Determination of Oxyethylene Distribution in Condensates of Primary Alcohols With Ethylene Oxide[1]

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Abstract

A new method has been developed that makes possible determination of the oxyethylene distribution of the condensates of mixed carbon number detergent-range, primary alcohols with ethylene oxide over a wide range. Circular thin layer chromatography of the 3,5-dinitrobenzoate ester derivatives is used to separate the condensates into a series of groups, each group containing all of the compounds present having the same number of oxyethylene units. These groups of esters are recovered and determined by a spectrophotometric procedure. Distribution curves are obtained that cover the range of added oxyethylene units from 0 to as high as 18. Higher adducts are recovered and determined as a group.

Introduction

Alkyl ether polyoxyethylene polymers, produced by condensation of alcohols with ethylene oxide, are widely used as surface active agents. Since these adducts contain a range of compounds having different numbers of added oxyethylene units, knowledge of this distribution is important and methods for its determination are needed.

Various procedures have been used for investigating the distribution in these and similar condensates, principally those from alkyl phenols. Kelly and Greenwald (1), Rosen (2) and Bürger (3) used column chromatography in work with alkyl phenols but adequate resolution was difficult to achieve and the chromatographic step was lengthy. Puthoff and Benedict (4) described a rapid method for separation and determination of the first few members of the adducts from primary alkyl ether condensates using column chromatography of the p-phenylazobenzoate esters. Konishi and Yamaguchi (5) and Skelly and Crummett (6) have used thin layer chromatography in work with the alkyl phenol condensates. Gas liquid chromatography (4) of the acetate esters (7) or the silyl ethers (8) has been shown to separate individual compounds having up to ten or more oxyethylene units. Calculation of results from these separations, except for the first few members of the series, has not been reliable because the many pure compounds necessary for determination of detector response are not easily obtained. Such compounds could probably be prepared (9) but an excessive amount of work would be required.

This paper presents a procedure for the determination of the oxyethylene distribution in polyoxyethylene condensates made from primary alcohols using a circular thin layer chromatographic separation of the 3,5-dinitrobenzoate (DNB) ester derivatives followed by a spectrophotometric determination of the recovered esters. This procedure is applicable to primary alcohol condensates from mixtures of alcohols, where normal and branched carbon chains and mixtures of carbon numbers are present. Distribution curves obtained cover the range of added oxyethylene units from 0 (unreacted alcohol) to 14 to 18 units, depending upon the average molar ratio of oxyethylene units to alkyl groups in the product.

Application of this procedure has made available samples having known distributions that will be useful for determination of gas liquid chromatographic detector response factors and for development of simpler, faster techniques.

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Experimental Procedures

Apparatus

Commercial water-repellent filter paper, Whatman No. 4, silicone treated, was used for the filtrations in preparation of the DNB esters. The circular thin layer chromatographic apparatus was similar to that described by Konishi and Yamaguchi (5) except that a motor driven syringe was used to feed the migration solvent. The syringe provided for delivery of up to 10 ml of solvent at a flow rate of 0.05 ml/min. A 120 mm section of the tip end of a 1 ml pipet (the feed tube), held in a clamp, was used to feed the solvent to the chromatographic adsorbent. A cover for the upper part of the apparatus was made by punching a hole in the center of a 2 in. diameter rubber disc and forcing it over the feed tube. Connection between the syringe and the feed tube was made with a length of $\frac{1}{16}$ in. O.D. Teflon tubing which slides into the feed tube and wedges into the interior taper near the tip. A 7.5 in. diameter spacer ring made from $\frac{1}{8}$ in. O.D. Teflon tubing separated the glass cover plate from the adsorbent surface.

Conventional 8 × 8 in. glass plates coated with an 0.3 mm (wet) layer of silica gel adsorbent were used. Sample solution was applied with a 1 μl "Microcap" (Drummond Scientific Corp.) and detection was with a 2540A ultraviolet lamp.

A small spatula with a chisel type tip, a thin dissecting needle with handle, a pair of ordinary magnifying glasses (3X), a small quill brush with bristles clipped to a length of 5 mm and fitted with a handle, glazed black paper and 4-dram screw-cap vials were used for recovering the sections of adsorbent containing the separated compounds.

Cheney type syringes, 1 ml and 5 ml, were used for addition of reagents in the extraction and color development steps. Membrane type filters, 1 in. diameter, Type Alpha-8 (0.2μ pore size) held in Easy Pressure Syringe Filter Holders (Gelman Instrument Co., No. 4320) were mounted on 10 ml syringe barrels fitted with 18 gage hypodermic needles. The filter units were held in a clamp arranged to permit filtration directly into the spectrophotometer cell. Air at about 5 psig, supplied through a line fitted with a suitable stopper and toggle valve, was used to speed the filtration. About 2 dozen filter units are recommended.

Spectrophotometric measurements were made with an extended adsorbance range spectrophotometer, such as the Beckman Model B, fitted to use 5 cm path cells that hold 5 ml or less.

