

of fragments would also provide insight in the performance of heterogeneous catalysts. Obviously, a pre-screening survey must be made before such detailed investigations are made. The proposed method has proved exceedingly useful in this respect.

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Analysis of Fatty Acid-Ethylene Oxide Adducts by Countercurrent Distribution¹

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Abstract

Countercurrent distribution (CCD) has been found to be a very satisfactory means for the direct determination of free polyol, monoester and diester in a wide range of fatty acid-ethylene oxide adducts in which the average polyoxyethylene (POE) chain length varies from 1-40 ethylene oxide units. A suggested procedure with three solvent systems, providing optimum separation over the entire scope of products, is presented in this paper.

Several fatty acid-ethylene oxide derivatives were analyzed and good separations were obtained as indicated by well-defined wt distribution curves. The results on POE-8-stearate verify earlier conclusions that the product consists of unesterified POE glycols and POE glycol mono- and diesters in the approximate molar proportions of 1:2:1.

CCD was also used to effect partial fractionation of the monoester according to POE chain length. The fractionation, although incomplete, is sufficient to permit estimation of polymer distribution.

Introduction

THE LITERATURE (1,2,3) reports several methods for the analysis of the products resulting from the reaction of long-chain fatty acids with ethylene oxide or POE glycols. The overall reaction results in an equilibrium mixture of free POE glycols, monoesters and diesters of the fatty acid as discussed by Birkmeier and Brandner (2).

Malkemus and Swan (1) developed a method for the analysis of POE glycol esters which they applied both to products made by esterifying POE glycol with fatty acid and to adducts of fatty acid and ethylene oxide. The free POE glycol is extracted from the product and discarded. The remaining ester portion is analyzed for saponification and hydroxyl numbers. From these constants and those of the original material, the quantities of free polyol, monoester and diester are calculated. The procedure is quite simple, but requires great accuracy in the determination of the analytical constants.

Birkmeier and Brandner (2) reported a procedure for the analysis of POE-8-stearate (Myrj® 45, Atlas Chemical Industries, Inc.). This method requires recovery and analysis of both the unesterified POE glycols and the mixed esters. The relative amounts of monoester and diester are calculated from the

saponification and hydroxyl numbers of the mixed ester portion after correcting for the small amounts of free fatty acid, ash and water which are present.

There is disagreement among the several investigators on the mole ratios of free polyol, monoester and diester in the products. Malkemus and Swan and Wrigley, Smith and Stirton (1,4,5) reported mole ratios of monoester to diester varying from 1:1-2:1. In the previously mentioned paper (2) the authors determined the mole ratio of free polyols to monoesters to diester to be ca. 1:2:1, and pointed out that this is the mole ratio expected if ester interchange is established during the ethylene oxide addition.

Since all of the foregoing estimates of composition were indirect, and, at most, involved separation of free polyol from the ester portion, but not of monoester from diester, a search for a more satisfactory separation procedure appeared desirable. Some trial was made of column chromatography which had been reported to be applicable (3), but incomplete separations were observed in our laboratory. Attention was then directed to the CCD technique developed by Craig (6).

The present paper describes the application of the CCD technique for the direct determination of free polyol, mono- and diesters in long chain fatty acid-ethylene oxide adducts. A solvent system, which had been reported by Drew and Schaefer (7) for the separation of reaction products resulting from the addition of ethylene oxide to long-chain alcohols, was found satisfactory for the analysis of products prepared with 1-8 moles of ethylene oxide/mole fatty acid. Modifications of the system were necessary for satisfactory separations of similar derivatives in which 20 and 40 moles ethylene oxide were added.

Experimental

Apparatus and Solvent Systems. The CCD apparatus employed is the Model No. 5-B (H. O. Post Scientific Instrument Co., Inc.). It has 100 cells with a capacity of 40 ml in either phase. Flasks for the evaporation of extract are extraction type, flat bottom, wide neck and 150 ml capacity.

The solvent systems used are as follows:

Solvent System Composition, % (V/V)			
System.....	A	B	C
Solvent			
Hexane.....	35	34	32
Chloroform.....	15	16	18
Absolute ethanol.....	40
3-A denatured ethanol.....	40	40
Water.....	10	10	10

¹ Presented in part at the AOCs meeting in St. Louis, 1961.

Hexane is a commercial grade solvent which is redistilled just prior to use. Chloroform is reagent grade. Denatured alcohol is formula 3-A, which consists of 5 gal commercially pure methyl alcohol added to 100 gal ethyl alcohol.

