

Quantitative Analysis of Ethoxylated Alcohols by Supercritical Fluid Chromatography¹

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This work was undertaken to develop a relatively simple, rapid, reproducible and accurate method for measuring the ethylene oxide distribution, overall ethylene oxide ratio, and percent free alcohol in ethoxylated alcohols. Using single isomer ethoxylate standards comprised of from one to eight ethylene oxide units per alcohol, a response factor correlation for the flame ionization detector on a supercritical fluid chromatograph was established. Response factors for ethoxylates with higher than eight ethylene oxide units were estimated by extrapolation of this correlation. Supercritical fluid chromatographic separation of ethoxylates was accomplished using a density-programmed carbon dioxide mobile phase and a poly(dimethylsiloxane) coated open tubular column. The validity and accuracy of this method was demonstrated by comparing its results for unreacted alcohol levels, ethylene oxide-to-alcohol average ratios, and weights of samples injected relative to internal standards with values measured independently by standard methods. In addition, supercritical fluid chromatographic determinations of ethylene oxide molar distributions are in agreement with theoretical Weibull-Nycander distributions.

Ethoxylated alcohols are widely used as nonionic surfactants in detergents, wetting agents and emulsifiers. They are prepared both commercially and in the laboratory by the addition of ethylene oxide (EO) to aliphatic alcohols. Under base catalyzed conditions, the distribution of oligomers in the product having different numbers of ethoxy groups is determined mainly by the relative rates of the initiation and propagation ethoxylation steps. Because this distribution can affect the chemical and end-use properties of these surfactants, its reliable determination is important for both performance and quality control considerations.

High performance liquid chromatography (HPLC) has been used for the separation and measurement of EO oligomers in ethoxylated alcohols (1-5). Because these compounds have no significant near-ultraviolet absorption, they must be derivatized before HPLC analysis with a UV detector (1,2). HPLC has the advantage that the molar response factors for the individual derivatized oligomers can be taken to be equal to each other. However, this advantage must be weighed against the time required for each analysis and against the need for a separate gas chromatographic analysis to determine the alcohol and low-ethoxy ethoxylate contents. Flame ionization detectors (FID) with HPLC have been used to analyze ethoxylated alcohols (3), but this is not a detector conveniently used with HPLC, and reproducibility is difficult to achieve. Refractive index detectors are also not suitable for HPLC analysis because they are not easily used with gradient elution, which is needed to separate high ethoxy content oligomers (4).

Analysis by conventional gas chromatography (GC) is currently limited to oligomers containing relatively few, that is, less than about 5 EO units (6), although high temperature GC recently has extended this range to 10 to 14 EO units (7). Converting the ethoxylates to esters, which are more volatile and therefore more amenable to GC separation, can extend the former procedure to higher oligomers. Separate peaks for adducts with up to 13 monomers of EO have been obtained for an ethoxylate derived from dodecyl alcohol (8). Probe distillation chemical ionization mass spectrometry has been used to determine the EO distribution in complex mixtures, and good agreement was obtained between its results and GC analysis of a simple mixture (9). However, this method requires relatively sophisticated equipment and expertise which are not readily available in routine laboratories. A recent publication (10) proposes the use of thin layer chromatography with flame ionization detection for the determination of EO distributions in nonionic surfactants. The procedure involves separation of the oligomers with silica gel coated rods, development of the rods in two separate solvent systems, and passing the rods through an FID. Unreacted alcohol and monoethoxylate concentrations are typically determined as a sum because of peak overlap. The authors also indicate that analysis by the thin layer chromatography method is difficult when oligomer distributions contain higher than 12-14 EO units. Detailed reviews of the analysis of nonionic surfactants, including ethoxylated alcohols, have been published elsewhere (11,12).

Supercritical fluid chromatography (SFC) has been shown to be an effective method for separating EO oligomers in ethoxylated alcohols (13,14). An excellent review of this analytical procedure has been published recently (15). However, to our knowledge it has not been developed beyond the point of producing results in area percentages (16). We are reporting here a simple-to-use SFC method which obviates all of the limitations of the above discussed methods and which yields mole percentages of the individual oligomers. In addition, the concentrations of unreacted alcohol and overall average EO/alcohol ratios are obtained in the same run.

EXPERIMENTAL

Materials. Standard mono-disperse ethoxylates containing 1-8 EO units used to determine SFC-FID response factors were purchased from Nikko Chemical Co., Ltd. Purity of each single isomer was shown by the supplier to be greater than 98% by high temperature GC. General reagents, such as the alcohols, EO and catalysts used in ethoxylations, were of analytical grade or higher purity.