Reagents

Commercial 3,5-dinitrobenzoyl chloride was recrystallized from carbon tetrachloride (digest 0.1 g/ml

at about 70 C, filter and cool in an ice bath). The product was evacuated to remove solvent and stored in a dessicator. Anhydrous pyridine was used; the benzene used in the esterification reaction was alcohol free. The thin layer adsorbent used was silica gel containing gypsum binder and a white fluorescent additive (Mallinckrodt Chemical Co., No. 7GF); it was passed through a 150 mesh/in. sieve to remove any large particles or agglomerates that might be present. Analytical reagent grade chloroform with 2% volume absolute ethanol added was used for migration solvent. The N,N-dimethylformamide and 1,2-propanediamine used for extraction and color development were commercial materials (Matheson, Coleman, and Bell).

Procedure

Preparation of DNB Esters. Dissolve 0.5 meq. of sample in 20 ml of benzene in a 100 ml boiling flask. Add 180 mg of 3,5-dinitrobenzoyl chloride plus 15 mg for every mg of water present in the sample taken, 0.2 ml of pyridine and a boiling chip and reflux for 90 min. Cool slightly, add 0.05 ml of water and reflux an additional 15 min. Cool and filter the contents of the flask through Whatman No. 4 silicone treated paper into a 100 ml separatory funnel fitted with a Teflon stopcock. Rinse the flask sparingly with benzene. Add 5 ml of 10% sodium bicarbonate solution to the funnel and shake for 3 min. Allow the phases to separate, discard the lower, aqueous phase, repeat the extraction twice more, and filter the benzene solution through Whatman No. 4 silicone treated paper into a weighed container. Immerse the container in hot water and evaporate to constant weight with a gentle stream of nitrogen. Redissolve the ester product in benzene to yield a concentration of 50 to 60 mg/ml.

Circular Thin Layer Chromatography. Hold the adsorbent coated plate with the adsorbent side down and tap it to dislodge any loose particles of adsorbent. Assemble the chromatographic apparatus and fill the solvent feed system being sure that the adsorbent coated plate is level, the spacer ring is centered on the plate and the 20 mm hole in the glass cover is over the center of the plate. Place weights on the cover to prevent accidental movement. Apply two 1 μl portions of sample solution to a quadrant of the plate placing the two portions side by side so that the edges of the wetted areas just touch and lie on the circumference of the 20 mm diameter circle defined by the hole in the cover. Up to four samples can be placed on one chromatogram. Place the glass cylinder over the hole in the cover and place two 20 × 70 mm strips of thick filter paper, which has been wet with migration solvent, on end in the cylinder so that they stand to the sides of the hole in the cover. Insert the solvent feed tube between the strips of paper and lower it until the tip is a few millimeters above the adsorbent surface. Slide the rubber disc down to close the top of the glass cylinder. Examine the arrangement to be sure that the solvent feed tube and glass cylinder are centered on the hole in the cover and that the lower ends of the paper strips are to the sides of the hole in the cover.

Wait 20 min for vapor equilibration, slide the solvent feed tube down into contact with the adsorbent surface and start the solvent feed. Continue migration for 20 to 30 min after the solvent front has reached the spacer ring. Stop the migration, remove the chromatogram and allow it to dry.

Recovery of Fractions. Place the chromatogram under the UV light and, with the small spatula, scrape approximately ⅛ in. wide radial grooves in the adsorbent at the sides of each sample sector. Scrape similar grooves a few millimeters outside the fastest moving sample components. Since short wavelength UV light is harmful to the eyes, wear eye protection and turn the lamp off when it is not needed. Hold the dissecting needle nearly flat against the chromatogram and, with long strokes, loosen the adsorbent on the unused areas of the chromatogram. Tilt and tap it to dislodge this adsorbent and, with a folded paper tissue, clean these areas, the back and the edges of the chromatogram. Recover, one at a time, the sections of adsorbent containing separated compounds. First scribe a line between the outermost zone and the next adjacent zone with the needle. This operation is most easily done while wearing magnifying glasses to provide sharp vision and scribing the line with a series of short, 2 to 4 mm strokes. Turn the needle as above and loosen the marked area with a series of short strokes. Transfer the loose adsorbent to a piece of glazed paper by tilting the chromatogram, tapping and using the small brush as necessary. Then transfer this adsorbent to a 4 dram vial. Continue in this manner until all of the sections of adsorbent containing visible, separated sample components have been removed; the remaining section of adsorbent for each sample is recovered as a single fraction that includes the origin.

Extraction and Spectrophotometry. Add 5.5 ml of N,N-dimethylformamide to each of a convenient number of the vials with a Cheney type syringe. Cap the vials and shake them vigorously. After 10 min add 0.55 ml of 1,2-propanediamine to one of the vials with a Cheney type syringe, cap it, shake briefly and pour the contents of the vial into a filter unit. Filter the color solution into a spectrophotometer cell using air pressure to speed the filtration and measure the absorbance of the solution at 525 mμ against N,N-dimethylformamide reference within 5 min after addition of the 1,2-propanediamine. Continue in this manner until all of the fractions have been processed. Determine a color reagent blank omitting the adsorbent but including the filtration step.

