

Preparation and Evaluation of Surface-Active Brassylic Acid-Ethylene Oxide Adducts¹

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Abstract

Both liquid and solid surface-active adducts of brassylic (tridecanedioic) acid were prepared by potassium hydroxide-catalyzed addition of ethylene oxide gas to the molten acid. The number-average molecular weights (\overline{MW}_n) of the adducts ranged from 500 to 3,000. These adducts cover a wide span in the ratios of hydrophilic to lipophilic portions of the molecule. They are unique in that hydrophilic end-groups sandwich a rather long chain of lipophilic methylene units. Treatment of some adducts with hot, saturated, aqueous sodium chloride induced transesterification and produced hydroxyl-terminated, multi-brassylic, poly(ethylene glycol) esters of \overline{MW}_n 1,000 to 4,000, all of which were efficient surface-active agents.

Average degrees of polymerization of the poly(ethylene oxide) (PEO) chains were determined by a) functional group analysis, b) weight increase, and c) methanolysis of the products, followed by gas-chromatographic analysis of the isolated poly(ethylene glycol) fraction. Surface tension, critical micelle concentration, emulsion stability, and efficiency as an emulsifying agent in the aqueous polymerization of vinyl acetate were measured to evaluate surfactant properties of products in which the degrees of polymerization of the PEO chains ranged from 1.4 to 44.

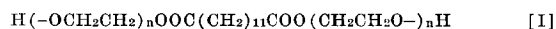
Introduction

FATTY ACID ESTERS of poly(ethylene glycol) (PEG) are efficient nonionic surfactants and lubricants (2). They are readily prepared by condensation of PEG with a fatty acid, transesterification of PEG with fatty acyl derivatives (2,8,12), or base-catalyzed addition of ethylene oxide (EO) to a fatty acid (28). The hydrophile-lipophile balance (HLB) (6) is adjusted by varying the PEG chain-length or the number of EO units added to the fatty acid. The mechanism of base-catalyzed EO addition to monocarboxylic fatty acids described by Wrigley et al. (28) and by Stockburger and Brandner (22) favors the complete conversion of the carboxyl groups to ethylene glycol monoesters before any elongation of the oxyethylene chains. (Glycol monoesters can also be called diesters of dicarboxylic acids. In this text, prefixes refer to the total number of ester linkages in the molecule. Polymers, other than diesters, up to decaesters are collectively called oligoesters.)

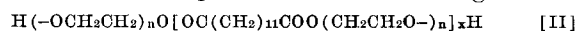
Although fatty dicarboxylic acids are used extensively in the preparation of polyesters (23), no report has been found on fatty dicarboxylic esters of PEG which possess terminal free hydroxyls. Niederhauser (15) has reacted EO with a complex mixture of polycarboxylic acids (by-product from caustic fusion of castor oil) and recovered surface-active esters of PEG that have terminal free hydroxyls. An ethylene

glycol ester, bis(2-hydroxyethyl) terephthalate, has been prepared by Kolb (9) by the reaction of EO and terephthalic acid in dimethylformamide. A similar compound, bis(2-hydroxyethyl) azelate, is commercially available as a monomer for copolyesters and urethane elastomers.

In a continuing study on the utilization of the erucic acid-rich seed oil from *Crambe abyssinica* (27), the authors have prepared brassylic (tridecanedioic) acid by oxidative ozonolysis of erucic acid (16) and have added EO in various quantities to prepare surface-active brassylic acid diesters of ethylene glycol and PEG, which were expected to have the following structure:



where n is the average degree of polymerization of the poly(ethylene oxide) (PEO) chains ranging from 1 to 50. Some of the products contained oligoesters:



and treatment with hot, saturated, aqueous sodium chloride increased their oligoester content. In Structure II, x is 2 for tetraesters, 3 for hexaesters, 4 for octaesters, and 5 for decaesters. Whether diesters or oligoesters, these products are unique in that hydrophilic end-groups sandwich a rather long chain of lipophilic methylene units. This arrangement is opposite to the monocarboxylic fatty acid diesters of PEG, which have lipophilic methylene units at the terminal positions. The surface-active brassylic acid-EO adducts ranged from 3.5 to 19.0 in HLB. Some of them were efficient emulsifiers for aqueous polymerization of vinyl acetate.