Solvents in the proportions indicated are mixed thoroughly and allowed to separate into two phases just before use. The volumes should be sufficient to yield at least 6 liters of either phase. Solvent System A is used for products containing 1-8 moles ethylene oxide/mole fatty acid. Systems B and C are used for products containing 20 and 40 moles, respectively, ethylene oxide.

Procedure. Approximately 6.25 g sample, weighed to the nearest cg, is dissolved in lower phase solvent and diluted to 250 ml in a volumetric flask. Lower phase solvent is transferred into the cells of the apparatus with the exception of the first five, which are left empty to receive the sample. Forty ml aliquots sample solution are then pipetted into the first five cells of the apparatus. Forty ml upper phase solvent is placed in each of the five sample cells, 0-4. It is also placed in the three cells, 5,6 and 7 immediately ahead of the sample cells in order to ensure conditioning of the lower phase in advance, and thus, minimize volume distortion. The robot drive mechanism of the CCD apparatus is set for 20 equilibration strokes. Time for settling is adjusted according to the time observed for the complete separation of layers following the first equilibration period. A fundamental distribution of 95 transfers is automatically carried out, using 40 ml upper phase solvent, delivered by the automatic filling device, for each transfer.

The entire contents of every second cell from 0-99 are siphoned into weighed 150-ml flasks. The solvent is evaporated on a steam bath during a period of ca. 2 hr and the residue which remains is dried in a vacuum oven at 60C for 1 hr. With products containing more than 8 moles ethylene oxide/mole fatty acid, it is advisable to pass a stream of nitrogen into the flask while on the steam bath to prevent excessive oxidative degradation of the polyoxyethylene moiety.

The flasks are finally reweighed to obtain the wt of solute. A wt distribution curve is then prepared in which wt of solute is plotted vs. cell number. Three peaks are obtained. The first, nearest cell 0, is that of free polyol. The second and third peaks are monoester and diester, respectively. The wt composition of the product is determined from the curve by adding the wt of solute contained in all of the cells under each peak. The per cent of each component is based on the total wt of the fractions in order to correct for a small loss which occurs in transferring the liquid phase to the flasks.

A somewhat modified procedure is recommended for adducts in which the mole ratio of ethylene oxide to fatty acid is less than 7 and where adducts are likely to contain significant amounts of volatile, low mol wt glycols. The contents of every second cell from 30-99 are analyzed gravimetrically in the manner previously described. However, the free polyol, which is contained within cells 0-29, must be measured by some suitable means in which there is no loss of volatile glycols (see Note 1).

Note 1. A general procedure has not been devised for the determination of the free polyol in all products containing less than 7 moles of ethylene oxide/mole fatty acid because of the volatility of the lower glycols. However, the following steps were found satisfactory for measurement of the free polyol content of one specific product in which 0.8 moles ethylene oxide were added: The combined cell contents, 0-29, were evaporated to a 5-ml vol at 60C, using a Rinco rotating evaporator and the predominantly aqueous solution which resulted was analyzed for ethylene, diethylene and triethylene glycols by gas chromatography. In this manner, both the quantity and composition of the free polyol were obtained.

Presumably the free polyol of products prepared from 2-6 moles ethylene oxide/mole fatty acid could be measured by a combination of gas chromatography and gravimetry. For example, lower glycols through triethylene could be measured before and after complete evaporation of the aqueous solution. The wt of the residue after evaporation could then be corrected for the loss of volatile glycols.

Results and Discussion

Fractionation of Fatty Acid-Ethylene Oxide Adducts into Free Polyol, Monoester and Diester. A complete analysis is easily accomplished within two days, since the countercurrent extraction may be run automatically overnight. Usually as little as 3 min is sufficient for a clean-cut separation of solvent layers. The solvent systems which are employed are unique in preventing stubborn emulsions which frequently occur when working with surface-active agents and other systems.

Wt distribution curves obtained by the CCD of various fatty acid-ethylene oxide adducts including POE-8-stearate, POE-8.5-oleate, POE-20-palmitate and POE-40-stearate (Myrj[®] 52, Atlas Chemical Industries, Inc.) show in Figures 1-5. Figures 1,2,3 and 5 represent distributions made with recommended solvent systems. Figures 4 and 5 for POE-40-stearate are both shown to illustrate the pronounced improvement in resolution effected by changing from solvent system A to solvent system C, which has a higher proportion of chloroform to hexane.