Calculations. Apply the color reagent blanks and normalize the resulting corrected absorbances. This step gives the molar distribution directly. To obtain the weight distribution, multiply each of the molar distribution values by the appropriate average molecular weight for the components present and use the resulting relative weights to calculate the weight per cent. The molar distribution data is used to calculate the average molar ratio of oxyethylene units to alkyl groups.

Nomenclature

Mixed primary alcohols are described by numbers indicating the carbon number range of the mixture. For example, 12–13 means a mixture of 12 and 13 carbon number alcohols, 12–15 means a mixture of the 12, 13, 14 and 15 carbon number alcohols. Mixtures are approximately 1:1 except for the 12–15 mixtures which are approximately 2:3:3:2. These alcohols contain approximately 75% normal or straight carbon chains and the remaining 25% is branched on the 2 carbon atom, predominately methyl but with decreasing amounts of the propyl and higher isomers.

Nominal molar ratios of oxyethylene units to alkyl groups in adducts are indicated by an additional num-

ber following the carbon number range. For example, 12–13–3 means a molar ratio of 3 oxyethylene units to 1 alkyl group.

Discussion

Thin layer chromatography was investigated because it frequently provides separations of similar compounds. Bürger (10) has shown that TLC separations can be made of the polyoxyethylene adducts of a variety of compounds including alcohols, phenols and amines where the separated zones contain only those adducts having the same number of oxyethylene units. For some similar compounds no indication of any significant effect from the hydrocarbon part of the molecules was observed. Qualitative TLC migrations with primary alcohol polyoxyethylene adducts in these laboratories showed similar results. Further study of this separation showed that, with these detergent range adducts, neither the number of carbon atoms in the alkyl group nor branching on the carbon chain influenced the separation provided the alcohols had a primary configuration. These adducts separated into a series of zones, each zone containing all of the compounds having the same number of oxyethylene units. Absolute proof of this behavior is difficult to achieve but no differences in migration behavior could be detected when polyoxyethylene adducts of normal primary alcohols were compared with those from mixed alcohols in the C_{12} to C_{15} range containing branched carbon chains (mostly the 2-methyl isomer) or highly branched alcohols prepared by propylene polymerization. Differences in migration behavior caused by the hydrocarbon portion of the molecules in such complex mixtures, if present, would be expected to produce complex and poorly resolved chromatograms that differed from those obtained from adducts of single alcohols. The absence of any detectable differences provided confidence that the separation was determined strictly by the number of oxyethylene units present. Circular thin layer chromatography (5) was used in this work because it gives better resolution than the conventional linear method.

Extension of the TLC separation of the alcohol adducts, as such, to quantitative measurements is difficult because they are not easily detected on chromatograms without using vigorous chemical methods that change them and, even if they are detected and recovered, rapid methods for the determination of the small amounts separable by TLC are not available. Methods such as charring with sulfuric acid followed by densitometry (11) might be used but such methods require calibration with pure compounds to enable calculation of the results.

Therefore conversion of the adducts to a derivative that could be detected and determined more easily was investigated. Bürger (12), in work with polyethylene glycols, used the 3,5-dinitrobenzoate ester derivatives. These esters are strong UV absorbers and can be seen directly as dark zones on adsorbents containing a fluorescent additive, when illuminated with UV light and a sensitive spectrophotometric procedure for their determination has been reported (13). Use of these derivatives was investigated and adopted.

The method given for preparation of the ester derivatives is similar to that used by Bürger but, with the primary alcohol adducts, the recommended method gives better recoveries, is faster because phase separation occurs more rapidly and it removes 3,5-dinitrobenzoic acid from hydrolysis of excess reagent more completely. This acid interfered because it streaked on the chromatogram and obscured the low R_f region. Filtration through water repellent paper removes water droplets from the benzene phase. Recoveries found for samples, based on weight of product, have been consistently within 95% of theory.

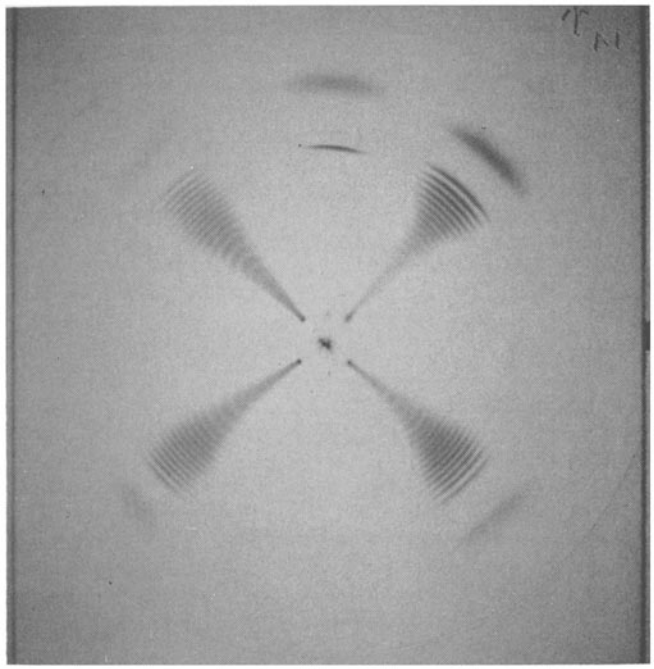

FIG. 1. Circular thin layer chromatographic separation of 3,5-dinitrobenzoate esters of primary alcohol polyoxyethylene condensates. Chloroform-ethanol (98:2) solvent. Samples clockwise from top: 5 μg each of mixed esters of 1-pentadecanol and trioxyethylated 1-pentadecanol, 12–13–3, 12–13–6.5, 12–15–9 and 14–15–11. See Nomenclature in text.