The size distribution among the PEO chains was determined by gas-liquid chromatography (GLC) of the PEG mixture which was isolated after methanolysis of the adducts.

Experimental Procedures

Brassylic Acid Purification

Brassylic acid was prepared by oxidative ozonolysis of erucic (*cis*-13-docosenoic) acid (16). A pilot-plant preparation (94% brassylic) was recrystallized from xylene (ACS, analyzed reagent) twice by dissolving one kg per liter of hot solvent and allowing it to stand overnight at 25°C. The recovered brassylic acid was decolorized by chromatography through a column of silicic acid-Celite 545 (1:2) with distilled chloroform as eluant. The colorless crystals (mp 113.5–114°C) represented 85 to 90% by weight of the pilot-plant preparation. GLC of the methyl ester (13) showed 98% purity, which would indicate 88 to 94% recoveries of brassylic acid. Remaining impurities were the homologous nonanedioic (trace), undecanedioic (1%), and pentadecanedioic (1%) acids.

Base-Catalyzed Oxyethylation

Brassylic acid (24.4 g, 0.200 equivalent) and powdered potassium hydroxide (0.3 g of 86.5%, ACS, analyzed reagent) were placed in a three-necked, 500-ml, round-bottom flask equipped with reflux con-

¹ Presented at the AOCs Meeting, Chicago, October 1967.

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denser, stirrer, thermometer, and gas inlet. The inlet and an outlet at the top of the condenser were connected to bubblers containing mineral oil that gauged the rate of EO addition and efflux. The system was flushed with nitrogen and heated to 125C. The nitrogen stream was replaced by 99.7% pure EO (7), and the temperature was maintained at 125C for 3 hr and then elevated to 155C. The uptake of EO was estimated by suspending the reaction and weighing the system. When the desired increase in weight was achieved, the system was heated under nitrogen for an additional hour. The increase in weight corresponded to 1, 5, 10, 20, or 50 moles of EO per equivalent of brassylic acid. The products were analyzed either per se, after deionization through an alumina column with dioxane as eluant, or after washing with hot, saturated, aqueous sodium chloride as described by Malkemus and Swan (10).

Analytical Constants

Acid value (AV) was determined in water, 95% ethanol, or benzene-ethanol (1:1) by titrating with standard 0.1 N aqueous NaOH to the phenolphthalein end-point under a nitrogen atmosphere. Saponification value (SV) was determined by refluxing with approximately 150% excess of 0.15 N ethanolic KOH for 45 min and titrating the excess alkali with standard 0.1 N aqueous HCl and a mixed indicator of one part cresol red to three parts thymol blue (0.04% aqueous solution). Hydroxyl value (OHV) was determined by the method of West et al. (25), modified slightly by using the acetic anhydride-pyridine reagent of Ogg et al. (18). Infrared spectrophotometry (1) was employed as a corroborative method for OHV determination.

Molecular Weights

The molecular weights of the products were determined by vapor-pressure osmometry with either dioxane (ACS, analytical grade, distilled at atmospheric pressure after refluxing with sodium) or water used as solvent (Mechrolab osmometer, Model 301A).

Solubility and Emulsion Tests

A 1% mixture (10 mg/ml) of each product in various solvents was agitated in a vibrating stirrer for 5 min at room temperature (25C) and allowed to stand for 1 hr. Its solubility was noted qualitatively

as soluble, partly soluble, insoluble, or cloudy. The emulsion test described by Martin et al. (11) was applied to 11 of the 16 products; i.e., 40 ml of a 0.10% aqueous solution of a product was shaken with 40 ml of mineral oil and the time required for 10 ml of aqueous phase to separate in a 100-ml graduated cylinder was recorded. Emulsions were also tested by the drop dispersion method (24) to determine whether they were oil-in-water or water-in-oil dispersions.

Surface Tension and Critical Micelle Concentration

Surface tension of aqueous solutions of the adducts was measured with a Cenco-du Noüy interfacial tensiometer at concentrations of 0.01 to 1,000 mg/100 ml at 25C (17). The critical micelle concentration (CMC) (3,21) was determined by plotting surface tension versus the logarithm of concentration and locating the point where a sharp change in slope occurred in the curve.