For every product which was analyzed, the material corresponding to each peak was recovered by combining the solutes encompassed by the peak. The frac-

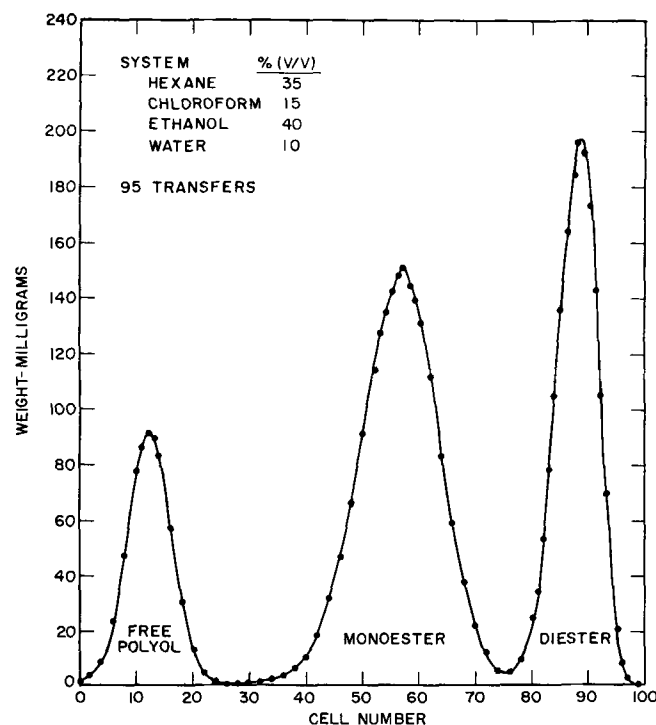


Fig. 1. CCD of POE-8-stearate, solvent system A.

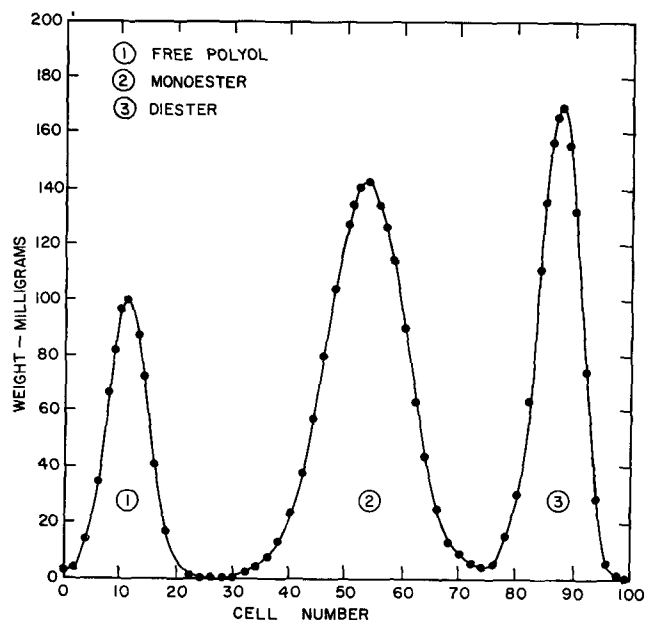


Fig. 2. CCD of POE-8.5-oleate, solvent system A.

tions were then identified by one or more of the following tests: 1) IR examination, 2) gas chromatography, 3) ester number and 4) hydroxyl number. Ester numbers were calculated from saponification and acid numbers which were determined essentially by AOCS methods (8). Hydroxyl numbers were determined by a modification of the method of West, Hoagland and Curtis (9).

POE-8-stearate was the first of the fatty acid-ethylene oxide adducts which were separated by CCD and therefore the component fractions were more fully tested than those obtained in succeeding product separations. A typical wt distribution curve for POE-8-stearate shows in Figure 1. The materials represented by the three peaks were identified as free polyol, monoesters and diesters by IR spectra, ester and hydroxyl numbers. The data which identify the fractions of POE-8-stearate show in Table I.

