Determination of Ethylene Oxide Oligomer Distributions in Alcohol Ethoxylates by HPLC Using a Rotating Disc-Flame Ionization Detector[1]

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ABSTRACT

A high performance liquid chromatographic (HPLC) method has been developed for the quantitative determination of ethylene oxide (EO) oligomer distributions (% wt) in acetylated alcohol ethoxylates, $R(OCH_2CH_2)_nOH$, from n=0, 1 to n=30 using a rotating disc-flame ionization detector. Both single carbon number and mixed carbon number alcohol-based (NEODOL® ethoxylates) samples have been analyzed by gradient elution with 2 different solvent systems on a Waters μ-Porasil column. With both solvent systems, 95% hexane is the initial solvent but with one system, 100% acetone is the final solvent and with the other, 10% methanol/90% acetone is used. The latter solvent elutes the higher ethoxylates from n=21 to n=30 quantitatively from the μ-Porasil column which the 100% acetone solvent fails to do. The 100% acetone solvent separates n=2 and n=3 from n=0,1 which the methanol-containing solvent does not do. Response factors for n=3 and n=8 have been experimentally determined and the response factors for the other EO units have been calculated from these 2 results. The corrected EO oligomer distributions for both NEODOL® 25-9 and NEODOL® 23-6.5 determined by HPLC are in good agreement with those determined earlier by circular thin layer chromatography (up to n=16 can be determined by this method). The average EO numbers determined by the HPLC method and by a wet chemical (phthalic anhydride) method are in excellent agreement for the above 2 samples and a sample of NEODOL® 23-7.5. The results are discussed in terms of Snyder's theory for gradient elution in HPLC using the gradient steepness parameter.

INTRODUCTION

Alcohol ethoxylate oligomers $[R(OCH_2CH_2)_nOH]$, prepared by reaction of alcohols with ethylene oxide in which n may vary from 0 to 30 and higher, are widely used as nonionic, surface-active agents. Several methods have been developed for the determination of ethylene oxide oligomer distributions in alcohol ethoxylates but all of them suffer from certain limitations.

Gas chromatography (GC) of the acetate esters (1) or the silyl ethers (2) was shown to separate single carbon number ethoxylates up to about 12 ethylene oxide units. K.F. Guin of this laboratory (unpublished data) determined the ethylene oxide oligomer distributions of 2-carbon number ($R=C_{12}$ and C_{13} or C_{14} and C_{15}) alcohol ethoxylates up to 14 ethylene oxide units by GC of the trimethylsilyl ethers. The alkyl units (R) derived from the alcohol were primary, containing about 75% normal and 25% branched carbon chains. Ethylene oxide (EO) units higher than 14 could not be resolved. Furthermore, this GC method was not applicable to 4-carbon number ($R=C_{12}$, C_{13}, C_{14}, and C_{15}) alcohol ethoxylates due to overlap of the C_{12} and C_{15} ethoxylate peaks.

Thin layer chromatography (TLC) has been used to separate some of the oligomers of alcohol ethoxylates. Using circular TLC of the 3,5-dinitrobenzoate ester derivatives, McCoy and Bullock (3) reported the EO oligomer distributions of several samples of types similar to that studied by Guin. Four-carbon number ($R=C_{12}$, C_{13}, C_{14}, and C_{15}) alcohol ethoxylates were successfully analyzed. However, EO units higher than 16 could not be separated and were determined together as a group. For other work on the TLC separation of ethoxylate oligomers, see references cited in ref. 4.

In 1975, Nakamura and Matsumoto (5) showed that the EO oligomers of commercially available, single carbon number alcohols could be separated by high performance liquid chromatography (HPLC) of the acetate derivatives using a Pye Unicam LCM-2 moving wire-flame ionization detector. The separation was effected on a Zorbax-SIL (5-μ silica) column using gradient elution with an initial solvent consisting of 10% acetone in hexane linearly programmed to 100% acetone over 18 min. However, in the chromatogram of an acetylated dodecanol ethoxylate in which the average molar ratio of EO to dodecyl groups was 10, EO units lower than 4 were not resolved and a baseline umbrella underneath peaks from n=10 to n=17 made quantitation difficult and subject to error. Furthermore, the highest EO unit that could be detected was only 19.

The most attractive method developed up to this point for the determination of EO oligomer distributions is an HPLC one reported recently by Allen and Linder (4). The separations were carried out on 2 μ-Porasil columns in series using phenyl isocyanate derivatives and ultraviolet (UV, 240 nm) detection. Two gradients were used. The first used 2-propanol (2-32% over 1 hr) in butyl chloride, and the second used 2-propanol (3-18% over 1 hr) in methylene chloride. The first gradient separated the n=1 through n=8 mole adducts whereas the second separated the n=4 through n=25 mole adducts. The percentage of free alcohol (n=0) can not be determined by this method and must be determined by a GC technique. This method can be used for the analysis of mixed carbon number ($R=C_{12}$ through C_{18}) alcohol ethoxylates because only peak broadening results from the presence of mixed carbon numbers. The only limitation is that in the chromatogram of a 9 mole-average dodecanol ethoxylate, the highest EO unit that was shown to be quantitated was 21.

This paper describes an HPLC method for the quantitative determination of EO oligomer distribution in acetylated alcohol ethoxylates. In a 9 mole-average alcohol ethoxylate, EO units as high as 30 can be quantitated. The instrument used for detection is a rotating disc-flame ionization detector (FID) previously described by Szakasits and Robinson (6) of this laboratory. Tracor manufactured the instrument under license from Shell Oil Company according to the design of Szakasits. To our knowledge this instrument is not available commercially from Tracor.

EXPERIMENTAL PROCEDURES

Materials

1-Dodecanol was obtained from Chemical Samples in greater than 99% purity. Tri-ethylene glycol dodecyl ether (C_{12}-3EO) and octa-ethylene glycol dodecyl ether (C_{12}-8EO) were obtained from Nikko Chemicals Company in about 98% purity. For solvents, hexane was obtained from Waters and ace-

[1]Presented at the AOCS meeting, New Orleans, May 1981.

tone and methanol were LiChrosolv® grade. The water content of the acetone as determined by Karl Fischer titration was 0.2-0.3%. Ethoxylate samples were supplied by D.B. Bright of this laboratory.