Emulsifier for Aqueous Polymerization

Initially, effectiveness of the products in emulsion polymerization of vinyl acetate was evaluated by observing the emulsion formed by a 2-min mechanical mixing of 1.00 ml of vinyl acetate (72-73C/750 mm), 6.00 ml of water, and 0.020 g of product at room temperature. For comparison, a readily available commercial surfactant, Tween 80 (polyoxyethylene-20-sorbitan monooleate, HLB = 15.0), was similarly tested. Five of the products and Tween 80 maintained emulsions for 18 hr or more whereas six others showed signs of breaking in the emulsion in less than 15 min. The five products that showed good emulsifying properties, along with Tween 80 alone, were then tested in azobis(isobutyronitrile)-initiated emulsion polymerizations by heating at 60C in a tumbler bath for 15 hr. The 20-ml polymerization tube contained 1.00 ml of vinyl acetate, 0.020 g of emulsifier, 0.010 g of initiator, and 6.00 ml of water, all in a nitrogen-saturated atmosphere. The amount of methanol-insoluble poly(vinyl acetate) recovered after thorough washing was taken as a measure for evaluating the efficiency of the EO adducts as emulsifiers.

GLC of PEG

The distribution in size of the PEO chains in the adducts was determined by GLC of the free PEG

TABLE I
Properties of Brassylic Acid-Ethylene Oxide Adducts

| Adduct No. | Moles of EO* added per carboxyl | Secondary treatment | Appearance of adduct | Melting point, C | Acid value | Saponification value | Hydroxyl value |
|------------|---------------------------------|--|------------------------|------------------|------------|----------------------|----------------|
| 1 | 1 | None | White wax | 59-63 | 0.0 | 322 | 226 |
| 2 | 6 | None | Light amber oil | -5+10 | 0.3 | 130 | 93 |
| 3 | 10 | None | Colorless oil | | 0.3 | 96 | 71 |
| 4 | | No. 3 washed with hot saturated NaCl | Colorless oil | | 0.4 | 99 | 41 |
| 5 | | No. 3 HCl-neutralized, washed with hot saturated NaCl | Colorless oil | | 0.4 | 99 | 43 |
| 6 | | No. 3 deionized | Colorless oil | | 0.3 | 104 | 52 |
| 7 | 11 | None | Dark amber viscous oil | 16-19 | 1.2 | 85 | 86 |
| 8 | 20 | None | Light yellow wax | 37-39 | 0.8 | 58 | 49 |
| 9 | | No. 8 washed with hot saturated NaCl | White wax | 37-40 | 0.3 | 62 | 30 |
| 10 | | No. 9 repeated | White wax | 36-37 | 0.3 | 57 | 28 |
| 11 | 20 | None | Light yellow wax | 36-41 | 0.2 | 51 | 38 |
| 12 | | No. 11 deionized | Yellow wax | 38-39 | 0.8 | 50 | 36 |
| 13 | 50 | None | Light yellow wax | 49-52 | 0.1 | 22 | 37 |
| 14 | | No. 13 washed with hot saturated NaCl | Light yellow wax | 50-52 | 0.1 | 24 | 33 |
| 15 | | No. 13 HCl-neutralized, washed with hot saturated NaCl | Light yellow wax | 50-52 | 0.1 | 27 | 30 |
| 16 | | No. 13 deionized | Light yellow wax | | 0.1 | 24 | 31 |

* Ethylene oxide.

TABLE II
Degree of Polymerization of Ethylene Oxide, Molecular Weight, and Hydrophile-Lipophile
Balance of Brassylic Acid-Ethylene Oxide Adducts

