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Fractionation of Some Polyethenoxy Lauryl Ethers

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WHEN ETHYLENE OXIDE is condensed with a fatty acid, alcohol, or alkylphenol to form polyethenoxy nonionic detergents, the average number of ethenoxy groups can usually be determined from the weights of starting materials or, in the case of the ester-type products, from saponification equivalents (1). It would be of interest to determine the exact composition and the distribution of ethenoxy groups in various ethenoxy substituted ethers or esters. The present paper deals with the molecular distillation of ether-based nonionic detergents prepared from lauryl alcohol and analysis of the various fractions to obtain such a distribution curve. In addition, detergency data are presented for the individual fractions illustrating the effect of ethenoxy substitution on soil removal and whiteness retention.

The nonionics reported herein were chosen in such a manner that the hydrophobic group would be a single substance rather than a mixture of isomers, and the molecular weight of the hydrophobe and hence of the nonionic was kept rather low in order to avoid decomposition. Distribution curves for the polyethylene glycols have been calculated by Flory (2) according to Poisson's Law, and experimental results obtained by molecular distillation of polyethylene glycol (3) support the theory.

Preparation of the Polyethenoxy Ethers

Lauryl alcohol (m.p. 21-22°C.) was condensed with ethylene oxide, using 0.5% by weight of potassium hydroxide catalyst according to directions previously described (4). The refractive index and composition of the products chosen for molecular distillation are recorded below.

Polyethenoxy lauryl ether A (6.88 ethenoxy units) was prepared by condensing 163 g. of ethylene oxide with 100 g. of the alcohol while B (9.90 ethenoxy units) was made from 234 g. of ethylene oxide and 100 g. of lauryl alcohol. A and B gave refractive indices (N_D^{20}) of 1.4564 and 1.4580, respectively.

Prior to distillation 100 ml. of the nonionic ether were treated with the exact amount of concentrated hydrochloric acid required to neutralize the potassium hydroxide used in the condensation.

Molecular Distillation and Analysis

One hundred ml. of each of the polyethenoxy lauryl ethers were carefully fractionated at approximately 0.02 mm., using a short-path type distillation apparatus, into 3 ml. fractions, each of which was analyzed by a carbon determination as well as by refractive

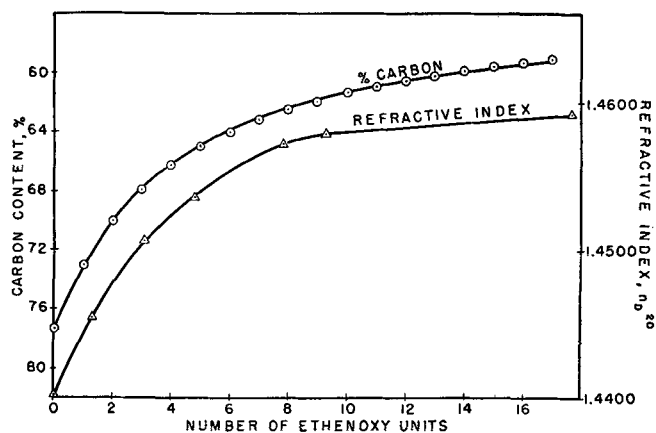


Fig. 1. Variation in carbon content and refractive index with ethenoxy chain length of polyethenoxy lauryl ethers.

index. Figure 1 illustrates the change in ethenoxy units of the lauryl ether with carbon content as well as with refractive index. The latter values were obtained by preparing a variety of lauryl ethers with a known average number of ethenoxy groups and measuring the refractive index of each composite sample. It was later found that refractive index values could be correlated fairly well with the carbon determinations on the individual distilled samples. After distillation a curve was plotted for variation