Rotating disc conveyors. Discs were prepared from 0.5 in × 5 in. diameter plates of 99% pure alumina (Coors Porcelain Co., Golden, CO) by our machine shop according to the specifications of Szakasits and Robinson (6). The discs were gradually heated in a high-temperature furnace to 900 C for 2 hr before use.

Acetylation reagent. Analytical reagent-grade *p*-toluene sulfonic acid monohydrate (14.4 g) was dissolved in 360 mL of ethyl acetate. Analytical reagent-grade acetic anhydride (120 mL) was then added slowly with stirring and the resulting reagent was stored in an amber bottle.

Acetylation

To a 100-mL, round-bottomed flask with a 24/40 joint (purged with dry nitrogen for 5 min) was added 2.0 g of sample. After diluting with 2 mL of toluene, 6 mL of acetylation reagent was pipetted into the flask. The flask was stoppered and placed in a water bath at 50 ± 1C for 15 min. During the first 2 min, the contents of the flask were swirled while being brought up to temperature. The product was quickly cooled to 20 C and transferred to a 125-ml separatory funnel. Toluene (20 mL) was used to wash the contents of the flask into the separatory funnel. The product was washed with 50 mL of 30% wt aq sodium chloride and then twice with 50 mL of a solution containing 5% wt sodium bicarbonate and 25% wt sodium chloride. Finally, the product was rewashed wilth 50 mL of 30% wt sodium chloride. The toluene solution was transferred to a bottle and dried with anhyd granular sodium sulfate (shaken vigorously). The drying agent was removed by filtration through Whatman no. 40 filter paper and washed twice with 5 mL of toluene. In the case of acetylated NEODOL® 25-9, the volume of the toluene solution was reduced to 28 mL by nitrogen flow on the steam bath. For acetylated NEODOL® 23-7.5 or acetylated NEODOL® 23-6.5, more concentrated solutions were used (final volume 16-24 mL).

The advantage of the above procedure is that it removes about 80% of the polyethylene glycol impurities which are present in the samples in the 0.5-2% range. Thus, when a polyethylene glycol sample of average molecular weight 400 was carried through the acetylation procedure, only 20% of it was recovered. The presence of significant amounts of polyethylene glycol impurities (10% and higher) may interfere with the determination of EO oligomer distributions.

Instrumentation

The disc speed potentiometer was adjusted to a setting of 200 on the duodial (9-10 in./min). For gradient B, the solvent removal heater was set at 75 C and for gradient A, it was set at 100 C. The input switch was set on A, the input attenuator was set on 1, and the output attenuator was set on 16. The air (instrument air cylinders) pressure was set at 50 psi and the air flow was adjusted to a reading of 65 on the detector air flow meter (about 1,000 cc/min) and to 55 on the oxidizer flow meter. The hydrogen (high-purity cylinders) pressure was set at 30 psi and the hydrogen flow was adjusted to a reading of 100 on the detector hydrogen flow meter (about 150 cc/min) and to 130 on the oxidizer flow meter. After igniting the flames, it is important to disconnect and ground the ignition system in order to obtain good analysis repeatability.

Two Water's Model 6000A solvent delivery systems, a Model 660 solvent programmer, a single 4.6 mm × 300 mm Waters μ-Porasil column, and a Valco, 6-port injection valve having a 25-μL sample loop were installed in conjunction with the detector. The splitter on the detector system was adjusted to a setting of 4 so that about 15% of the effluent flows onto the disc. The solvent flow was 2 mL/min and solvent applicator needle was positioned about 0.01-0.02 in from the disc edge so that the solvent flow was taken up continuously and smoothly by the disc.

The recorder used was a Leeds and Northrup XL600 set at 10 mV span and the chart speed was 0.4 in./min. The baseline was adjusted to 5 on a 100-unit basis. Either gradient A or gradient B (linear, curve 6) over a 20-min period was commenced. The baseline should rise no more than one unit during the course of the gradient and level out smoothly at the completion of the gradient. The solvent gradient was reversed using a 5-min program. When the baseline returned to its original value of 5, the instrument was ready for sample introduction.

Sample Analysis

The detector was tied into an in-house, centralized data acquisition system called CENDAT. A solution of the appropriate sample concentration (described above) in toluene was used. The Valco valve in the load position was flushed with about 1 mL of toluene before the introduction of each new sample. The sample solution (0.2 mL) was loaded into the Valco valve so that extensive dropwise overflow occurred. At the same time as the sample was injected, either gradient A or gradient B (40 or 45 min initially) was commenced, the run button was activated on the CENDAT system control box, and the recorder was marked at the initial time. Different μ-Porasil columns were used for gradients A and B. When gradient A reached 70% completion, the gradient time was reduced to either 30 min (23-7.5 or 23-6.5 samples) or 25 min (25-9 samples). When the baseline leveled out permanently at the final solvent position, the run was terminated on the CENDAT system control box and the solvent gradient was reversed (5 min). The time (±10 sec) at each valley between peaks corresponding to the ethylene oxide oligomer distribution was marked on the chromatogram. Using valley-to-valley baseline integration on the CENDAT system, the percentage of each ethylene oxide oligomer in the sample was determined.

Gradient B was used to determine the ethylene oxide oligomer distribution from n=0,1 to n=20. Gradient A was used to determine the ethylene oxide oligomer distribution from n=21 to as high as n=30. The results of the 2 runs were then merged, yielding an overall distribution. The uncorrected ethoxylate distribution was then corrected by response factors. For a set of 4 samples, the typical analysis time was 2.5-3 hr/sample.

Ordinarily, with gradient B, the n=0 and n=1 peaks which are only partially resolved are integrated together. However, it is possible to estimate the relative amounts of n=0 and n=1 present. To carry out this estimate, a straight line (see Fig. 4, vide infra, for example) at the separation of n=0 from n=1 was dropped to the baseline and the areas were determined at this dividing line. The area of n=1 thus determined was then increased by 25% and the area of n=0 was decreased by the same amount. The latter correction represents the branched carbon chain isomers of n=1 which are buried underneath the n=0 peaks. The average value of the branched chain isomers from n=2 to n=5 is about 25% of the total. The n=0 and n=1 values thus obtained were within 5% of that determined by GC so our estimate appears to be reasonably reliable.