As expected, the IR examination of the diester showed no $-OH$, more $-COOR$ and less $-C-O-C-$ unit wt than the IR spectrum of the monoester. For

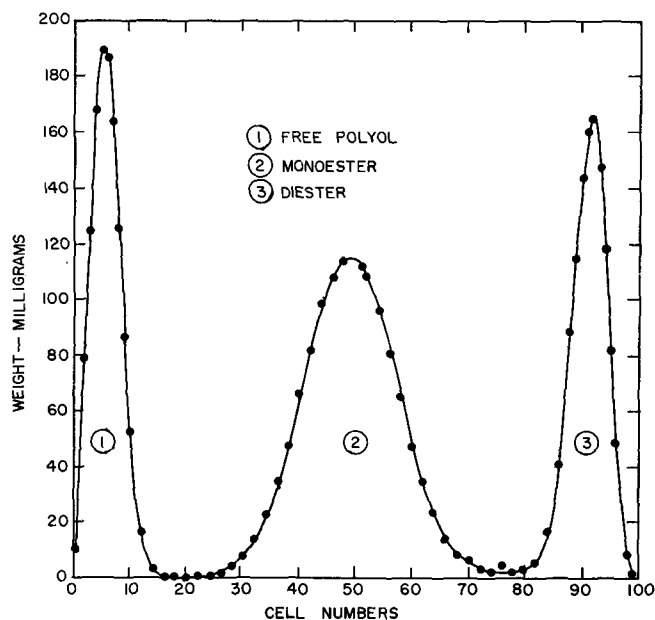


Fig. 3. CCD of POE-20-palmitate, solvent system B.

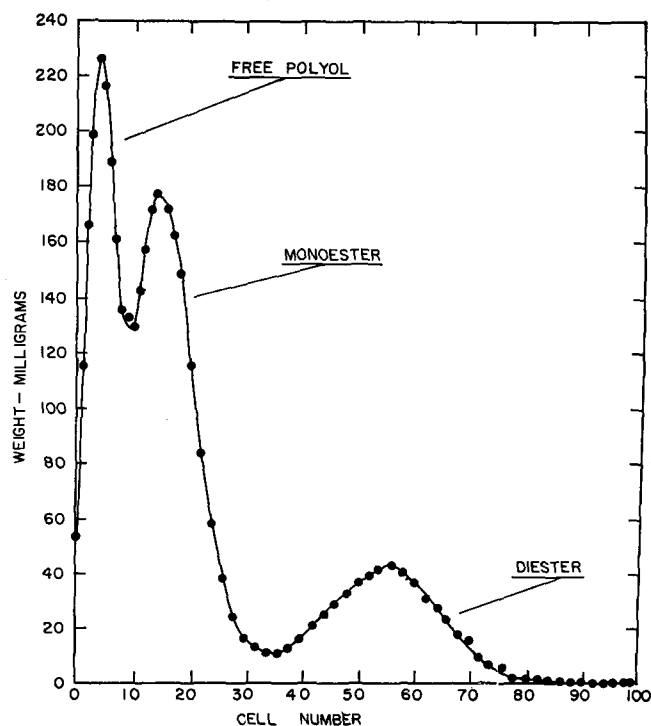


Fig. 4. CCD of POE-40-stearate, solvent system A.

all of the products tested, regardless of the solvent system used, the fastest moving fraction in the countercurrent extractor was the diester; the slowest was the free polyol.

Oxidative degradation during recovery of fractions was quite pronounced for products in which the mole ratio of ethylene oxide to fatty acid was 20 or 40. Air oxidation leads to the formation of aldehydes, acids and esters which produce falsely high saponification numbers. These can be prevented by introducing nitrogen into the flasks while heating the cell contents on the steam bath. No difficulty with air oxidation was observed for products containing 1-8 moles of ethylene oxide. Air oxidation particularly of the longer chain lengths must be prevented so that fractions may be identified by their chemical constants. This need is clearly evident from the saponification

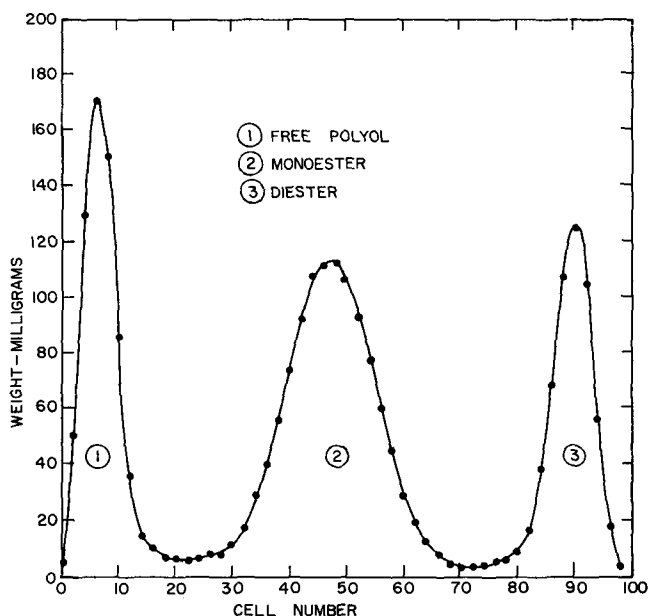


Fig. 5. CCD of POE-40-stearate, solvent system C.