Procedures. Alcohol ethoxylations were carried out batch by batch in a one-l, stirred autoclave at temperatures from 100 to 150°C. The autoclave was charged with alcohol and catalyst, the latter usually being anhydrous potassium alkoxide prepared beforehand from potassium hydroxide and the alcohol to be ethoxylated. EO was then

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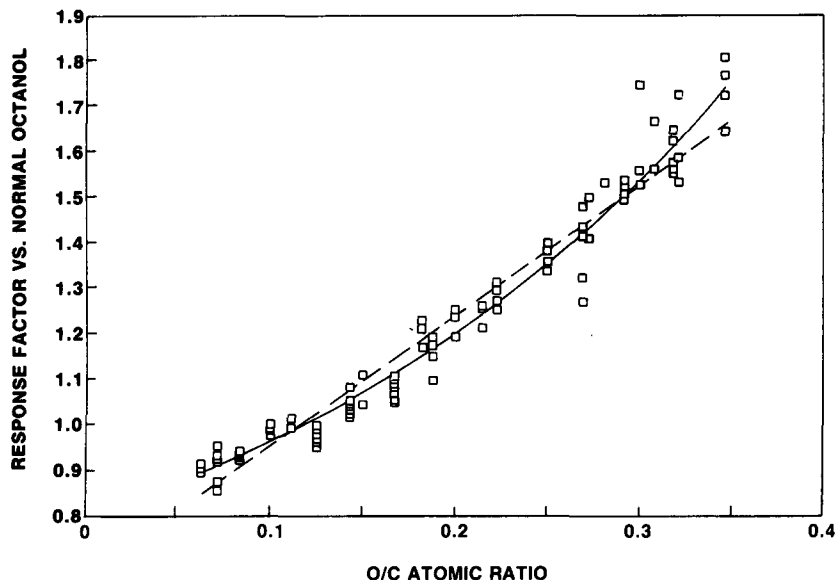


FIG. 1. SFC-FID response factor as a function of oxygen-to-carbon ratio in standard ethoxylated alcohols (open squares, data points; dashed line, linear transformation correlation; response factor, $2.85 \times (O/C) + 0.67$; solid curve, transformed dependent variable correlation); response factor = $[1/(1.12 - 1.054 \times (O/C))]^2$.

added from a weigh tank to a predetermined pressure. The system was isolated and EO allowed to react until no further pressure decrease was observed. EO addition was repeated intermittently until the desired amount of ethoxylation had taken place. Product alcohol ethoxylate was recovered after removing the basic catalyst by hot filtration through acidic clay.

Proton NMR was used to determine the overall average EO/alcohol ratio by determining the number of protons attached to carbon atoms that have no adjacent oxygen atoms relative to the number of protons that do have oxygen atoms adjacent to their carbon atom. This ratio is obtained directly from the integrated NMR results and, based on the chemical formula for the ethoxylate, is also equal to $(2n + 1)/(4m + 2)$, where n is the alcohol carbon number minus one and m is the average number of moles of EO/mole of alcohol.

Conventional GC methods using methyl benzoate as an internal standard were used to determine independently the amounts of unreacted alcohol present in ethoxylated alcohol samples.

SFC analyses were performed with a Lee Scientific Model 501 unit equipped with an FID detector interfaced with a Hewlett-Packard 1000 computer and 3357 Laboratory Automation System software. Separation of ethoxylates was achieved using a 20-m long, poly(dimethylsiloxane) coated, 100-micron i.d. capillary column, porous frit restrictor, and carbon dioxide as the supercritical eluent at a flow rate of ca. 0.5 cc/min through the column. The density of the latter was programmed asymptotically from 0.20 to 0.72 g/cc after a 2-min hold at initial conditions. The SFC oven and FID temperatures were held constant at 100°C and 375°C, respectively, throughout the analyses, which typically required one hour. All samples and standards were dissolved at about 5% by volume in acetone and injected using an LC automatic sampler with the sample valve held at 10°C.

RESULTS AND DISCUSSION

Determination of response factors. Earlier work in our laboratories had established a correlation between the response factors of various oxygenated hydrocarbons for GC-FID analyses and their oxygen-to-carbon atom ratios. Because standard single isomer ethoxylates containing more than eight moles of EO/mole of alcohol were not readily available to us, we tested whether anything similar to our previous correlation would also apply in SFC-FID analysis. The response factors relative to normal octanol were measured for ca. 80 samples of standard ethoxylates of C-10, C-12, C-14 and C-16 normal alcohols containing 1–8 EO units. Figure 1 shows the correlation between these response factors and the oxygen-to-carbon atom ratio, using both a linear regression of the raw data and the best transformed-variable regression found. In this work, the latter equation was used to calculate response factors and to extrapolate them for ethoxylates containing higher amounts of EO. Using the oxygen-to-carbon ratio, a large change in EO content (from 8 to 25 units) can be represented by a relatively small change in atomic ratio (from 0.35 to 0.42 for a C-12 ethoxylate system), thereby introducing significantly less error into the extrapolation to high EO levels. Periodically, and whenever changes (such as alteration of the sample flow-split ratio) were made in the SFC, the response factor correlation was re-determined.