TLC experiments, similar to those described for the alcohol adducts, showed that the separation of the DNB esters was again determined by the number of oxyethylene units present. Separation in this manner is particularly suitable for the desired determination of oxyethylene distribution. Figure 1 shows the appearance of a chromatogram and the separation obtained for a number of primary alcohol adducts. The sector at the top shows the separation of a mixture of about 5 μg each of the esters of 1-pentadecanol and its trioxyethylene adduct, moving clockwise the other samples are the esters from the adducts of mixed primary alcohols with 3, 6.6, 9 and 11 mole ratios of ethylene oxide; the respective carbon number ranges were 12 and 13, 12 and 13, 12 through 15 and 14 and 15 mixed at approximately equal concentrations. The zones furthest from the center are the esters of the unreacted alcohols and, moving towards the center, the number of oxyethylene units progressively increases. The duller regions visible towards the side of the photograph resulted from uneven illumination with 2540A ultraviolet light when the photograph was taken.

TABLE I

Molar Absorptivities of Some 3,5-Dinitrobenzoate Esters in the Spectrophotometric Procedure

3,5-DNB ester of	Absorptivity, liters/mole-cm
n-Dodecanol	1.59×10^4
n-Pentadecanol	1.59×10^4
Trioxyethylated n-dodecanol	1.55×10^4
Trioxyethylated n-pentadecanol	1.64×10^4

TABLE II

Comparison of Molar Ratio of Oxyethylene Units to Alkyl Groups Calculated From Distribution Data and Determined Directly

Sample[a]	Molar ratio	
	Directly on sample[b]	Calculated from distribution
12–13–3	3.1	3.0
12–13–3	2.9	2.9
12–15–3	3.0	3.1
12–13–6	5.7	5.7
12–13–6.5	6.6	6.6
12–15–9	8.8	8.7
14–15–11	11.2	10.5

[a] See section on Nomenclature in text.
[b] By nuclear magnetic resonance[14].

The samples were applied as 1 μl portions of benzene solutions containing from 60 to 70 μg of the DNB esters. The application pattern differs from that used in the recommended procedure because only single spots were applied; in the procedure two 1 μl portions are applied side by side to increase the amount applied without overloading the adsorbent and each sector shows two closely adjacent migration paths that merge on the common edges in the high R_f region. In the separation shown the solvent flow was continued for about 20 min after the solvent front reached the spacer ring.

The migration solvent used, chloroform with 2% volume additional ethanol added was selected by experiment, using the apparatus and flow rates described, at a room temperature of 72 ± 1 F. Systems of this type where only a low concentration of a polar solvent is present tend to be sensitive to the experimental conditions and, if used in other locations, some changes in composition of the migration solvent might be required to achieve the same separation. Some indications were obtained that a solvent flow rate slower than the 0.05 ml/min used would improve the separation, but this was not investigated.

The adsorbent coated plates were prepared using a conventional hand-operated spreader. Slurries used were a little more fluid than are normally used and the controlling edge of the floating spreader gate was straightened by grinding on a glass lap. This was done to achieve uniform thickness of the adsorbent layer. Uniform thickness and symmetry in the experimental arrangement are important for achieving a reasonably symmetrical chromatogram. The silica gel adsorbent used was chosen because weak dark zones are easily seen against the brilliant white fluorescence; any organic impurities present did not interfere. Pre-coated commercial plates are available, but the one lot tried contained excessive amounts of organic impurities that obscured the separation.

In this work the many pure compounds needed for calibration of the spectrophotometric part of the procedure were not available. However, the method was developed and tested without having the pure compounds. This was possible because all of the fractions, including the unresolved group near the origin, were recovered and analyzed. Recovery and analysis of all of the fractions from the sample allowed an assumption to be made and the resulting distribution curves calculated. The molar ratio of oxyethylene units to alkyl groups in the original sample was then calculated from this distribution data. This ratio was determined directly on the original samples by a nuclear magnetic resonance method (14). Comparison of these ratios provides evidence for the validity of the assumption. The assumption made was that the molar absorptivities of the color developed by the DNB esters of all of the adducts was a constant. Such an assumption is not unreasonable because the color forming part of the molecule is the DNB ester group and the remaining parts of the molecules present are quite similar, the principal difference being the number of oxyethylene units in the chain. Kelley and Greenwald (1) found constant molar absorptivities for the UV absorbances of alkylphenol oxyethylene adducts. A few compounds were available for direct measurement of the molar absorptivities in the low end of the series the region where differences would be expected to be the greatest. The DNB esters of two primary alcohols and their trioxyethylene adducts were prepared, purified by recrystallization, and their molar absorptivities were measured by the recommended method. Table I shows that, within the accuracy of the measurements, the absorptivities are constant. Table II compares the molar ratios of oxyethylene groups to alkyl groups calculated from the distribution data and determined directly by nuclear magnetic resonance for a number of samples; agreement in nearly all cases is within the accuracy of the nuclear magnetic resonance method (±0.1 unit) showing that the assumption of constant molar absorptivity is valid. This agreement also provides strong evidence that the entire procedure is sound and that the results are meaningful.