RESULTS

NEODOL® (registered trademark of Shell Chemical Com-

pany) ethoxylates are prepared from mixed primary alcohols and ethylene oxide. The carbon number range of the mixture is described by numbers. For example, 23 means a mixture of 12- and 13-carbon number alcohols, 25 means a mixture of 12-, 13-, 14- and 15-carbon number alcohols. These alcohols contain about 75% normal carbon chains and the remaining 25% are branched on the 2-carbon atom. Average molar ratios of ethylene oxide units to alkyl groups are indicated by an additional number following the carbon number range. Thus, NEODOL® 23-6.5 signifies an average molar ratio of 6.5 ethylene oxide units to 1 alkyl group. An alternate way of describing this material is to use the expression $C_{12\text{-}13}$-6.5 ethoxylate.

Initial experiments on the determination of ethylene oxide oligomer distribution were done on a single carbon number ethoxylate, a 7.5 mole average tridecanol ethoxylate (C_{13}-7.5, 75% normal, 25% branched). It was found that the presence of some methanol in the solvent gradient (see Table I for gradient A) was necessary to elute the higher EO units from n=21 to n=26 sharply enough for quantitation. The chromatogram for the separation of acetylated C_{13}-7.5 using gradient A (40 min gradient time) from n=0-3 to n=26 is shown in Figure 1. Using gradient A with a 2-carbon number ethoxylate, acetylated NEODOL® 23-7.5, (an experimental ethoxylate which is not available commercially) the main effect of the presence of mixed carbon numbers is peak broadening, but good sample baseline resolution is still achieved (Fig. 2). To sharpen the peaks from n=23 through n=26, the gradient time was reduced from 40 to 30 min at 70% gradient completion. The amount of methanol in the acetone is quite critical, with larger amounts than 10% producing umbrella baseline effects.

In both Figures 1 and 2, the lower EO units (n=0-n=3) are not resolved and are integrated together as a group. To separate the lower EO units in the acetylated $C_{12\text{-}13}$-7.5 ethoxylate, gradient elution with an initial solvent consisting of 5% acetone in hexane linearly programmed to 100%

TABLE I

Summary of Gradient A Conditions

Initial solvent	*Final solvent*	Gradient time
0.5% Methanol/ 4.5% acetone/ 95% hexane	10% Methanol/ 90% acetone	40-45 min initially, changed to 25 or 30 min at 70% completion with NEODOL ethoxylates

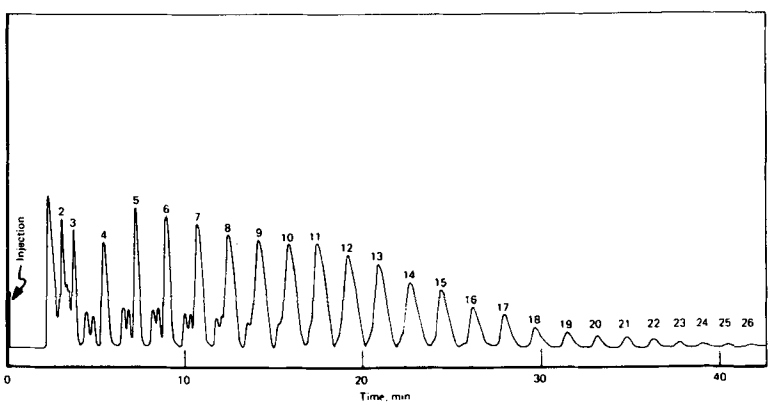

FIG. 1. HPLC separation of acetylated C_{13}-7.5 using gradient A. Column: Waters 1/4 in. X 1 ft μ-Porasil; solvent: hexane/acetone/methanol gradient—initial, 0.5% methanol/4.5% acetone/95% hexane; final, 10% methanol/90% acetone; gradient time: 40 min; flow rate: 2 mL/min; chart speed: 0.4 in./min.

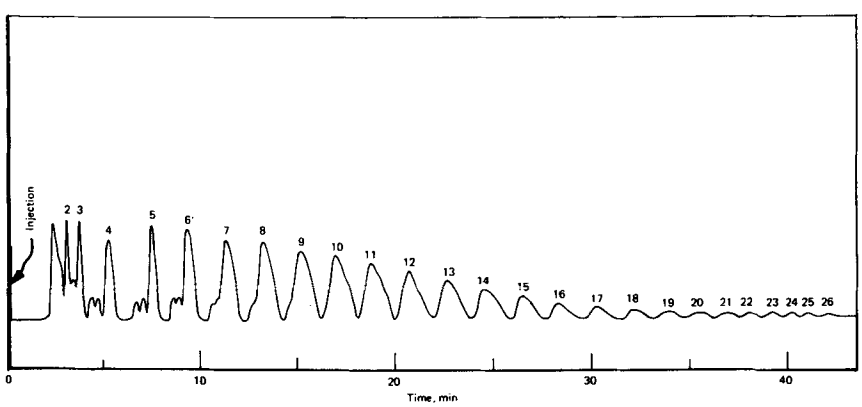

FIG. 2. HPLC separation of acetylated NEODOL® 23-7.5 using gradient A. Column: Waters 1/4 in. X 1 ft μ-Porasil; solvent: *n*-hexane/acetone/methanol gradient—initial, 0.5% methanol/4.5% acetone/95% hexane; final, 10% methanol/90% acetone; gradient time: 45 min initially, changed to 30 min at 70% completion; flow rate: 2 mL/min; chart speed: 0.4 in./min.

acetone over 40-45 min (gradient B) was used. The chromatogram presented in Figure 3 with gradient B shows excellent sample baseline resolution from n=0,1 to n=21. If shorter gradient times such as those used by Nakamura and Matsumoto (18 min) are used, a baseline umbrella was found underneath the peaks from n=7 to n=13 that prevented quantitative determination of the relative areas. In Figure 3, the n=1 peak is only partially resolved from the n=0 peaks and are ordinarily integrated together but a method of estimating the relative amounts of n=0 and n=1 is described in the Experimental Procedures section. For n=2, 3, 4 and 5, the branched carbon chain ethoxylates are partially resolved from the main normal carbon chain peaks, but by n=9, branched and normal carbon chain ethoxylates have completely merged.

Table II is a comparison of the results (average of 4 determinations ± σ) using gradient B (all values in the tables are in % weight unless otherwise specified) with the results using gradient A. The agreement from n=0-3 to n=21 is excellent for the 2 gradients. For gradient B, the coefficient of variation is in the 2-3% range from n=0,1 to n=13 and in the 3-6% range from n=14 to n=20. The complete EO oligomer distribution from n=0,1 to n=26 is obtained by merging the results from the 2 gradients.

