Determination of Oxyethylene Distribution in Condensates of Primary Alcohols With Ethylene Oxide

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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 Bürg er (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 (7) 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.

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 1/8 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 1/8 in. O.D. Teflon tubing separated the glass cover plate from the adsorbent surface.

Conventional 8 x 8 in. glass plates coated with a 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 (2X), 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 (0.2µm 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 12 dozen filter units were used.

Spectrophotometric measurements were made with an extended absorbance 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

1 Presented at the AOCS Meeting in New York, October, 1966.
at about 70°C, filter and cool in an ice bath. The product was evacuated to remove solvent and stored in a desiccator. 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 (Malinskreutz Chemical Co., No. 7G0F); 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 each of a convenient number of 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 μm 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. Recover, one at a time, the remaining section 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. 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 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 cover and place two 20 x 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 1/2 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 the 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 μm 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-