In order to calculate the weight distribution a second assumption is made. This is necessary because the average molecular weight of each separated group of adducts is used in the calculation; this weight is not known for the adducts present in the higher, unresolved region and an approximated value is used in the calculation. This assumption does not have an important effect on the distributions obtained in this work because the unresolved group represents only a small part of the total, less than 15% in most cases, and an approximation suffices. The average molecular weight assumed for the unresolved group in this work was that for the adduct having three oxyethylene units more than that for the last resolved adduct. It should be possible to calculate a more accurate value from the shape of the molar distribution curve.

The most delicate part of the method is recovery of the sections of adsorbent containing the separated adducts. Patience and care are needed to scribe the lines between the adjacent separated groups and to loosen the adsorbent because the entire separation takes place in a distance of about 80 mm. In some regions the clear space between separated zones is not much over 1 mm. This recovery step is not overly difficult provided reading glasses of moderate magnification (3X) are worn to provide a good view of the placement of the needle point. The needle itself is held nearly vertical and steadied by placing one or two fingers against the glass plate. A series of short, 2 to 4 mm, movements are used both to scribe the line and, later, with the needle held nearly flat with the point at the scribed line, to loosen the absorbent. The loosened adsorbent is transferred to a folded piece of black glazed paper, placed on a larger piece to allow recovery in case of a spill, by tilting and tapping the glass plate. Recovery is completed with a small brush and the adsorbent is then poured from the paper into a vial. With a little practice it is possible to recover one section every 4 to 5 min.

The spectrophotometric method used (13) involves measurement of a reddish nitroquinoid color (15) that develops when the base, 1,2-propanediamine, is added to a N,N-dimethylformamide solution of the

TABLE III

Oxyethylene Distributions Found for Primary Alcohol Adducts

n = [a]	12–13–3[b]		12–13–6.5[b]		12–15–9[b]		14–15–11[b]	
	% Mole	% Wt	% Mole	% Wt	% Mole	% Wt	% Mole	% Wt
0	26.5	15.8	8.2	3.3	4.7	1.6	4.2	1.4
1	14.6	10.6	3.9	1.9	2.5	1.1	2.5	1.0
2	14.3	12.2	6.1	3.5	3.3	1.6	2.9	1.3
3	12.2	12.2	7.9	5.3	4.6	2.6	3.3	1.7
4	9.3	10.6	8.8	6.7	5.5	3.6	4.0	2.4
5	6.7	8.6	9.6	8.2	6.7	4.9	4.5	2.9
6	4.6	6.4	9.2	8.7	7.3	5.8	5.2	3.7
7	3.4	5.2	8.3	8.6	7.6	6.6	5.3	4.1
8	2.4	4.1	7.4	8.4	8.1	7.7	5.9	5.0
9	1.8	3.2	7.0	8.5	8.0	8.1	6.3	5.7
10	1.2	2.5	5.6	7.4	7.5	8.1	6.5	6.3
11	1.0	2.0	4.6	6.5	6.6	7.7	6.6	6.8
12	0.6	1.4	3.5	5.3	6.3	7.9	6.5	7.1
13	0.5	1.3	2.8	4.5	4.9	6.4	6.0	6.9
14	0.4	1.1	1.8	3.0	3.7	5.1	5.4	6.7
15	....	....	1.6	2.8	3.0	4.4	4.7	6.0
16	....	....	....	....	2.7	3.4	4.1	5.6
17	....	....	....	....	....	....	3.3	4.7
18	....	....	....	....	....	....	3.0	4.4
Higher[c]	1.2	3.4	3.5	7.3	7.6	13.3	9.9	16.5

[a] Value of n in equation $R-(OC_2H_4)_n-OH$.
[b] See section on Nomenclature in text.
[c] Adducts higher than last discrete value shown.

DNB esters. Tests showed that N,N-dimethylformamide, when used as a migration solvent, moved the DNB esters at the solvent front, showing that the solvent for the color procedure is also effective for eluting or extracting the esters from the adsorbent. This is convenient and avoids any necessity for using other solvents. A potential complication in the color development step is that the color is not overly stable and must be measured within 5 min. Color development and measurement proved to be a simple and rapid process and this limitation is not important. In the recommended technique the esters are extracted from the silica gel by soaking it in N,N-dimethylformamide for a few minutes, 1,2-propanediamine is added to develop the color in the presence of the adsorbent and the color solution is filtered directly into the spectrophotometer cell. Pressure filtration through membrane type filters removes extremely small solid particles (16) and proved to be so fast, 10 to 15 sec for 5 ml, that it is practical to develop the color in the presence of the adsorbent and complete the filtration and measurement within the 5 min limit. The average time from addition of the base to completion of a color measurement is about 2 min; ample time remains to check the instrument zero and verify the value.