TABLE I
Identification of CCD Fractions—POE-8-Stearate

	Peak 1 (Free polyol)		Peak 2 (Monoester)		Peak 3 (Diester)	
	Found	Calc'd	Found	Calc'd	Found	Calc'd
% Yield.....	17.10	49.6	33.3
% Sulfated ash.....	0.83
Acid no.....	1.3	0.0
Ester no. ^a	96.0	95	134.0	133
Hydroxyl no. ^a	316.00	338	91.0	95	0.0	0

^a Found values for ester and hydroxyl numbers are corrected for impurities. Calc'd values are derived from the acid number (208) and hydroxyl number (338) of the fatty acid and total polyol, respectively.

numbers for POE-20-palmitate in Table II.

An alkaline catalyst is usually employed in the preparation of the fatty acid-ethylene oxide adducts. The finished product therefore contains a small, equivalent amount of sodium soap which can be calculated from the sulfated ash content. Some free fatty acid may also be present in the product and can readily be estimated from the acid number.

From the data found for the CCD fractions of POE-8-stearate (Table I), it is evident that the sodium soap and the free fatty acid of the original product are recovered in the free polyol and monoester fractions, respectively. The sulfated ash and acid number balances are as follows:

Sulfated Ash—17.1% free polyol x 0.83% sulfated ash = 0.14% on original product basis versus 0.17% found.

Acid number—49.6% monoester x 1.3 acid number = 0.65 on original product basis versus 0.54 found.

The finding of the sodium soap in the free polyol fraction was expected because of the almost negligible solubility of soap in the upper phase solvent, which is predominantly hexane. Similar calculations showed that the 17% free oleic acid in POE-0.8-oleate was carried into the monoester fraction.

The observations regarding the location of free fatty acid apply to separations made with solvent system A. For other products, requiring solvent systems B or C, the location of free fatty acid, if present, can readily be determined. The yields of free polyol and monoester may be corrected for soap and free fatty acid, if the quantities indicated by the chemical constants of the original product make this desirable.

The composition of POE-8-stearate determined by

TABLE II
Effect of Air Oxidation on Saponification Numbers—CCD Fractions of POE-20-Palmitate

Fraction	Saponification number		
	Found after evaporation		Calc'd
	Air present	Air absent	
Free polyol.....	30.8	1.0	0
Monoester.....	73.3	49.0	49.3
Diester.....	100.3	85.0	81.5

TABLE III
Composition of POE-8-Stearate

Component	By countercurrent distribution			By chemical method ^a
	Uncorrected dry basis	Corrected		
		Dry basis	Dry, soap-free, fatty acid-free basis	
% Sodium soap.....	0.7
% Free polyol.....	17.1 ^b	16.4	16.6	15.6
% Free fatty acid.....	0.3
% Monoester.....	49.6 ^c	49.3	49.8	48.9
% Diester.....	33.3	33.3	33.6	35.5

^a Method of Birkmeier and Brandner (2).

^b Contains sodium soap.

^c Contains free fatty acid.

TABLE IV
Weight Per Cent^a and Mole Ratio^a of POE-8-Stearate Fractions

Batch of POE-8-stearate	Wt %			Mole ratio		
	Free polyol	Monoester	Diester	Free polyol	Monoester	Diester
A.....	16.6	49.8	33.6	1.16	2.12	1.00
B.....	17.0	49.6	33.4	1.20	2.12	1.00

^a On a dry, soap-free, fatty acid-free basis.

CCD shows in Table III, both on an uncorrected and a corrected (for soap and ash) basis. For comparison, the composition of the same lot determined by the method of Birkmeier and Brandner (2) is included.

With POE-8-stearate the correction for soap and free fatty acid does not seriously change the proportions of the major fractions as obtained directly from the CCD wt distribution curve.