| Adduct No. | OHE ^a SE | n ^b | EO units per molecule of adduct | Molecular Weight × 10 ⁻³ | | | HLB ^c |
|------------|------------------------|----------------|---------------------------------|-------------------------------------|-----------------------|--|------------------|
| | | | | By VP osmometry | By end-group analysis | Calculated as diester from weight increase | |
| 1 | 1.4 | 1.4 | 3.5 | 0.55 | 0.50 | 0.34 | 6.0 |
| 2 | 1.4 | 8 | 20 | 1.3 | 1.2 | 0.8 | 14.3 |
| 3 | 1.4 | 12 | 29 | 1.6 | 1.6 | 1.1 | 15.8 |
| 4 | 2.4 | 15 | 50 | 2.0 | 2.7 | ... | 15.7 |
| 5 | 2.3 | 14 | 47 | 2.9 | 2.6 | ... | 15.7 |
| 6 | 2.0 | 13 | 38 | 2.0 | 2.2 | ... | 15.5 |
| 7 | 1.0 | 12 | 24 | 1.3 | 1.3 | 1.2 | 16.3 |
| 8 | 1.2 | 21 | 46 | 2.1 | 2.3 | 2.0 | 17.5 |
| 9 | 2.1 | 24 | 75 | 3.2 | 3.8 | ... | 17.3 |
| 10 | 2.0 | 26 | 80 | 2.8 | 4.0 | ... | 17.5 |
| 11 | 1.3 | 26 | 60 | 2.3 | 3.0 | 2.0 | 17.8 |
| 12 | 1.4 | 26 | 63 | 2.2 | 3.0 | ... | 17.8 |
| 13 | 0.6 | 40 | 65 | 2.6 | 3.0 | 4.7 | 19.0 |
| 14 | 0.7 | 42 | 73 | 3.6 | 3.4 | ... | 18.9 |
| 15 | 0.9 | 42 | 79 | 3.2 | 3.7 | ... | 18.8 |
| 16 | 0.8 | 44 | 77 | ... | 3.6 | ... | 18.9 |

^a Hydroxyl equivalent/saponification equivalent.

^b Average degree of polymerization of poly(ethylene oxide) chain.

^c Hydrophile-lipophile balance (4).

concentrate which was recovered from the products of HCl-catalyzed methanolysis of the adducts. Methyl brassylate was removed by extraction with ethyl ether from an aqueous methanolic mixture. The glycols were identified by initially utilizing the linear plot of logarithm of isothermal retention versus degree of polymerization (n in formulas I and II) of PEO chains with mono-, di-, and tri(ethylene glycols) as standards. This plot identified the components from ethylene glycol to octa(ethylene glycol), which were then used for identifying the longer glycols up to heptadeca(ethylene glycol) in the linear plot of programmed-temperature retention versus degree of polymerization of PEO chains. Since components greater than $n=8$ could not be detected by our standard procedures (13), a glass column (0.25 cm ID, 0.62 cm OD, 55.0-cm long), packed with 3% JXR on 100–120 mesh Gas-Chrom Q (Applied Science Laboratories Inc.) for on-column injection into an F&M 810 gas chromatograph and attached to a flame ionization detector, was utilized to separate components up to $n=17$. Programming rate was 8C/min starting at 50C.

Results and Discussion

Properties of Products

The number of moles of EO added per mole of carboxyl, the secondary treatment applied, the physical appearance, and the chemical constants for each product are listed in Table I.

The average degree of polymerization (n) of the PEO chains, listed in Table II, was calculated from the saponification equivalent (SE) and the hydroxyl equivalent (OHE) by a) finding the average equivalent weight of the PEO attached to each carboxyl

group (SE—brassylic equivalent), b) applying a correction factor for every PEO chain that is esterified at both ends (number of ester linkages in molecule/number of PEO chains in molecule), and c) dividing the corrected weight by the equivalent weight of monomeric EO.

$$n \text{ of PEO} = (\text{SE} - 122.16) \times \frac{2(\text{OHE}/\text{SE})}{1 + (\text{OHE}/\text{SE})} \div 44.05$$

SE and OHE were calculated from the SV and OHV listed in Table I. Evidently the simple method of gauging molecular-weight increase by EO uptake is an adequate means for attaining the desired chain-lengths of PEO in the adduct.

The number of EO units per molecule was determined by multiplying the number of PEO chains per molecule ($1 + \text{OHE}/\text{SE}$) by the degree of polymerization of each PEO chain.

The number-average molecular weight (\overline{MW}_n) by vapor-pressure osmometry generally agreed well with that by end-group analysis (Table II). The latter was calculated as follows:

$$\overline{MW}_n = 2(\text{OHE corrected for free acid}) \\ = 112,216/(\text{OHV} + \text{AV})$$

HLB (6), which can vary from 0 for pure brassylic acid to 20 for pure PEG, was calculated from the formula: $\text{HLB} = 20 [1 - (\text{SV of product}/\text{AV of brassylic acid})]$, where AV of brassylic acid is 459.3 mg KOH/g. Respective theoretical values for bis(2-hydroxyethyl) brassylate and cyclic (or high-polymer) ethylene glycol brassylate are 5.3 and 3.1.