Use of Cheney type syringes to dispense measured volumes is rapid and convenient. The absolute volumes used are not important, provided they are constant, because the data are normalized before calculation. Normalizing is done to avoid any necessity for placing accurately known weights of sample on the chromatogram. The total volume of the color solution to be used is determined by the volume required to fill the spectrophotometer cell. This volume should be minimized to avoid undue dilution and can be set at any value by appropriate adjustment of the syringes. The ratio of 10 to 1 between reagents should be maintained. Use of an extended absorbance range spectrophotometer is advantageous because all measurements in a distribution can be made with the same light path cell and solution volume.

This procedure involves a relatively large number of operations and, as a result, is slow. A minimum of 3 to 3.5 man-days are needed to complete two samples in duplicate. There does not appear to be any possibility for making any significant reduction in the time required. However, application of the method has made available samples having known

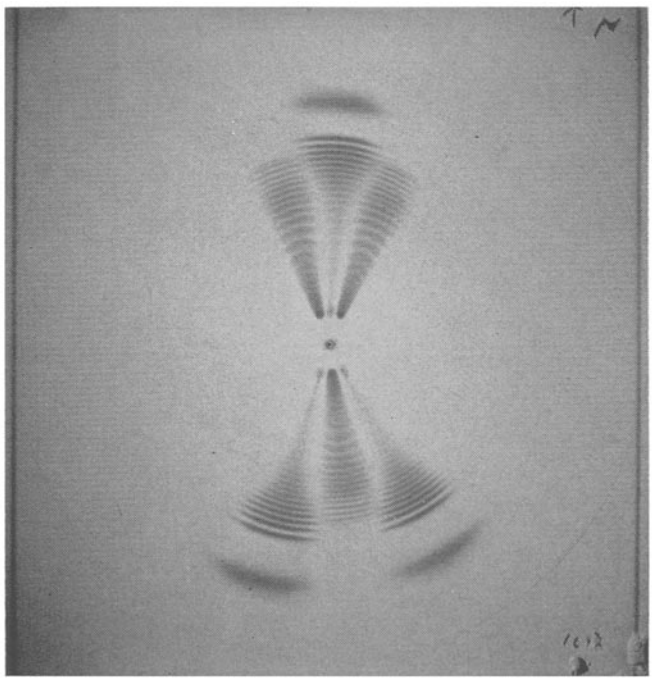

FIG. 2. Comparison of migration behavior of esters of a polyoxyethylene condensate of a primary alcohol and polyethylene glycol. Chloroform-ethanol (98:2) solvent. Center path at top is polyethylene glycol esters, both side paths are esters from primary alcohol condensate. Bottom section is the opposite arrangement of same esters.

distributions that makes possible investigation and calibration of other, possibly faster techniques. Response factors for gas liquid chromatography (GLC) can now be determined and results can be obtained for samples having a substantial part of their distribution in the GLC range. Investigation of techniques for direct scanning of chromatograms likewise becomes possible; such techniques would require less time. Preliminary scanning experiments made using 2500A ultraviolet light and measuring the reduction in intensity of fluorescent light, which occurs at locations where the esters are present, are encouraging.

Polyethylene glycols, frequently present at low concentration in these adducts, would form DNB esters and could separate in a similar fashion (12). The migration behavior of these esters was determined in the chloroform-ethanol solvent using the glycols recovered by extraction (17) from a typical condensate made by reaction of the alcohol with three moles of ethylene oxide. The recovered glycols were converted to their DNB esters and their migration behavior compared directly with that of the esters of the alcohol adduct. Direct comparison was made by placing about 50 μg of one of the two preparations, between two similar amounts of the other; both combinations were used. The resulting chromatogram, Figure 2, shows that the migration behavior is similar but not identical. The polyethylene glycol esters are at the sides in the upper part and at the center in the lower. Interference, both in the chromatographic step and in the color measurement, would be expected if significant amounts of polyethylene glycols were present. In such cases the extraction method of Weibull (17) could be used for their prior separation. Only small amounts, less than 2%, of polyethylene glycols were present in the samples analyzed and no significant interference would occur. The presence of this small amount would explain a slight darkening

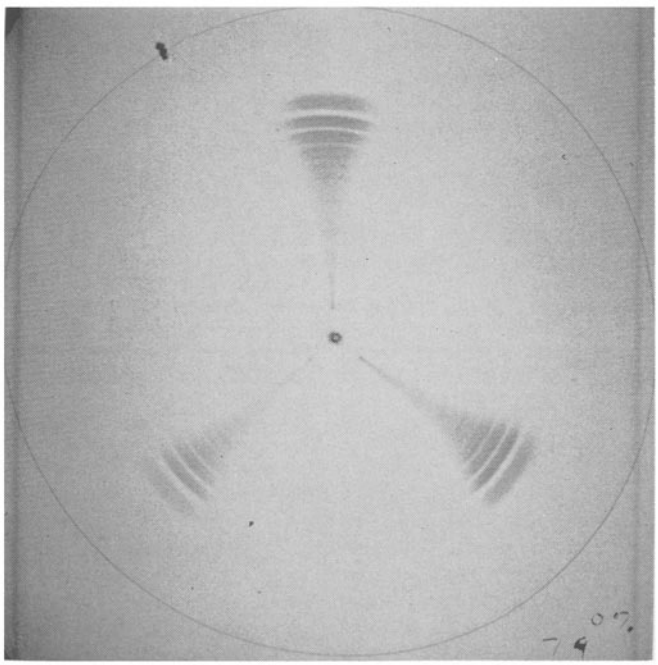

FIG. 3. Separation of 3,5-dinitrobenzoate esters of a secondary alcohol polyoxyethylene condensate. Chloroform solvent, 25, 50 and 75 μg of same ester sample.