Response factors for n=3 and n=8 have been determined to be 1.12 ± .01 and 1.31 ± .01 mV-sec, respectively, by HPLC analyses of equal weights of acetylated 1-dodecanol and acetylated tri-ethylene glycol dodecyl ether and equal weights of acetylated 1-dodecanol and acetylated octa-ethylene glycol dodecyl ether. As pure ethoxylates higher than n=8 are unavailable, no response factors for them could be experimentally determined. However, the results with n=3 and n=8 indicate that each additional EO unit adds about 0.04 units to the response factor. Hence, response factors have been calculated for all of the other EO numbers. In Table III, the EO oligomer distribution of the C_{12-13}-7.5 ethoxylate from n=0,1 to EO=26 corrected by response factors is summarized.

The average molecular weight of the starting alcohol was determined by GC analysis to be 195. From the original chromatogram, it was estimated that the n=0,1 peaks contained 60% n=0 and 40% n=1 so a molecular weight of 213 was used to calculate the moles/100 g of n=0,1. The complete summary of the calculation of the EO oligomer distribution in moles/100 g (average ± σ) from all 4 determinations in % wt (to check for error propagation) is presented in Table IV. From these results an average molecular weight of 518 ± 7 was calculated which corresponds to an average EO number of 7.34 ± .10. The coefficient of variation is 1.35%, so the error propagation is small.

Figure 4 shows the HPLC chromatogram from n=0,1 to n=20 for the separation of an acetylated C_{12-13}-6.5 ethoxylate using gradient B. Once again, the sample baseline resolution is excellent but the higher ethoxylates (n=21-23) do not elute sharply enough for quantitation. The HPLC chromatogram from n=0-3 to n=23 using gradient A is presented in Figure 5. Table V summarizes a comparison of the results (average of 4 determinations ± σ) using gradient B with the results using gradient A. The agreement from n=0-3 to n=20 is excellent for the 2 gradients. For gradient B, the coefficients of variation are about the same as those observed in the analysis of the acetylated C_{12-13}-7.5 ethoxylate.

Table VI gives the EO oligomer distribution of the C_{12-13}-6.5 ethoxylate from n=0,1 to n=23 corrected by

TABLE II

Comparison of Gradient A with Gradient B in the Analysis of Acetylated NEODOL® 23-7.5

EO no. (n)	Uncorrected gradient B ave ± σ	Uncorrected gradient A ave ± σ
0,1	6.0 ± .13	
2	3.7 ± .12	14.0 ± .3
3	4.7 ± .13	
4	5.6 ± .12	5.6 ± .13
5	6.6 ± .12	6.6 ± .13
6	7.9 ± .18	8.1 ± .20
7	8.9 ± .20	8.7 ± .20
8	8.9 ± .20	8.9 ± .25
9	8.8 ± .20	8.7 ± .25
10	8.1 ± .20	8.3 ± .25
11	7.2 ± .18	7.3 ± .22
12	6.3 ± .15	6.3 ± .19
13	4.7 ± .13	4.6 ± .15
14	3.6 ± .13	3.7 ± .15
15	2.6 ± .12	2.6 ± .13
16	1.9 ± .09	2.0 ± .12
17	1.25 ± .06	1.3 ± .08
18	0.9 ± .05	0.88 ± .05
19	0.7 ± .04	0.72 ± .04
20	0.5 ± .03	0.53 ± .03
21	0.4 ± .03	0.42 ± .03
22		0.27 ± .03
23		0.18 ± .02
24	0.8	0.13 ± .02
25		0.10 ± .02
26		0.08 ± .02

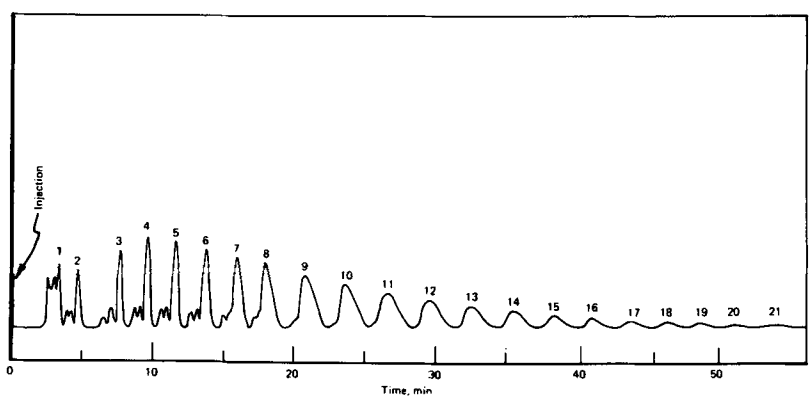

FIG. 3. HPLC separation of acetylated NEODOL® 23-7.5 using gradient B. Column: Waters 1/4 in. × 1 ft μ-Porasil; solvent: *n*-hexane/acetone gradient—initial, 5% acetone/95% hexane; final, 100% acetone over 40 min; flow rate: 2 mL/min; chart speed: 0.4 in./min.

TABLE III

Corrected HPLC Analysis of Acetylated NEODOL® 23-7.5

EO no. (n)	Uncorrected ave ± σ	Response factor	Corrected ave ± σ
0,1	6.0 ± .13	1.02	4.5 ± .10
2	3.7 ± .12	1.08	3.0 ± .10
3	4.7 ± .13	1.12	3.9 ± .11
4	5.6 ± .12	1.16	4.85 ± .10
5	6.6 ± .12	1.20	5.9 ± .11
6	7.9 ± .18	1.24	7.3 ± .17
7	8.9 ± .20	1.28	8.5 ± .19
8	8.9 ± .20	1.32	8.8 ± .20
9	8.8 ± .20	1.36	8.95 ± .20
10	8.1 ± .20	1.40	8.5 ± .21
11	7.2 ± .18	1.44	7.75 ± .19
12	6.3 ± .15	1.48	7.0 ± .17
13	4.7 ± .13	1.52	5.3 ± .15
14	3.6 ± .13	1.56	4.2 ± .15
15	2.6 ± .12	1.60	3.1 ± .14
16	1.9 ± .09	1.64	2.3 ± .11
17	1.25 ± .06	1.68	1.65 ± .08
18	0.9 ± .04	1.72	1.2 ± .05
19	0.7 ± .04	1.76	0.9 ± .05
20	0.5 ± .03	1.80	0.67 ± .04
21	0.4 ± .03	1.84	0.54 ± .04
22	0.27 ± .03	1.88	0.38 ± .04
23	0.18 ± .02	1.92	0.26 ± .03
24	0.13 ± .02	1.96	0.20 ± .03
25	0.10 ± .02	2.00	0.15 ± .03
26	0.08 ± .02	2.04	0.12 ± .03