Solubilities of the adducts in organic solvents are given in Table III. All adducts were soluble in water except that which had only 1 mole of EO added per mole of carboxyl. Adducts with 6, 10, and 11 EO

TABLE III
Solubility of Brassylic Acid-Ethylene Oxide Adducts

| Adduct No. | Solubility in Organic Solvents ^a | | | | | | | | | | | | |
|------------|---|---------|------------|---------|-------------------|--------------------|---------|---------|-------------|--------|----------|-------------|----------|
| | Acetone | Benzene | Chloroform | Diglyme | Dimethylformamide | Dimethyl sulfoxide | Dioxane | Ethanol | Ethyl ether | Hexane | Methanol | Mineral oil | Pyridine |
| 1 | Ins | Ins | S | S | Ins | Partly S | S | Ins | Ins | Ins | Cloudy | Ins | S |
| 2 | S | S | S | S | S | S | S | S | S | S | S | S | S |
| 3 | S | S | S | S | S | S | S | S | S | S | S | S | S |
| 7 | S | S | S | S | S | S | S | S | S | S | S | S | S |
| 8 | S | S | S | S | S | S | S | S | S | S | S | S | S |
| 10 | Cloudy | S | Ins | Ins | S | S | S | Ins | Ins | Ins | S | Ins | S |
| 11 | S | S | S | S | S | S | S | S | S | S | S | Ins | S |
| 12 | S | S | S | S | S | S | S | S | S | S | S | Ins | S |
| 13 | S | S | S | S | S | S | S | S | S | S | S | Ins | S |
| 14 | Ins | S | Ins. | S | S | S | Ins | S | S | S | S | Ins | S |
| 15 | Ins | S | Ins. | Ins | S | S | Ins | S | S | S | S | Ins | S |
| Tween 80 | S | S | S | S | S | S | S | S | S | S | S | S | S |

^a S = soluble, Ins = insoluble; 10 mg/ml at 25C.

TABLE IV
Surface Properties of Brassylic Acid-Ethylene Oxide Adducts

| Adduct No. | Critical Micelle Concentration, 25C | | | Surface tension dynes/cm | Emulsion Test Mineral oil-water separation, min | Emulsifier for aqueous polymerization of vinyl acetate |
|------------|-------------------------------------|-------|------|--------------------------|--|--|
| | mg/100 ml | mM | | | | |
| 1 | | | | | Insoluble | |
| 2 | 1.2 | 0.009 | 45 | 45 | 3 | Excellent |
| 3 | 1.2 | 0.008 | 45 | 45 | 4 | Good |
| 7 | 1.8 | 0.014 | 49 | 49 | 4 | Very good |
| 8 | 2.0 | 0.010 | 51 | 51 | 2 | Good |
| 10 | 3.3 | 0.012 | 53 | 53 | 2 | Fair |
| 11 | 1.0 | 0.004 | 51 | 51 | 4 | Poor |
| 12 | 2.8 | 0.013 | 52 | 52 | 6 | Poor |
| 13 | 38 | 0.15 | 52 | 52 | 2 | Poor |
| 14 | 65 | 0.18 | 52 | 52 | 4 | Poor |
| 15 | 43 | 0.13 | 54 | 54 | 5 | Poor |
| Tween 80 | 14 | | 47 | 47 | 4 | Good |

added per carboxyl were soluble in all the 13 organic solvents. Tween 80 (polyoxyethylene-20-sorbitan monooleate, HLB = 15.0) is included for comparison.

Surface properties of some adducts are listed in Table IV. Representative surface-tension curves for CMC determination are shown in Fig. 1. The 6- and 10-mole adducts (No. 2, 3) had twice as steep a slope ($d\gamma/d\ln c$) as Tween 80 in the region below the CMC. This change in surface tension per increment of concentration diminished as the amount of EO added per molecule increased. The 20-mole adducts had slopes nearly the same as that for Tween 80 whereas the 50-mole adducts had slopes only half as steep. One of the 20-mole adducts, No. 11, had an unusually low CMC and showed no tendency to level off even at rather high concentrations.

