

# Fractionation of Ethoxylated n-Dodecanol into Molecular Species by Countercurrent Distribution and Determination of Some of Their Physical Properties

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## ABSTRACT

Ethoxylated n-dodecanol, containing an average 4.2 moles of ethylene oxide, was separated into 13 members of a series of dodecyoxypoly (ethoxy) ethanol using a 200 tube counter current distribution apparatus. Purity of each homologue was checked by thin layer chromatography, and its distribution constant, mp and refractive index were determined.

## INTRODUCTION

Ethoxylation of an alcohol, such as n-dodecanol gives an adduct ( $C_{12}H_{25}[OC_2H_4]_n-OH$ ), where n represents the average moles of ethylene oxide attached to the hydrophobe. After addition of 1 mole ethylene oxide, further addition occurs at the newly formed hydroxyl group to produce a mixture of homologues of poly (ethoxy) ethanol following a Poisson distribution (1-3). Pure homologues can be prepared by Williamson's ether synthesis for comparative determination of physical and physicochemical characteristics; but this is cumbersome, especially for the higher members in which n is above six (4-6). Accordingly, the separation of ethoxylated mixtures occasionally has been attempted using silicic acid column chromatography with mixed chloroform acetone eluents (7,8).

Countercurrent distribution (CCD) has been used for the direct determination of free polyol monoester and diester in a wide range of fatty acid ethylene oxide adducts and also to affect partial fractionation of the monoester according to polyoxyethylene chain length (9). The reaction product of a long chain alcohol-ethylene oxide adducts (10,11) was separated into homologous ethers and polyethylene glycols. However, CCD has not been used for the preparation of pure molecularly homogeneous ethylene oxide adducts. Such separation has been achieved in the present work. This method is fairly quantitative, can be used on a preparative scale, and, unlike partition chromatography, can be monitored at any stage using thin layer chromatography.

## EXPERIMENTAL PROCEDURES

### Base Materials

Dodecyoxypoly (ethoxy) ethanol was prepared by the reaction of chemically pure n-dodecanol (1 mole) with 10 moles ethylene oxide (reagent grade) in the presence of 1% NaOH as catalyst under a constant stream of oxygen-free nitrogen at a temperature of 180 C. After the reaction, the alkali was neutralized with a calculated amount of concentrated hydrochloric acid and the precipitated sodium chloride was separated. The product obtained was a light color, and was liquid at room temperature ( $n_D^{35}$  1.4460). The average moles of ethylene oxide units found by NMR spectroscopy (12) was 4.2.

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### Solvents

All solvents, except hexane (reagent grade), were of commercial grade and distilled fresh just before use.

### Apparatus

For preselection of a suitable solvent system, a small bench-scale hand operated apparatus consisting of 10 tubes was used (13). The actual separation was carried out in a 200 tube all glass fully automatic CCD apparatus (14), with a capacity of 25 ml in either phase. The robot drive mechanism was set for 6 cycles/hr, each cycle consisting of shaking to equilibration, separation of phases, and transfer of the upper phase to the next tube.

### Identification of Reaction Products

Small portions of the samples, either in the solvent system used for CCD or dissolved in methanol, were spotted on TLC plates quoted with 0.5 mm thickness of Silica Gel G. A solvent system (15), consisting of butanone saturated with water (for the lower adducts), and a solvent mixture (16) of ethyl acetate: acetone: water, 55:35:10 (v/v/v) for the higher adducts were used. The TLC plates were sprayed either with a modified Dragendorff reagent (15), producing reddish brown spots on a yellow background for the ethoxylate and red spots for the polyglycols, or with 2,7-dichlorofluorescein to reveal the unreacted dodecanol under UV light.

### Solvent System for CCD

Criteria in selecting a solvent system were: (A) quick separation of phases, implying large differences in density and surface tension of the layers; (B) large separation factors; and (C) an average distribution coefficient lying between 0.2-5.0 for the components of the mixture being separated. A number of solvent mixtures, consisting of hexane, trichloroethylene, butanol, methanol, and water, in various proportions were pretested (16). The best results were obtained with a mixture of hexane, trichloroethylene, methanol, and water in the ratio of 6:4:8:2 (v/v/v/v) equilibrated into upper and lower phases.

### Procedure

Ethoxylated dodecanol (25.8 g) was dissolved in lower phase solvent and diluted to 250 ml in a volumetric flask. Aliquots (25 ml) of sample solution then were pipetted into the first 8 tubes of the apparatus, followed by 25 ml upper phase solvent in each of the 8 sample tubes. The remaining tubes then were filled with 25 ml upper phase and 25 ml lower phase solvent. The apparatus was set for recycling so that tube no. 1 was connected with tube no. 200. The robot drive mechanism of the apparatus was set for 200 transfers. The separation was checked by TLC of every fifth tube. Tube nos. 0-25 contained n-dodecanol and  $C_{12}H_{25}(OC_2H_4)OH$  and tubes nos. 170-200,  $C_{12}H_{25}(OC_2H_4)_{17}OH$  and polyglycol. Each of these tubes was emptied and refilled with 25 ml fresh lower and upper phase solvent, and 100 more transfers were carried out. At