TABLE IV

Calculation of Average Ethylene Oxide Number of NEODOL® 23-7.5

EO no. (n)	% wt ± σ	MW	Moles/100 g ± σ
0,1	4.5 ± .1	213	.0211 ± .00043
2	3.0 ± .1	283	.0102 ± .00042
3	3.9 ± .11	327	.0119 ± .00037
4	4.85 ± .1	371	.0131 ± .00032
5	5.9 ± .11	415	.0142 ± .00030
6	7.3 ± .17	459	.0159 ± .00041
7	8.5 ± .19	503	.0169 ± .00038
8	8.8 ± .2	547	.0161 ± .00035
9	8.95 ± .2	591	.0151 ± .00032
10	8.5 ± .21	635	.0134 ± .00030
11	7.75 ± .19	679	.0114 ± .00028
12	7.0 ± .17	723	.0097 ± .00017
13	5.3 ± .15	767	.0069 ± .00015
14	4.2 ± .15	811	.0052 ± .00015
15	3.1 ± .14	855	.0036 ± .00014
16	2.3 ± .11	899	.0025 ± .00013
17	1.65 ± .08	943	.0018 ± .00010
18	1.2 ± .05	987	.0012 ± .00007
19	0.9 ± .05	1031	.00088 ± .00004
20	0.67 ± .04	1075	.00062 ± .00004
21	0.54 ± .04	1119	.00048 ± .00003
22	0.38 ± .04	1163	.00032 ± .00003
23	0.26 ± .03	1207	.00022 ± .00003
24	0.20 ± .03	1251	.00016 ± .00002
25	0.15 ± .03	1295	.00012 ± .00002
26	0.12 ± .03	1339	.00009 ± .00002
Total			.1930 ± .0026

TABLE V

Comparison of Gradient A with Gradient B in the Analysis of Acetylated NEODOL® 23-6.5

EO no. (n)	Uncorrected gradient B ave ± σ	Uncorrected gradient A ave ± σ
0,1	7.6 ± .16	
2	4.75 ± .13	17.9 ± .3
3	5.8 ± .14	
4	7.0 ± .14	6.9 ± .16
5	8.3 ± .18	8.2 ± .19
6	9.0 ± .20	8.8 ± .20
7	9.0 ± .20	8.8 ± .24
8	8.9 ± .19	8.9 ± .23
9	8.0 ± .18	8.2 ± .21
10	7.3 ± .18	7.4 ± .21
11	6.4 ± .14	6.5 ± .17
12	4.8 ± .13	4.9 ± .14
13	3.7 ± .12	3.8 ± .12
14	2.8 ± .1	2.7 ± .11
15	2.2 ± .08	2.2 ± .10
16	1.5 ± .06	1.6 ± .08
17	1.1 ± .05	1.1 ± .06
18	0.75 ± .04	0.77 ± .04
19	0.48 ± .03	0.50 ± .04
20	0.32 ± .03	0.34 ± .03
21		0.18 ± .03
22	0.4	0.12 ± .02
23		0.08 ± .02

response factors. The average molecular weight of the starting alcohol (195) was the same as that used for the C_{12-13}-7.5 ethoxylate. From the original chromatogram, it was estimated that the n=0,1 peaks contained 57% n=0 and 43% n=1, so a molecular weight of 214 was used to calculate the moles/100 g of n=0,1. The complete EO oligomer distribution in moles/100 g from all 4 determinations in % wt was calculated in a manner similar to that described for the C_{12-13}-7.5 ethoxylate (Table IV). From these results, an average molecular weight of 482 ± 7 was calculated which corresponds to an average EO number of 6.52 ± .1.

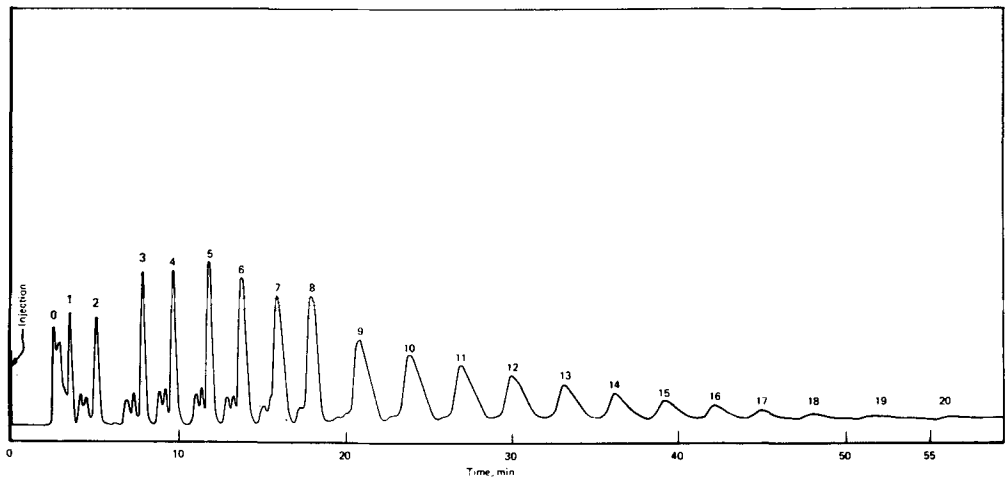

FIG. 4. HPLC separation of acetylated NEODOL® 23-6.5 using gradient B. Column: Waters 1/4 in. × 1 ft μ-Porasil; solvent: *n*-hexane/acetone gradient—initial, 5% acetone in hexane; final, 100% acetone over 45 min; flow rate: 2 mL/min; chart speed: 0.4 in./min.