The emulsion tests showed all adducts, except the 1-mole adduct, to be efficient emulsifiers for systems with oil dispersed in water. In testing the efficiency of the adducts as emulsifiers for aqueous polymerization of vinyl acetate, the polymerization reactions were not carried to completion. Evaluation therefore was made by comparing recoveries relative to that from the Tween 80 polymerization. Recoveries less than, equal to, double, and triple that from Tween 80 were judged as fair, good, very good, and excellent respectively. The six adducts that failed the initial emulsifier test were listed as poor.

GLC of PEG

Untreated liquid adducts No. 2 and 3 and a concentrated dioxane solution of solid adduct No. 8 were injected into a gas chromatograph under isothermal and programmed-temperature conditions that ordinarily separated PEG up to heptadeca(ethylene glycol). No peaks could be detected. A concentrated dioxane solution of solid Adduct No. 13 however showed trace

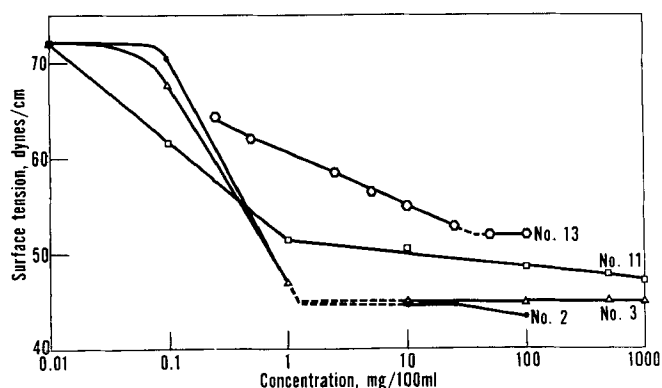


FIG. 1. Surface-tension curves for determination of critical micelle concentration of brassylic acid-ethylene oxide adducts. No. 2 = 6-mole adduct, No. 3 = 10-mole adduct, No. 11 = 20-mole adduct, and No. 13 = 50-mole adduct.

quantities of ethylene glycol and PEG of a low degree of polymerization, which probably were formed by EO addition to OH^o ions during the prolonged addition reaction of 50 moles of EO per mole of carboxyl. The OHE/SE ratio of 0.6 for Adduct No. 13 suggests the presence of free glycols which do not result from transesterification. These findings indicate the absence of any appreciable transesterification reaction, during EO addition, that would release free ethylene glycol or PEG (see discussion on oligoester formation). Yet the PEG fraction isolated from methanolysis products of Adducts No. 2 and 3 gave large peaks that covered a wide continuous spectrum of PEG sizes. The concentration versus degree of polymerization of PEO plots showed normal distributions similar to those from earlier reports (4,19,26). Fig. 2 shows the relative abundance of each PEG recovered from methanolysis of Adduct No. 2. The area-percentage by GLC does not necessarily represent weight-percentage, but the mean, mode, and median, all equal to $n = 6$, were lower than the $n = 8$ calculated for Adduct No. 2 (Table II). Apparently the relative detector response decreases with increasing polymer size. Similarly, Adduct No. 3 showed a wide dispersion ($n = 1 \sim 17$).

Oligoester Formation

When hot, saturated, aqueous sodium chloride was used to wash the adducts, as described by Malkemus and Swan (10), extensive transesterification occurred.

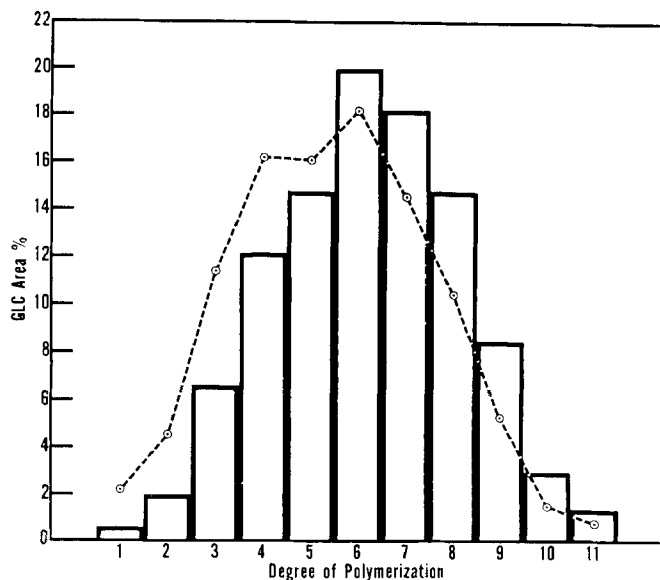
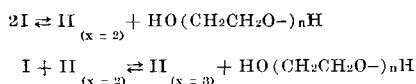