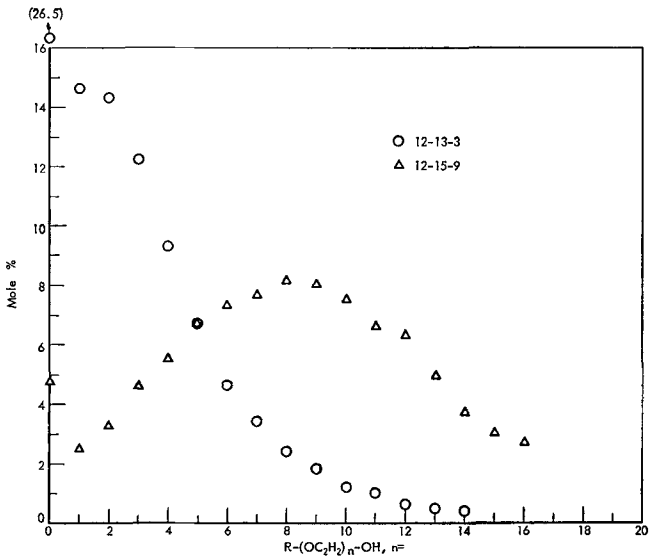

FIG. 4. Oxyethylene distributions found for some primary alcohol condensates.

of the adsorbent in the regions between separated adducts that is sometimes visible on chromatograms. This separation of the esters of the polyethylene glycols indicates that the method could also be used for determination of their oxyethylene distribution. No attempts were made to test this possibility.

In this work no interference from organic impurities, normally present in varying degrees in thin layer chromatographic adsorbents, could be detected. Blank extracts from chromatograms gave the same values as the blanks for the color reagents only; these values are low, less than 0.005 for a 5 cm path cell. Therefore chromatographic blanks were normally omitted although an occasional check, particularly when a new lot of adsorbent is used, should be made. In running color reagent blanks it is necessary to filter them even though no adsorbent is present because the 1,2-propanediamine develops turbidity on exposure to air; presumably the insoluble carbonate salt forms.

This work was concerned with relatively low condensates; products made with molar ratios of ethylene oxide to alkyl groups higher than 11 were not tried. Applicability to a somewhat higher level is expected but more work will be required to extend applicability to markedly higher ratio condensates. Two points would have to be established: quantitative recovery in the preparation of the DNB esters, and a different migration solvent capable of resolving the higher adducts. In this higher region, use of known, single adducts on the chromatogram for reference purposes to identify the separated groups, would probably be required. This requirement arises when the concentrations of the lower members of the series become too low for detection and the oxyethylene content of the first detectable zone is not obvious.

In principle, the method could also be applied to other types of polyoxyethylene condensates such as those made from secondary alcohols or alkyl phenols. The primary requirement would be that a thin layer chromatographic separation of the adducts into groups, each group containing all of the adducts having the same number of oxyethylene groups, could be obtained. A circular thin layer chromatographic separation of the DNB esters of the oxyethylene adducts of a commercial secondary alcohol condensate having a carbon number range from 11 to 15, containing the secondary alcohol isomers, and having an average molar ratio of ethylene oxide units to alkyl groups of 3, was made. The resulting chromatogram, made using chloroform (containing only the usual 0.75% ethanol preservative) migration solvent and three different amounts of the sample, 25, 50 and 75 μg, shown in Figure 3, indicated that a useful separation was obtained. However, more work would be necessary to ascertain whether the separation is on the basis of the number of oxyethylene groups. No work was done with adducts of the alkyl phenols.

This method was developed for the polyoxyethylene condensates of primary alcohols. Although it might be applicable to adducts from secondary alcohols or alkyl phenols by using appropriate migration solvents it is not applicable to mixtures of adducts from the two types of alcohols because different solvent mixtures are needed for the separation of the esters. As a result, even if separations were obtained, each of the separated zones would contain compounds having different numbers of oxyethylene units. Migration behavior of the esters of alkyl phenols has not been determined but it is unlikely that it would be the same as that of the primary alcohol esters.