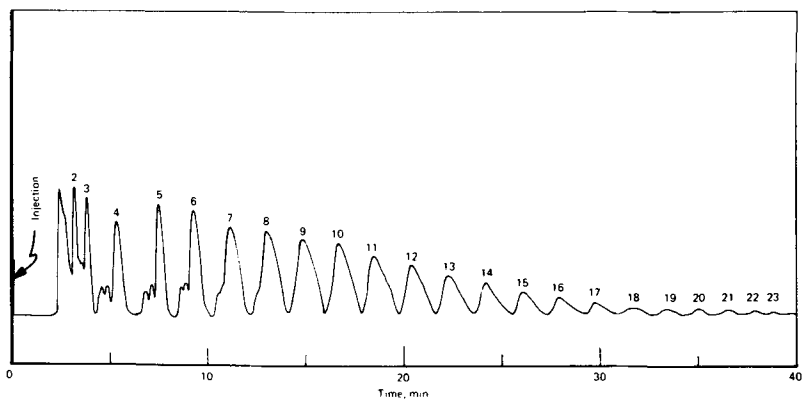

FIG. 5. HPLC separation of acetylated NEODOL® 23-6.5 using gradient A. Column: Waters 1/4 in. × 1 ft μ-Porasil; solvent: *n*-hexane/acetone/methanol gradient—initial, 0.5% methanol/4.5% acetone/95% hexane; final, 90% acetone/10% methanol; gradient time: 45 min initially, changed to 30 min; flow rate: 2 mL/min; chart speed: 0.4 in./min.

TABLE VI

Corrected HPLC Analysis of Acetylated NEODOL® 23-6.5

EO no. (n)	Uncorrected ave ± σ	Response factor	Corrected ave ± σ
0,1	7.6 ± .16	1.02	5.9 ± .13
2	4.75 ± .13	1.08	3.9 ± .11
3	5.8 ± .14	1.12	5.1 ± .12
4	7.0 ± .14	1.16	6.4 ± .13
5	8.3 ± .18	1.20	7.8 ± .17
6	9.0 ± .20	1.24	8.6 ± .19
7	9.0 ± .20	1.28	8.8 ± .20
8	8.9 ± .19	1.32	8.8 ± .19
9	8.0 ± .18	1.36	8.3 ± .19
10	7.3 ± .18	1.40	7.8 ± .19
11	6.4 ± .14	1.44	6.9 ± .16
12	4.8 ± .13	1.48	5.5 ± .15
13	3.7 ± .12	1.52	4.3 ± .14
14	2.8 ± .1	1.56	3.2 ± .11
15	2.2 ± .08	1.60	2.7 ± .10
16	1.5 ± .06	1.64	1.9 ± .08
17	1.1 ± .05	1.68	1.4 ± .06
18	0.75 ± .04	1.72	1.0 ± .05
19	0.48 ± .03	1.76	0.64 ± .04
20	0.32 ± .03	1.80	0.45 ± .04
21	0.18 ± .03	1.84	0.25 ± .04
22	0.12 ± .02	1.88	0.17 ± .03
23	0.08 ± .02	1.92	0.12 ± .03

A sample of the C_{12-13}-6.5 ethoxylate was analyzed by McCoy and Bullock (3) using circular TLC of the 3,5-dinitrobenzoate ester derivatives to separate the ethoxylates. Ethoxylates higher than n=15 could not be separated and were determined as a group. A comparison of the HPLC analysis with the TLC analysis of the C_{12-13}-6.5 ethoxylate is presented in Table VII. The agreement is excellent (less than 6% deviation) from n=3 through n=15 and fair (10-12% deviation) for n=0,1 and n=2.

The HPLC chromatogram from n=0,1 to n=20 for the separation of an acetylated C_{12-15}-9 ethoxylate (sample 26A) using gradient B is shown in Figure 6. The sample baseline resolution is excellent but the higher ethoyxlates (n=21-30) do not elute sharply enough for quantitation. Figure 7 presents the HPLC chromatogram from n=0-3 to n=30 using gradient A. The sample size was somewhat smaller than that used with the acetylated C_{12-13}-7.5 ethoxylate and the final gradient time was 25 min rather than 30 min. Using gradient A, the sample baseline resolution with the acetylated C_{12-13}-9 ethoxylate is not as good as that observed with the acetylated C_{12-13}-7.5 ethoxylate (the valleys in between most of the peaks are smaller) due to the presence of 4 carbon numbers rather than 2, but is still adequate. Table VIII is a comparison of the results (average of 4 determination ± σ) using gradient B with the results

TABLE VII

Comparison of HPLC and TLC Analyses of NEODOL® 23-6.5

EO no. (n)	HPLC analysis		TLC analysis		% Deviation
0,1	5.9		5.2		12
2	3.9		3.5		10
3	5.1		5.3		4
4	6.4		6.7		5
5	7.8		8.2		5
6	8.6		8.7		1
7	8.8		8.6		2
8	8.8		8.4		5
9	8.3		8.5		3
10	7.8		7.4		5
11	6.9		6.5		6
12	5.5		5.3		4
13	4.3		4.5		4
14	3.2		3.0		6
15	2.7		2.8		4
16	1.9				
17	1.4				
18	1.0				
19	0.64	6		7	
20	0.45				
21	0.25				
22	0.17				
23	0.12				

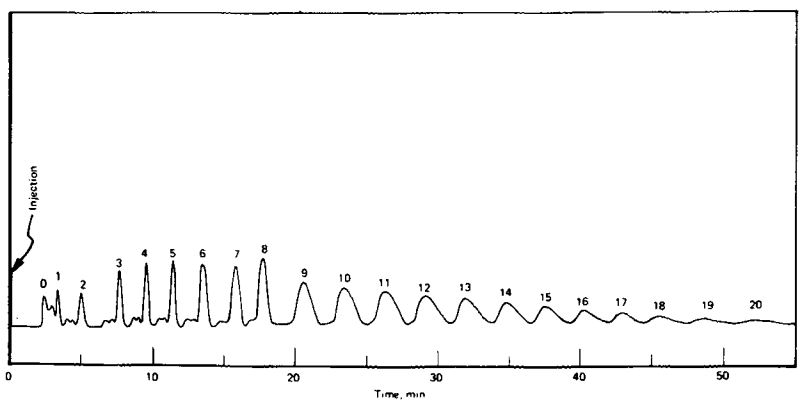

FIG. 6. HPLC separation of acetylated NEODOL® 25-9 using gradient B. Column: Waters 1/4 in. × 1 ft μ-Porasil; solvent: *n*-hexane/acetone gradient—initial, 5% acetone/95% hexane; final, 100% acetone over 40 min; flow rate: 2 mL/min; chart speed: 0.4 in./min.