FIG. 2. Distribution of poly(ethylene glycol) recovered from methanolysis of brassylic acid-ethylene oxide Adduct No. 2. Dotted curve indicates mole %, assuming GLC area % to equal weight %.

The OHE/SE ratios for the 10- and 20-mole adducts, No. 3 and 8, increased by nearly one unit when treated with the hot brine. This change is equivalent to an interaction of all the diester molecules either with each other to form a tetraester or with other oligoesters in the reaction mixture to form oligoesters that have two additional ester linkages. For example, the OHE/SE ratio 1.4 for No. 3 indicates its equivalency to a mixture of 60% diester and 40% tetraester. The change to 2.4 after washing indicates its conversion to an equivalency of 60% tetraester and 40% hexaester.

PEG molecules are displaced during transesterification.



The mechanism proposed by Wrigley et al. (28) and by Stockburger and Brandner (22) would predict that the transesterification and PEG formation would occur before hot-brine treatment. If such a prediction were true, the OHE/SE ratio of the total reaction product, before hot-brine treatment, would be 1.0. Instead results were obtained which suggest that the primary EO addition reaction incurs side reactions of greater complexity than reported by these investigators, and the liberation of PEG occurs during the secondary hot-brine treatment.

When neither free ethylene glycol nor PEG was detected by GLC in unwashed Adducts No. 2, 3, and 8, Adduct No. 8 was further analyzed by paper chromatography but again contained no PEG. As expected, its washed product No. 9 also had none; however the washings contained a large quantity. In these experiments, paper chromatograms were developed by ascending dioxane-acetic acid-water (2:1:2 by volume) on Whatman No. 1 paper. The spots were viewed under long-wave UV light after the chromatograms were dipped into 0.015% methanolic quercetin (14). The washed and unwashed products showed a single bright blue spot at R_f 0.83. The concentrate from aqueous washings and the hydrolysate from unwashed adduct each showed two spots; a faint blue unknown spot at R_f 0.90 and a bright yellow PEG spot at R_f 0.63.

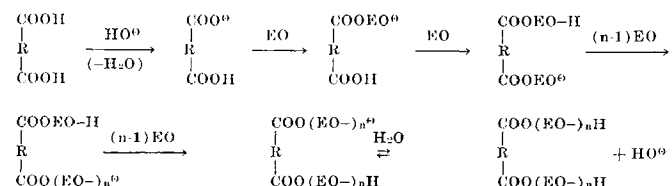
Further evidence for the incurrence of side reactions during hot-brine treatment was obtained when untreated Adduct No. 8 was dissolved and heated in distilled water at 99C for 15 min and allowed to stand for 1 hr. A dense, white precipitate formed whereas, when another portion of the same adduct was dissolved in distilled water but shaken vigorously at 25C for 15 min, the solution remained clear even after standing for two weeks. When a third portion was dissolved in 10% aqueous sodium chloride (1 g in 10 ml) and shaken vigorously at 25C for 15 min, a slight turbidity was observed after standing for 24 hr although only a small amount of precipitate formed after two weeks.

Inspection of the 10-mole Adducts No. 3, 4, 5, and 6 in Table I shows that neutralization of the excess base before hot-brine treatment failed to prevent transesterification and that the process of deionization through an activated alumina column at room temperature also induced transesterification in the adduct.

These observations warn against the indiscriminate application of purification procedures, such as hot-brine treatment, to PEG fatty esters. Furthermore the absence of free PEG in the original reaction

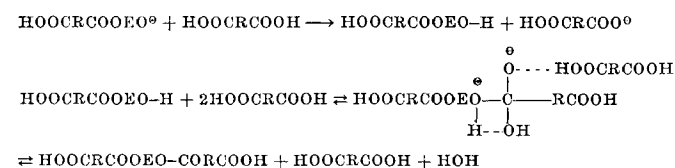
product and the product's OHE/SE ratio greater than 1.0 suggest a pathway to oligoester formation that does not require the release of a glycol molecule, $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$.