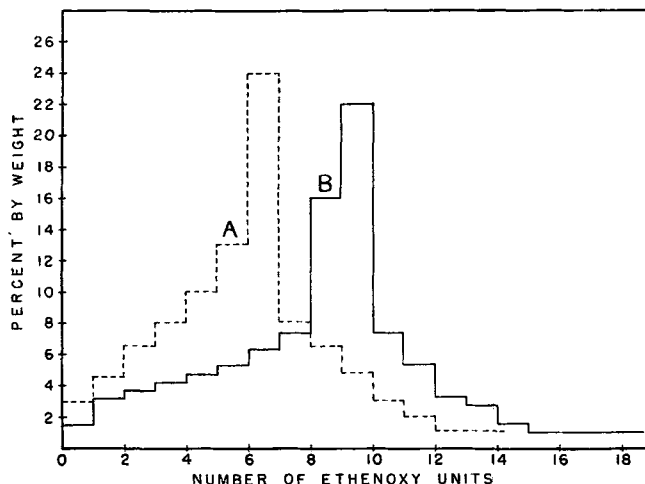


Fig. 2. Distribution of polyethenoxy lauryl ethers in terms of weight proportion at each ethenoxy level. (A = 6.88 and B = 9.90 ethenoxy units.)

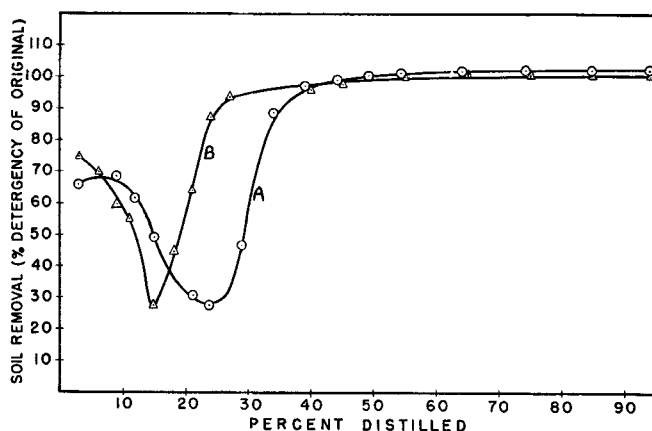


Fig. 3. Variation in soil removal in soft water with percentage polyethenoxy lauryl ether distilled. (A = 6.88 and B = 9.90 ethenoxy units.)

in ethenoxy content with each 3-ml. sample of the distillate, and from these curves Figure 2 was constructed. This latter figure illustrates percentage by weight of total distillate at each ethenoxy level. That pure isomers were obtained at each level should not be inferred. It should be noted that the distillation range in both cases was 125–250°C. with the bath temperature at the end being in the 350–370°C. range. Toward the very end of both distillations it was noted that the pressure rose to 0.07 mm., and some slight decomposition occurred. It would therefore be quite difficult to distill nonionic ethers with longer ethenoxy chains or with much larger hydrophobic groups. An attempt was made to distill a lauryl ether with an average of 14 ethenoxy units. However the latter portion of the distillate darkened considerably, indicating possible decomposition.

Detergency Data

It seemed desirable to assay the various fractions obtained for soil removal and whiteness retention values (5) in soft water in comparison with the original (undistilled) lauryl ether taken as the standard (100%). Therefore 0.4 g. of each distillate from the 6.88 ethenoxy ether admixed with 1.6 g. of builder

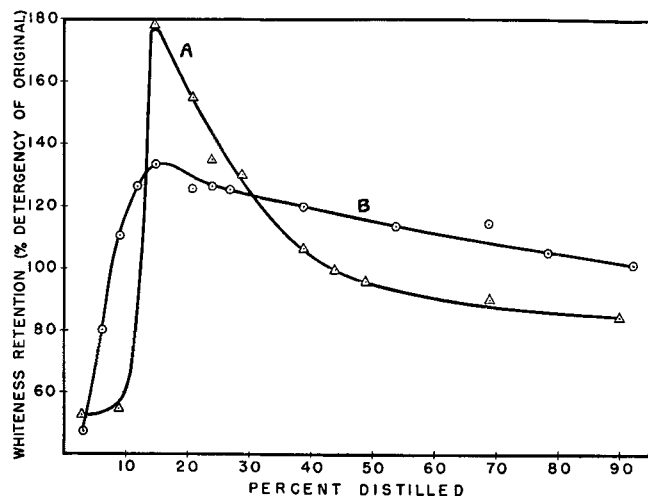


Fig. 4. Variation in whiteness retention in soft water with percentage polyethenoxy lauryl ether distilled. (A = 6.88 and B = 9.90 ethenoxy units.)