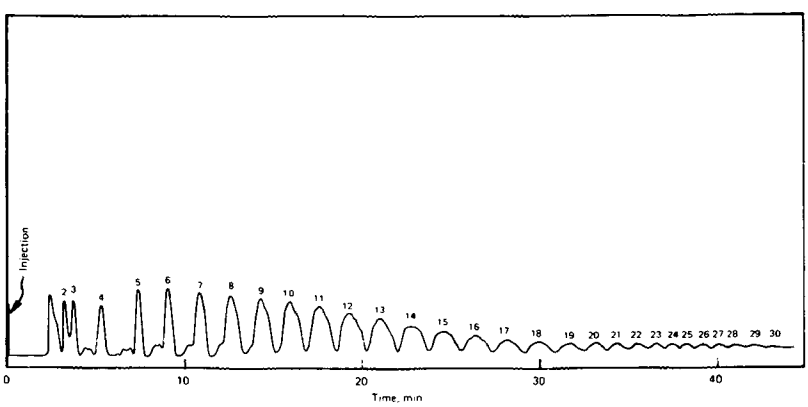

FIG. 7. HPLC separation of acetylated NEODOL® 25-9 using gradient A. Column: Waters 1/4 in. × 1 ft μ-Porasil; solvent: *n*-hexane/acetone/methanol gradient—initial, 0.5% methanol/4.5% acetone/95% hexane; final, 90% acetone/10% methanol; gradient time: 45 min initially, changed to 25 min at 70% completion; chart speed: 0.4 in./min; flow rate: 2 mL/min.

TABLE VIII

Comparison of Gradient A with Gradient B in the Analysis of Acetylated NEODOL® 25-9 (26A)

EO no. (n)	Uncorrected gradient B ave ± σ	Uncorrected gradient A ave ± σ
0,1	3.7 ± .12	
2	2.2 ± .09	9.5 ± .25
3	3.3 ± .10	
4	4.2 ± .12	4.4 ± .14
5	5.5 ± .13	5.7 ± .15
6	6.4 ± .15	6.7 ± .17
7	7.1 ± .16	7.3 ± .19
8	8.0 ± .18	8.2 ± .21
9	8.3 ± .18	8.1 ± .21
10	8.3 ± .17	8.5 ± .22
11	8.0 ± .17	7.9 ± .20
12	7.5 ± .16	7.3 ± .18
13	5.95 ± .14	5.85 ± .17
14	4.6 ± .12	4.5 ± .14
15	3.8 ± .12	3.6 ± .13
16	2.9 ± .10	2.8 ± .13
17	2.5 ± .09	2.3 ± .11
18	1.9 ± .07	1.8 ± .09
19	1.4 ± .06	1.3 ± .07
20	1.0 ± .05	0.95 ± .06
21		0.80 ± .05
22		0.60 ± .04
23		0.49 ± .04
24		0.37 ± .03
25	3.3	0.29 ± .03
26		0.23 ± .03
27		0.19 ± .03
28		0.13 ± .02
29		0.10 ± .02
30		0.08 ± .02

TABLE IX

Corrected HPLC Analysis of Acetylated NEODOL® 25-9 (26A)

EO no. (n)	Uncorrected Ave ± σ	Response factor	Corrected Ave ± σ
0,1	3.7 ± .12	1.02	2.7 ± .09
2	2.2 ± .09	1.08	1.6 ± .07
3	3.3 ± .10	1.12	2.65 ± .08
4	4.2 ± .12	1.16	3.5 ± .10
5	5.5 ± .13	1.20	4.75 ± .11
6	6.4 ± .15	1.24	5.7 ± .13
7	7.1 ± .16	1.28	6.5 ± .15
8	8.0 ± .18	1.32	7.6 ± .17
9	8.3 ± .18	1.36	8.2 ± .18
10	8.3 ± .17	1.40	8.3 ± .17
11	8.0 ± .17	1.44	8.1 ± .17
12	7.5 ± .16	1.48	7.9 ± .17
13	5.95 ± .14	1.52	6.5 ± .15
14	4.6 ± .12	1.56	5.2 ± .14
15	3.8 ± .12	1.60	4.3 ± .14
16	2.9 ± .10	1.64	3.4 ± .12
17	2.5 ± .09	1.68	3.0 ± .11
18	1.9 ± .07	1.72	2.35 ± .09
19	1.4 ± .06	1.76	1.75 ± .07
20	1.0 ± .05	1.80	1.3 ± .06
21	0.80 ± .05	1.84	1.05 ± .06
22	0.60 ± .04	1.88	0.81 ± .05
23	0.49 ± .04	1.92	0.67 ± .05
24	0.37 ± .03	1.96	0.52 ± .04
25	0.29 ± .03	2.00	0.41 ± .04
26	0.23 ± .03	2.04	0.34 ± .04
27	0.19 ± .03	2.08	0.28 ± .04
28	0.13 ± .02	2.12	0.20 ± .03
29	0.10 ± .02	2.16	0.16 ± .03
30	0.08 ± .02	2.20	0.13 ± .03

using gradient A. The agreement from n=0-3 to n=20 is very good for the 2 gradients. For gradient B, the coefficient of variation is in the 2-4% range from n=0,1 to n=19 and is in the 6-8% range from n=20 to n=24 for gradient A.

Table IX summarizes the EO oligomer distribution of the C_{12-15}-9 ethoxylate (sample 26A) from n=0,1 to n=30 corrected by response factors. The average molecular weight of the starting alcohol was determined by GC analysis to be 205. From the original chromatogram, it was estimated that the n=0,1 peaks contained 60% n=0 and 40% n=1, so a molecular weight of 223 was used to calculate the moles/100 g of n=0,1. The complete EO oligomer distribution in moles/100 g from all 4 determinations in % wt was calculated in a manner similar to that described for the C_{12-13}-7.5 ethoxylate (Table IV). From these results, an average molecular weight of 592 ± 9 was calculated which corresponds to an average EO number of 8.80 ± .14.

A sample of the C_{12-15}-9 ethoxylate was analyzed by McCoy using circular TLC but the ethoxylates higher than n=16 could not be separated and were determined as a group. A comparison of the HPLC analysis with the TLC analysis of the C_{12-15}-9 ethoxylate is presented in Table X. The agreement is excellent (1-5% deviation) from n=0,1 through n=16.

A second C_{12-15}-9 ethoxylate sample (26B) was also analyzed using the same procedure. The chromatograms using gradients B and A were quite similar to those presented in Figures 6 and 7. A summary of both the uncorrected and corrected EO oligomer distributions from the merger of the 2 gradients (n=0,1-n=30) is presented in Table XI. From these results, an average molecular weight of 589 ± 10 was calculated which corresponds to an average EO number of 8.75 ± .15.