The general scheme for potassium hydroxide-catalyzed EO addition to brassylic acid is as follows:



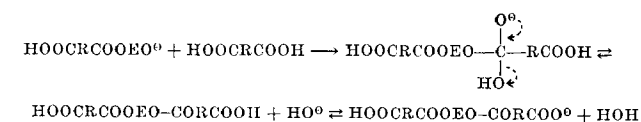
where $\text{R} = (\text{CH}_2)_{11}$. The potassium hydroxide regenerated at the end of the reaction can produce free glycols if the reaction time of EO addition is prolonged.

The origin of oligoesters formed without concomitant liberation of glycols probably lies at the early stages of EO addition. When the quantity of EO to be added is small and when the rate of EO uptake is held at a minimum, the initial adducts, surrounded by a large quantity of unreacted brassylic acid molecules in the form of a melt, would not be able entirely to avoid interaction with the brassylic acid. The ratio of nonionized carboxyl to ionized carboxylate (potassium salt) is 42 to 1 at the beginning of the reaction. Therefore the alkoxide ion, upon neutralization, would react with the abundant nonionized carboxyl (acid-catalyzed by another carboxyl) to form an ester and liberate a molecule of water.



Interaction between the hydroxyl in 2-hydroxyethyl hydrogen brassylate and the carboxylate in the mono-dissociated brassylate anion is not a logical reaction because the negatively charged carboxylate ion is not ordinarily subject to a nucleophilic attack by alcohols or their conjugate bases (5). For example, Equation 11 in the report by Stockburger and Brandner (22) should favor the reverse saponification reaction rather than the forward esterification reaction.

A nucleophilic attack by the alkoxide ion however can occur at the acyl carbon of a nonionized brassylic acid with subsequent elimination of a hydroxyl ion (20), thereby providing another route to oligoesters without liberation of glycol. The elimination of hydroxyl ion is facilitated by (i.e., it immediately reacts with) another nonionized carboxylic acid, which forms a stable carboxylate ion that can participate in an EO addition reaction.



During early attempts at preparing the 1-mole Adduct No. 1, uptake of EO ceased at less than 1 mole per equivalent of carboxyl when EO was introduced at 150–160C immediately instead of at a preliminary 125C as described in the procedures above. On two occasions only 0.81 and 0.46 mole was absorbed even after prolonged bubbling of EO. The products were essentially acid-free ($\text{AV} = 0.2, 0.0$), and the OHE/SE

ratios were 9.7 and 6.6, indicating extensive formation of linear or cyclic polyesters. The respective HLB values were 5.6 and 3.5; the degree of polymerization of the PEO chains, 2.3 and 1.3; and the \overline{MW}_n 2.9×10^3 and 2.0×10^3 . Osmometric molecular weights determined for these products were 3.3×10^3 and 2.0×10^3 , providing additional evidence for their polymeric nature. The virtual nonexistence of free glycols in these samples supports the mechanism proposed above for the formation of oligoesters without ester interchange.

Adducts with higher degrees of polymerization of PEO chains show greater stability to purification treatments. The 50-mole Adduct No. 13 showed no evidence of transesterification during the hot-brine treatment. Instead the treatment was effective in removing free glycols as originally reported by Malkemus and Swan (10). If the glycols were products of transesterification, as a side reaction during the EO addition, the OHE/SE ratio of the total system would have been 1.0. Its value 0.6 would suggest that the free glycols were produced, as discussed earlier, by the reaction of EO with the HO° ion which was regenerated when all the carboxyl groups had consumed their limit of EO. Analysis of Adduct No. 13 by GLC showed the presence of small quantities of PEG of a low degree of polymerization in the untreated adduct. Even after removal of the free glycols by hot-brine treatment, the OHE/SE ratio did not exceed 1.0, and the \overline{MW}_n remained lower than would be expected of a mixture containing oligoesters.

ACKNOWLEDGMENTS

Advice and consultation were given by R. G. Bates, W. J. DeJarlais, F. H. Otey, and J. C. Rankin.

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[Received November 6, 1967]