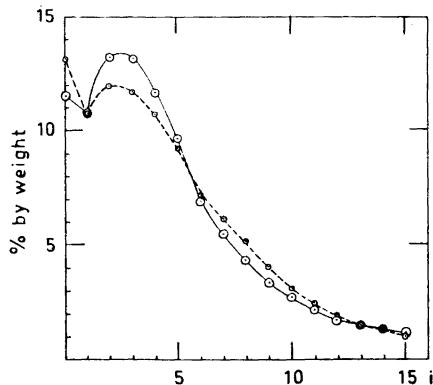


Fig. 2. The composition of two ethylene oxide adducts with an average molecular weight of 325. Solid curve: 0.1 % KOH used as a catalyst (Expt. No. 4). Dashed curve: 0.1 % NaOH (Expt. No. 7).

From Table 4 it is obvious that the observed compositions differ significantly from those expected from the Weibull-Nycander theory. The theoretical values in Table 4 were calculated using a value of the distribution constant $c=2.5$. From Fig. 3 it is seen that changing the distribution constant to $c=3.0$ gives a value for the amount of unreacted alcohol closer to the observed figure, but no better fit of the other values is obtained. Indeed it is not possible to describe the complete observed distribution accurately with the theory, even if the distribution constant is varied over a wide range (Table 5).

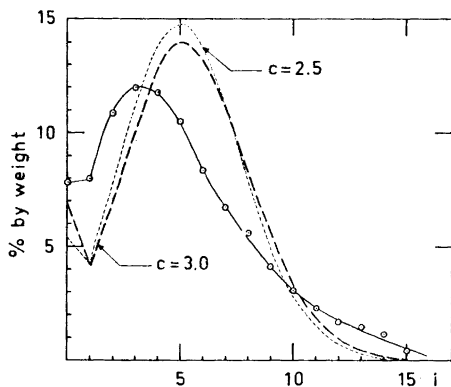


Fig. 3. Molecular weight distribution of an ethylene oxide adduct with an average molecular weight of 370 (Expt. No. 2). Dashed curves represent the corresponding Weibull-Nycander composition for two different distribution constants.

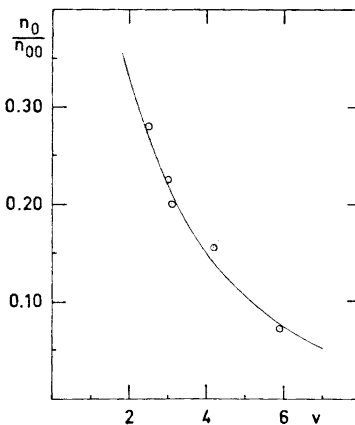


Fig. 4. Mole fraction (n_0/n_{00}) of unreacted dodecanol as a function of molar ratio v in the series of adducts obtained by KOH-catalyzed oxyethylation. The circled points represent observed values, whereas the curve was calculated from the Weibull-Nycander equation for $c=3.0$.

Table 5. Comparison of observed with calculated compositions using different distribution constants.

Glycol ether ^a <i>n</i>	Composition, % by weight					
	Expt. No. 5	Theoretical for $v=3.00$ ^b				
		$c=1.5$	$c=2.0$	$c=2.5$	$c=3.0$	$c=3.5$
0	13.2	5.9	8.5	10.8	12.8	14.5
1	11.4	9.9	9.0	8.2	7.5	7.0
2	13.3	16.5	14.4	12.7	11.4	10.3
3	13.2	19.8	17.7	15.9	14.4	13.2
4	11.6	18.2	17.2	16.2	15.2	14.3
5	9.4	13.5	13.8	13.8	13.5	13.2
6	6.4	8.4	9.3	9.9	10.4	10.6
7	5.3	4.4	5.4	6.2	6.9	7.4
8	4.3	2.0	2.7	3.4	4.1	4.6
9	3.3	0.8	1.3	1.7	2.1	2.6
10	2.7	0.3	0.5	0.7	1.0	1.3
11	2.2	0.2	0.2	0.3	0.4	0.6
12	1.7	0.1	0.1	0.1	0.2	0.3
13	1.4		0.0	0.0	0.1	0.1
14	1.3				0.0	0.0
15	1.2					
Total	101.9	100.0	100.1	99.9	100.0	100.0

^a C₁₂H₂₅O(CH₂CH₂O)_{*n*}H.^b Weibull-Nycander.

In the series of KOH-catalyzed adducts investigated, the amount of unreacted dodecanol varies with the average molar ratio v in the way shown in Fig. 4. A good correlation with the Weibull-Nycander equation for $c=3.0$ was obtained.* Thus, while the amount of unreacted material can be accurately described by the Weibull-Nycander theory, this does not seem to be the case when going to the higher species in the mixture. The distribution curves obtained indicate that differences in reactivity exist, not only between dodecanol and oxyethylated components, but also between the oxyethylated components themselves.

The results can be interpreted in the following way. In the alkali-catalyzed reactions between dodecanol and ethylene oxide the first step is considerably slower than those following. These proceed, at least for the lower members, with increasing rates. The explanation may be that the system's polarity is gradually increasing during the reaction.

* In contrast to the observations of Weimer and Cooper,¹⁰ who applied direct gas chromatography to different fatty alcohol-ethylene oxide adducts, obtained during widely varying conditions.

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