The standard method at Westhollow Research Center for

TABLE X

Comparison of HPLC and TLC Analyses of NEODOL® 25-9 (26A)

EO no. (n)	HPLC analysis	TLC analysis	Deviation
0,1	2.7	2.8	4
2	1.6	1.6	–
3	2.65	2.6	2
4	3.5	3.6	3
5	4.75	4.9	3
6	5.7	5.8	2
7	6.5	6.6	2
8	7.6	7.7	1
9	8.2	8.1	1
10	8.3	8.1	3
11	8.1	7.7	5
12	7.9	7.9	–
13	6.5	6.4	2
14	5.2	5.1	2
15	4.3	4.4	2
16	3.4	3.4	–
Higher	13.0	13.2	2

determining the average EO number of NEODOL® ethoxylates is by calculation from the average molecular weight as determined from the hydroxyl number using the phthalic anhydride method (7). Table XII shows results comparing the average EO numbers determined by the HPLC method and by the phthalic anhydride (PA) method. The agreement between the HPLC and PA results is excellent, with differences varying from only 0.04 to 0.1 units. These differences are within the repeatabilities of the PA method (1.5%) and the HPLC method (1.4-1.7%).

TABLE XI

Uncorrected and Corrected HPLC Analyses of Acetylated NEODOL® 25-9 (26B)

EO no. (n)	Uncorrected ave	Corrected ave
0,1	3.7	2.7
2	2.3	1.7
3	3.3	2.65
4	4.3	3.6
5	5.6	4.8
6	6.6	5.9
7	7.1	6.5
8	8.1	7.7
9	8.5	8.3
10	8.4	8.4
11	8.2	8.35
12	7.4	7.8
13	6.0	6.55
14	4.6	5.2
15	3.6	4.1
16	2.8	3.3
17	2.3	2.8
18	1.8	2.25
19	1.3	1.65
20	0.95	1.25
21	0.73	0.97
22	0.57	0.77
23	0.44	0.61
24	0.35	0.50
25	0.27	0.39
26	0.21	0.31
27	0.17	0.25
28	0.13	0.20
29	0.09	0.15
30	0.07	0.12

TABLE XII

Comparison of Average EO Numbers Determined by HPLC and PA Methods

NEODOL® type	Identification no.	Average EO number	
		HPLC method	PA method
23-7.5	19-1	7.34	7.30
23-6.5	19-3	6.52	6.62
25-9	26A	8.80	8.86
25-9	26B	8.75	8.71

DISCUSSION

The excellent agreement of the average EO numbers determined by the HPLC and the PA methods are consistent with the HPLC determination of EO oligomer distributions being an accurate method. The agreement of the HPLC results with the TLC results provides further evidence that the entire procedure is sound and that the results are meaningful. In particular, the use of calculated response factors for the higher ethoxylates appears to be reliable.

In their separation of an acetylated dodecanol ethoxylate of average EO number=10, the failure of Nakamura and Matsumoto to detect EO units higher than 19 is attributed to their use of 100% acetone as a final solvent in their gradient on 5-μ silica. Acetone is not a polar enough solvent to elute in a quantitative manner the higher ethoxylates from n=21 to n=30 in a 10 mole-average ethoxylate. But, as our results show, 10% methanol/90% acetone is a polar enough solvent to elute the higher ethoxylates (n=21-30) in a 9 mole-average ethoxylate of similar type from μ-Porasil.

In the separation of a 9 mole-average dodecanol ethoxylate (derivatized), Allen and Linder failed to quantitate EO units higher than 21 (4). Some reasons which probably contribute to our ability to quantitate the higher EO units (n=22-30) in a similar type sample are described next. In our work, we used much higher sample concentrations which permit our FID to see at least 4-5 times as much sample (splitting taken into account) as the UV detector of Allen and Linder. Furthermore, because we used only one μ-Porasil column rather than 2, our reduced void volume increased the sample size that our FID detector sees by an additional factor of 1.4 over that which the UV detector sees. Finally, the % wt values of the FID are 2-3 times greater than the mole % values of the UV detector in the n=22 to n=30 range. Thus, we have been able to detect EO units which have values as low as 0.1% wt whereas the lowest values on the high end detected by Allen and Linder for alcohol ethoxylates were in the 0.4-0.8% wt range.

Snyder et al. and Dolan et al. (8-10) have developed a theoretical basis for gradient elution in HPLC which applies to most of the work reported here. For linear solvent strength (LSS) gradients (approximated by linear gradients) Snyder has introduced the gradient steepness parameter b which is defined as:

$$b = \frac{\Phi S\, t_o}{100},$$

where Φ = %/min change in concentration of E in a D to E gradient; S = the solvent strength of the pure solvent E; and t_o = column dead time in min which varies with the chromatographic system.

The reciprocal of the gradient steepness parameter b increases for gradients with smaller values of Φ. Snyder et al. have shown that the quantity 1/b plays an almost identical role in gradient elution as the parameter k′ does in isocratic separation. Resolution increases as b decreases, but so does the separation time. For a given separation, the optimal value of b is 0.1 to 0.3. S for a 10% methanol/90% acetone solvent is about 4. The column dead time (t_o) in our chromatographic system is estimated to be about 2 min. For a gradient time of 40 min (Fig. 1), Φ is 2.4%/min. From these values, the value of b=0.19 for the separation of acetylated C_{13}-7.5 is calculated which is within the optimal range established by Snyder et al.

Snyder's theory predicts that, for LSS gradient programs, the widths of the eluted bands should be approximately the same throughout most of the chromatogram except at the very beginning. This is caused in part by the "band compression phenomenon" which arises from the faster migration of the tail of the bands in gradient elution versus the equal migration of all parts of the band in isocratic elution. Band compression is a function of the gradient steepness parameter. For the separation of acetylated C_{13}-7.5 (Fig. 1), the band widths at the baseline are about the same from EO=5 to EO=20 as predicted by Snyder. The band widths from EO=21 to EO=26 are smaller than the other band widths but this may be more apparent than real.

Snyder has also shown that the detector sensitivity increases as b is increased. This is due to an increase in peak height as a result of the "band compression phenomenon" already described. Accordingly, in the separation of acetylated NEODOL® 23-7.5 (Fig. 2), decreasing the gradient time from 45 to 30 min (increases Φ) at 70% gradient completion increases peak heights (decreases band widths) and hence the detection limits of the higher EO oligomers (n=22-26).

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