Table IV shows the composition of two different batches of POE-8-stearate in terms of both wt per cent and mole ratio, expressed on a dry, soap-free, fatty acid-free basis.

The average mol wt of the free polyol used to convert wt per cent to moles was calculated from the hydroxyl number of the free polyol fraction, after correcting for the soap present. The mol wt of the mono- and diesters were calculated from their ester numbers. The mole ratio of free polyol to monoester to diester is approx 1:2:1. These results are in agreement with those in the literature (2), namely, an average mole ratio of 1.12:1.99:1.00 for free polyglycols, monoester and diester, respectively. As pointed out in the cited paper, the slight deviation from a 1:2:1 mole ratio can be accounted for by the basic catalyst and traces of water in the reactants.

The polymer length (average number of oxyethylene units) of the free polyol was determined from its hydroxyl number. The polymer lengths of the monoesters and diesters were calculated both from the ester number and from the per cent oxyethylene (10) of fractions separated by CCD. These data (Table V) show that the three component fractions of POE-8-stearate have essentially the same polymer length.

The compositions of the various other fatty acid-ethylene oxide adducts which were analyzed by CCD are listed in Table VI.

Data in Tables III and IV show that corrections for soap and free fatty acid are minor except for POE-0.8-oleate. It was considered needless to apply corrections to the CCD yields of free polyol, monoester and diester obtained from the higher mol wt prod-

TABLE V
Polymer Length of POE-8-Stearate Fractions^a

	Free polyol	Monoester	Diester
Ester no.....	95.60	133.70
Polymer length from ester no.....	7.20	7.21
% Oxyethylene (C ₂ H ₄ O).....	59.90	37.30
Polymer length from % C ₂ H ₄ O.....	7.17	7.07
Hydroxyl no. (OH no.).....	316.00
Polymer length from OH no.....	7.67

^a Data shown for free polyol are corrected to a soap-free basis; data for monoester are corrected to fatty acid-free basis.

TABLE VI
Composition of Fatty Acid—Ethylene Oxide Adducts by CCD

Fatty acid Moles ETO.....	Description of adduct				
	Oleic 0.8	Oleic 8.5	Oleic 20	Palmitic 20	Stearic 40
	Wt per cent				
Sodium soap.....	1.3	0.6
Free polyol.....	0.8	17.6	30.2	24.1	28.5
Free fatty acid.....	17.3	0.3
Monoester.....	66.4	49.8	46.2	49.3	47.8
Diester.....	14.2	31.7	23.6	26.6	23.6

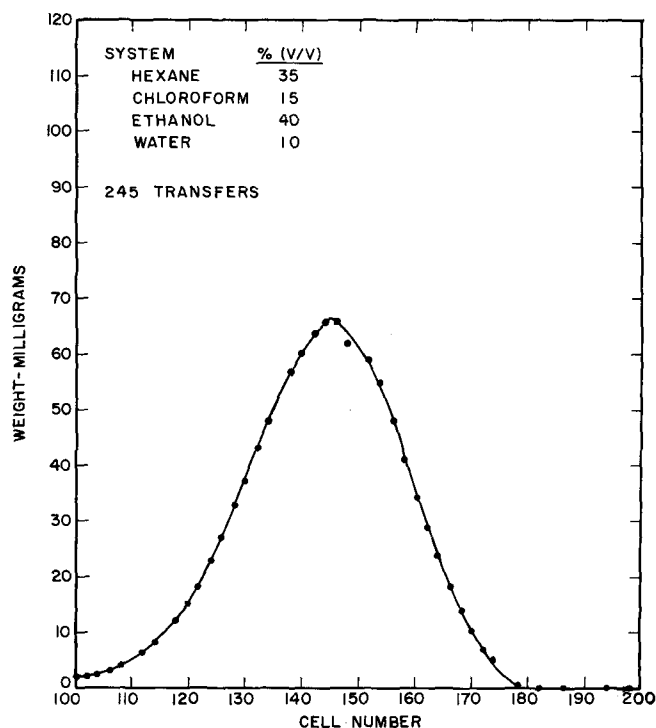


Fig. 6. CCD of POE-8-stearate monoester fraction, solvent system A.

ucts containing 20 and 40 moles ethylene oxide.

Fatty acid-ethylene oxide adducts are esters. Similar products are often manufactured by the direct esterification of POE glycols with fatty acids. Consequently, the CCD technique described in this paper should also be applicable to such products, within the mol wt range of the fatty acid-ethylene oxide addition products which have been studied.