(see Ref. 4 for composition) per liter were compared (Curve A) to similar quantities of the original 6.88 ethenoxy ether and builder for both soil removal (Figure 3) and whiteness retention (Figure 4). In the same way the built fractions from the lauryl ether, containing 9.90 ethenoxy units, were compared to the built 9.90 ether taken as 100% (Curve B on Figures 3 and 4).

Discussion of Results

It becomes evident from Figure 1 that, once the standard curves are prepared, the ethenoxy content of a substance with a pure hydrophobic group can be analyzed by the carbon value or by refractive index. However above 10 ethenoxy units any analysis becomes progressively less dependable.

Based on these analyses, the distribution curves of the two lauryl ethers, A with 6.88 and B with 9.90 ethenoxy units, respectively, are shown on Figure 2. The curves, in general, follow the theoretical distribution curves for the polyglycols proposed by Flory (2). In a talk before the Glycerine Producers Association Bramston-Cook (6) mentioned that the ethylene oxide condensate from isomeric nonylphenols with an average of 10 ethenoxy units will have a wide variety of chain lengths present with approximately 80% falling between eight and 16 ethenoxy units. By comparison our studies, e.g., with the 9.90 lauryl ether, reveal that about 60% of the distillate falls between eight and 16 ethenoxy units.

Detergency assays on the individual fractions from both ethers A and B indicate some rather startling results. In both cases the soil removal curve takes a downward trend until about 24% of A or 15% of B (4–5 ethenoxy units) are distilled, after which the soil removal attains about the same detergency as the original sample, remaining so throughout the remainder of the distillate. The optimum soil removal for A is reached at about 40–50% of distillate (6–7 ethenoxy units) and for B at about 30–40% (7–8 ethenoxy units). However the whiteness retention assay is somewhat remarkable in that the peak values are obtained in the low ethenoxy range, in fact, where soil removal is very poor, and then declining slowly throughout the rest of the distillate. For example, the highest whiteness retention for A and B is reached at about 15% of the distillate (3–4 ethenoxy units for A and 4–5 for B). These data would indicate that soil removal and whiteness retention are not as interrelated as one would suppose and that a single substance with good soil removal characteristics need not possess good whiteness retention. It should also be pointed out that in a practical sense it is indeed fortunate that nonionics possess the type of distribution of polymers to include materials which give both good soil removal and whiteness retention properties to the final product.

This inflection in the whiteness retention curve at low ethenoxy substitution was noted in the earlier work on the ethers (4) particularly with the decyl ether. However it is demonstrated much more emphatically herein.

Summary

Molecular distillation was applied to the fractionation of lauryl ether-ethylene oxide condensates. It was shown that the distribution, in general, follows Poisson's Law as applied to polyethylene glycols by

Flory. Detergency studies on the individual fractions indicate optimum soil removal at approximately seven ethenoxy units and optimum whiteness retention at about four ethenoxy units.

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Determination of Soaps by Ion Exchange Resins

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SALTS OF ORGANIC ACIDS are commonly analyzed by combustion to the sulfate or carbonate (1, 2). The sulfate is determined gravimetrically while the carbonate is determined by the usual volumetric procedure. Non-aqueous titration in ethylene-glycol-isopropanol solvent has recently been adapted to the determination of carboxylic acid salts (3, 4). Salts of high molecular weight fatty acids, such as the soaps, are commonly analyzed by acidification followed by ethyl ether extraction of the water-insoluble fatty acid (5).