This procedure has been applied to a number of polyoxyethylene condensates of mixed detergent range primary alcohols. These alcohols were in the 12 to 15 carbon number range and were mixtures. Carbon number mixtures were 12 and 13, 12 through 15, and 14 and 15 and, in all mixtures, about 75% of the carbon chains were normal or straight; the remainder were branched on the 2-carbon atom, predominately methyl with decreasing amounts of the propyl and higher isomers. Table III shows typical data obtained for both the molar and weight distributions and Figure 4 and 5 show the resulting molar distribution curves. The weight distribution curves are similar but are weighted more towards the higher members because the molecular weights are increasing. The highest discrete value of n, the number of oxyethylene groups,

TABLE IV
Repeatability of Data for Oxyethylene Distribution

N = [a]	Found, % Mole								
	12–13–3[b]				14–15–11[b]				
	Run A	Run B	Run C	Avg.	Run A	Run B	Run C	Run D	Avg.
0	26.3	26.6	26.7	26.5	3.9	4.0	4.8	4.2	4.2
1	14.5	14.6	14.6	14.6	2.3	2.4	2.6	2.6	2.5
2	14.5	13.9	14.4	14.3	2.6	2.9	3.2	2.8	2.9
3	12.3	12.1	12.3	12.2	3.5	3.3	3.3	3.1	3.3
4	9.2	9.5	7.6[c]	9.3	3.8	4.0	4.2	4.1	4.0
5	6.9	6.7	6.6	6.7	4.6	4.4	4.4	4.5	4.5
6	4.4	4.4	4.8	4.6	4.8	5.2	5.2	5.5	5.2
7	3.4	3.2	3.5	3.4	5.1	5.2	5.4	5.4	5.3
8	2.4	2.4	2.5	2.4	5.8	5.9	6.0	6.0	5.9
9	1.7	1.8	1.9	1.8	6.6	6.3	6.3	6.0	6.3
10	1.3	1.2	1.3	1.2	6.4	6.7	6.4	6.5	6.5
11	1.0	1.0	0.9	1.0	6.9	6.3	6.6	6.4	6.6
12	0.6	0.6	0.7	0.6	6.5	6.7	6.0	6.7	6.5
13	0.6	0.4	0.6	0.5	6.3	6.0	6.0	5.7	6.0
14	0.4	0.5	0.4	0.4	5.4	5.5	5.5	5.3	5.4
15	....	....	....	....	4.8	4.7	4.5	4.7	4.7
16	....	....	....	....	3.9	4.2	4.1	4.3	4.1
17	....	....	....	....	3.5	3.4	3.3	3.3	3.3
18	....	....	....	....	3.4	2.7	3.1	2.9	3.0
Higher[d]	1.2	1.2	1.1	1.2	9.8	10.3	9.3	10.0	9.9

[a] Values on n in equation $R-(OC_2H_4)_n-OH$.
[b] See section on Nomenclature in text.
[c] Omitted from average.
[d] Adducts higher than last discrete value shown.

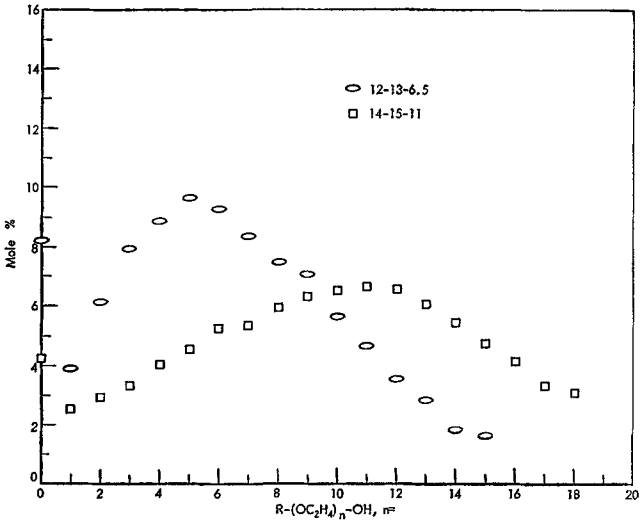

FIG. 5. Oxyethylene distributions found for some primary alcohol condensates.

shown for each sample, represents the point at which the last discrete fraction could be recovered from the chromatogram. The limiting point depends upon the distribution in the sample; condensates prepared using low molar ratios of ethylene oxide contain too low a concentration of the higher members for them to be detected on the chromatogram while, for higher molar ratios, the higher members were not resolved well enough for them to be recovered separately.

The data obtained in this work indicate that a relative precision of about ±5% was obtained. Accuracy, as measured by comparison of molar ratios of oxyethylene units to alkyl groups calculated from the distribution data and measured directly on the unseparated sample by nuclear magnetic resonance (Table II), is believed to be of the same order. Table IV shows all of the data obtained for two samples; one run in triplicate and the other in quadruplicate. Inspection of these data show that nearly all of the values are within ±0.3% absolute of the average.

In a method of this type the precision and accuracy achieved will depend, to a large extent, on the quality of the thin layer chromatographic separation and the care taken in isolating and recovering the sections of adsorbent containing the separated groups of compounds. Errors in this operation will cause part of a group to be recovered with an adjacent group and cause a corresponding error in the results. Therefore the practice in this work was to run samples in duplicate to minimize the effect of such errors and to provide an estimate of the reliability of the particular determination. Duplicate determinations also provide a means for estimating a missing value in the event that one of the many determinations made in the procedure is lost; normalizing the data for calculation requires that all values be used.

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