Polymer Distribution of Monoester Fraction of POE-8-Stearate. A study was made of the feasibility of fractionating POE-8-stearate monoester according to the length of the POE chain by CCD. Using solvent system A, the monoester was quantitatively sep-

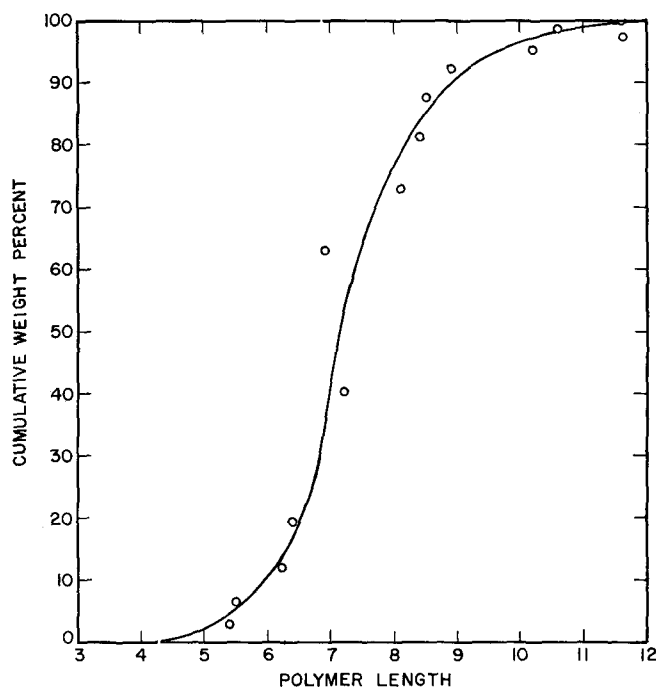


Fig. 7. Polymer length distribution of POE-8-stearate monoester fraction.

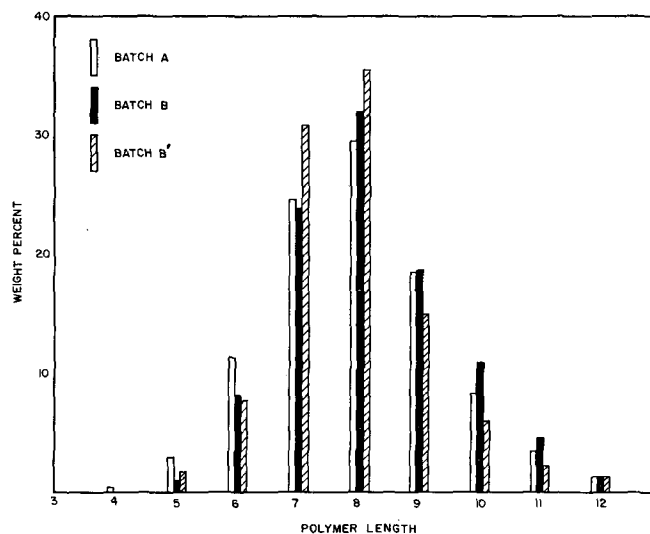


Fig. 8. Polymer distribution of POE-8-stearate (polyol basis).

arated from free polyol and diester by the application of 127 transfers. The separation involved removal of the diester by the single withdrawal technique and removal of free polyol by siphoning the contents of cells 0-30 at the completion of the distribution. The emptied cells were refilled with fresh solvent phases and the monoester fraction remaining in the instrument was recycled for 118 more transfers, making a total of 245. A typical wt distribution curve for POE-8-stearate monoester after 245 transfers shows in Figure 6.

The solutes recovered from successive groups of four cells were subjected to saponification number determinations. The average mol wt and polymer length of each fraction was calculated from the saponification number. An integral distribution curve was prepared, plotting polymer length against cumulative wt per cent (Fig. 7).

The polymer distribution of the POE glycol in the monoester portion of POE-8-stearate was then calculated from the integral curve. Figure 8 shows, by a bar graph, the results of three different determinations on two batches of POE-8-stearate. The percentages are expressed on the polyol basis. These values differ somewhat both from the values predicted by Flory (11) and those obtained by Birkmeier and Brandner (2) by fractional distillation. Examination of several of the fractions showed them to be contiguous mixtures of polymers. This work shows that CCD has some merit as a rapid means of obtaining an approx polymer distribution, but lacks discrimination.

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