TABLE I

Distribution Constants, mp, and Refractive Indices of Ethoxylated n-Dodecanol ( $C_{12}H_{25}[C_2H_4O]_nOH$ )

n	Distribution constant G	Molecular wt	mp, C	$n_D^{35}$	$n_D^{40}$
1	0.06	230.4	20.1-20.5	1.4393	--
2	0.11	274.4	18.2-18.6	1.4423	--
3	0.18	318.5	16.5-17.0	1.4450	--
4	0.28	362.5	19.4-19.8	1.4472	--
5	0.39	406.5	21.5-22.4	1.4489	--
6	0.52	450.6	24.5-25.2	1.4520	--
7	0.67	494.7	22.3-22.8	1.4528	--
8	0.85	538.7	29.6-30.1	1.4545	--
9	1.09	582.8	31.9-32.4	1.4540	--
10	1.38	626.9	35.2-35.6	--	1.4530
11	1.73	671.0	35.5-36.5	--	1.4535
12	2.16	715.1	36.8-37.3	--	1.4540
13	2.68	759.2	35.5-36.5	--	1.4546
14	3.31	--	--	--	--
15	4.10	--	--	--	--
16	5.10	--	--	--	--

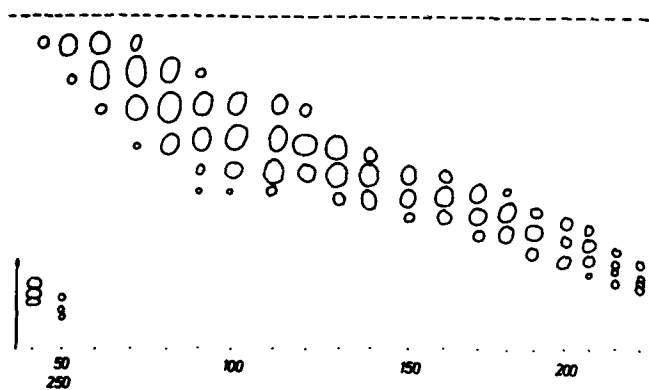


FIG. 1. Thin layer chromatogram showing separation of one fraction after 300 transfers. Solvent system: butanone saturated with water. Indicator: modified Dragendorff reagent.

this stage, almost all the tubes contained some material. The contents of all tubes, except nos. 55-90, were emptied into separate containers and set aside for further separation. The tubes were refilled with upper and lower phase and the distribution continued, checking the separation occasionally by TLC. Analogous separations were carried out with nos. 91-125, 126-160, 161-185, 186-200 and 1-10, and 11-32 and 35-45. Ca. 1200-1450 transfers were required to obtain good separations.

All fractions were checked by TLC with authentic compounds obtained by synthesis (5). Overlapping fractions were discarded. The fractions found to be pure by TLC were combined, and the solvent was removed by vacuum stripping with a nitrogen stream under minimal heat. To avoid autoxidation, 0.1% (based upon the expected wt of residue) of 4-ethyl-,2,5-bis-tert-butyl-phenol was added during solvent removal. The isolated substances were recrystallized from acetone or hexane.

## RESULTS AND DISCUSSION

### Distribution Constants

The distribution constant, G, was calculated for each homologue from the formula:

$$G = r_{\max}/(n - r_{\max}),$$

where  $r_{\max}$  is the tube number with the maximum amount of the particular homologue and n is the number of transfers affected. The results are shown in Table I. The distribution constant increases with increasing degree of ethoxylation. The number of transfers necessary to affect any

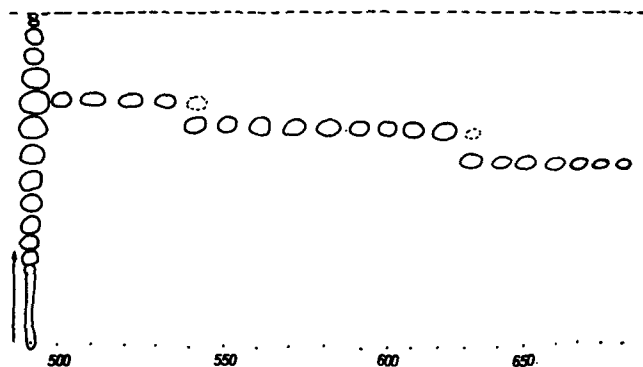


FIG. 2. Thin layer chromatograph of ethylene oxide adducts of n-dodecanol after 1450 transfers along with starting material. The 3 components were identified as homologues with 6, 7, and 8 moles ethylene oxide. Solvent system: butanone saturated with water. Indicator: modified Dragendorff reagent.

degree of separation is calculated from the distribution constant. To obtain adducts of 90% purity, ca. 1000 transfers are necessary, to get 95% purity, ca. 1250 transfers, and for 97.5% purity, ca. 1450 transfers.

The homologues present in the ethoxylated dodecanol were identified by comparison of the TLC spots with those produced by pure synthetic compounds. Figure 1 shows the TLC of a fraction obtained after 300 transfers. Every tenth tube is spotted. Some tubes contain as many as four components. The TLC is not quantitative, since an excess of substance was spotted to show up the impurity. An estimate of the homologue in tubes 620-635 showed only ca. 5.5% of contamination from the fractions in the earlier tubes 555-619 (in this series the tubes were numbered 500-699). After 1450 transfers, fractions were obtained that contained only a single component, as shown in Figure 2.

The mp and refractive indices of pure homologues of the dodecyoxypoly (ethoxy) ethanol also are shown in Table I. The mp are ca. 0.5 C lower than the best values reported in the literature, owing perhaps to the presence of the antioxidant added in the present work. However, it was not possible to isolate condensates with more than 15 ethylene oxide units in sufficient amount, since, initially, the condensates were prepared using low molar ratios of ethylene oxide resulting in lower concentrations of the higher members.

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