The use of cation exchange resins for the determination of salts of organic acids has been reviewed by Samuelson (6). Van Etten and Wiele employed Dowex 50 resin to convert organic salts to the free acids (7). These studies were concerned mainly with the determination of short chain, polybasic, and aromatic acids.

A rapid method for the determination of soap in the presence of neutral fat was desired. The use of cation exchange resins with organic solvents proved successful. The analysis of pure soap solutions prepared from authentic fatty acids was studied. Conversion of soap to fatty acid averaged 99.80% recovery. A single determination could be run in 20-30 min. The soap in a series of commercial products was also determined by the method. The total fatty acid values were compared with values obtained by extraction and titration.

Materials Required

Dowex 50 ion exchange resin
 Chamber burette, 100-ml. capacity
 The neck above the chamber is removed, leaving a reservoir of approximately 45 ml. above the graduated burette.

Standardized 0.1N alcoholic sodium hydroxide
 Standardized 0.1N alcoholic potassium hydroxide
 Phenolphthalein indicator, 1% in 95% Alcohol
 Ethyl alcohol, formula 3A containing 5% methanol and 5% water
 Benzene, C. P.

Column Preparation

The resin was prepared for use by allowing 50 g. to stand overnight in 6N hydrochloric acid. It was washed 6 times by decantation with 200-ml. volumes of distilled water. A volume of 200 ml. of 50% alcohol was added to the resin and allowed to remain in contact for 1 hr. The resin was then washed six times with 50% alcohol and twice with 95% alcohol by decantation.

A glass wool plug 2 cm. in length was placed next to the stopcock in the burette. The burette was filled with alcohol, and the resin was added slowly with tapping. A bed of approximately 45 ml. of resin was added. Alcohol was then passed through the column until 150 ml. of effluent consumed no more than 0.3 ml. of 0.1N caustic.

A column so prepared has a total capacity of 90 milliequivalents. In actual practice the resin was replaced after 15-20 milliequivalents had been passed through. No attempt to test the effective capacity of the column was made.

Analysis of Synthesized Soap

A 0.2- to 0.5-g. sample of fatty acid was placed in a 150-ml. beaker and dissolved in 20-30 ml. of alcohol. Three drops of phenolphthalein indicator were added, and the fatty acid was titrated to the first permanent pink with standard alcoholic base. The volume of base was recorded, and the milliequivalents of soap formed was calculated. This alcoholic soap solution was then passed through the column at a rate of 6-8 ml. per minute. It was followed by 100 ml. of alcohol.

The effluent, totaling *ca.* 150 ml., was collected in a 250-ml. Erlenmeyer flask. Three drops of phenolphthalein indicator solution were added, and the fatty acid was titrated with the same strength base used to form the soap. The volume was recorded, and the milliequivalents of fatty acid were calculated. A blank amounting to the total volume of alcohol in the effluent was passed through the column and titrated. This value was subtracted from the final titration.

Results

The conversion and subsequent analysis of 13 soaps are presented in Table I. Average recovery was 99.80%. The lauric, myristic, and palmitic acids were

TABLE I
 Conversion and Analysis of Typical Synthesized Soaps

Soap	Milli-equivalents Added	Milli-equivalents Recovered	% Recovered
Potassium heptanoate.....	3.234	3.216	99.44
Potassium pelargonate.....	3.938	3.927	99.72
Potassium caprate.....	1.710	1.702	99.53
Sodium undecylenate.....	3.843	3.843	100.00
Potassium laurate.....	2.055	2.060	100.24
Sodium laurate.....	1.959	1.959	100.00
Potassium myristate.....	2.278	2.277	99.96
Potassium palmitate.....	1.149	1.143	99.48
Sodium palmitate.....	1.097	1.097	100.00
Potassium stearate.....	1.785	1.789	100.22
Sodium oleate.....	1.157	1.143	98.79
Potassium oleate.....	2.550	2.550	100.00
Potassium linoleate.....	2.974	2.974	100.00

Average Recovery = 99.80%.