Comparison of SFC results with standard methods. In order to test the validity of these response factors, ethoxylations of normal octanol and 2-ethylhexanol separately and also as a 1:1 mixture, were carried out at three EO/alcohol ratios, nominally 3, 6 and 9. The products were analyzed for average EO content and percent unreacted alcohol by conventional methods and by SFC. A hand drawn copy of a typical SFC of an ethoxylate made from the mixture of normal octanol and 2-ethylhexanol is

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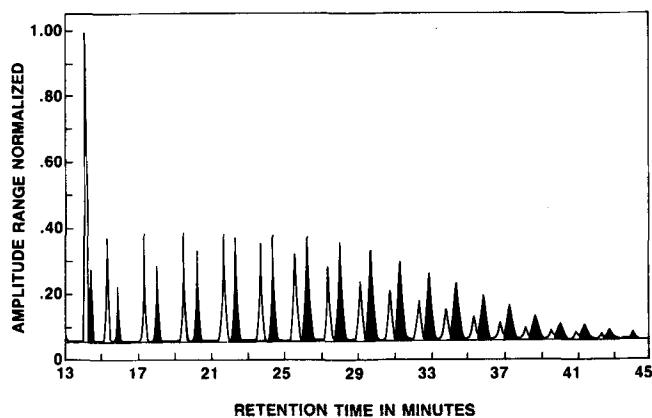


FIG. 2. SFC chromatogram of 6 EO ethoxylate of 2-ethylhexanol normal octanol equimolar mixture (open peaks, 2-ethylhexanol ethoxylates; shaded peaks, normal octanol ethoxylates).

shown in Figure 2. The original trace showed no unusual peak shape or baseline truncation, and complete, almost baseline, separation of the two series of ethoxylated C-8 alcohols was achieved. The trace clearly demonstrates that 2-ethylhexanol is ethoxylated more slowly than normal octanol, with the latter's distribution containing less unreacted alcohol and more of the higher EO ethoxylates. Through the response factor correlation, all SFC peak areas were converted to relative weights and then to relative molar concentrations. Using a LOTUS®123 spreadsheet to simplify the repeated calculations, average molar ratios of EO/alcohol and molar percent free alcohols were determined from these values. Table 1 compares these SFC results with the conventional measurements for the nine products. The close agreement between the two sets of results is striking. In addition, two of the samples were also analyzed by SFC with normal octanol added as an internal standard. The ratios of the ethoxylate sample weights to the internal standard were then compared to those calculated from the SFC data. In both cases, the agreement between the two values was within 10%. Subsequent to these initial tests, many other runs have been made which show equally good agreement; their sum total is taken to be a validation of the SFC method and the response factor correlation.

Reproducibility of SFC analysis. A brief reproducibility study was carried out by analyzing a 5.5-mol ethoxylate of normal octanol nine times and an 8.8-mol ethoxylate of normal octanol eight times. For the first, the average EO/alcohol ratio was found to be 5.53 with a

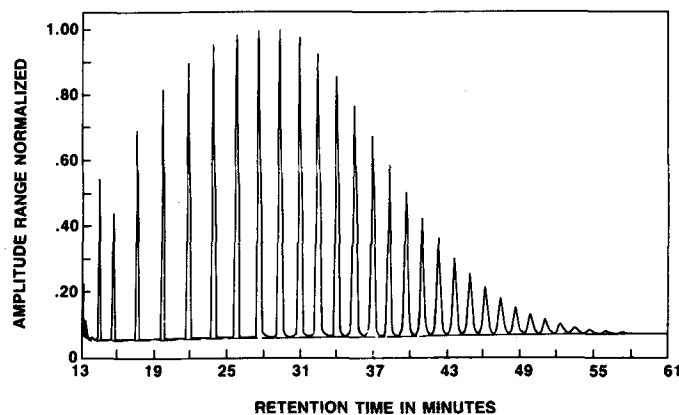


FIG. 3. SFC chromatogram of 9 EO ethoxylate of 2-ethylhexanol.

relative standard deviation (RSD) of 0.9%. Average ethoxylate molar concentrations varied from 10.9% (at 5 EO) to 0.11% (at 19 EO), while the RSDs for the individual ethoxylates of the EO distributions were in the range of 0.16 to 3.9%, with an average value of 1.6%. For the higher ethoxylate, the average EO/alcohol ratio was found to be 8.74 with an RSD of 0.9%. Average ethoxylate concentrations varied from 9.1% (at 7 EO) to 0.5% (at 23 EO), while the RSDs were in the range of 0.5 to 4.1%, with an average value of 2.1%. In both cases, RSD increased with increasing EO content of the ethoxylate for the last peaks eluted, while the lowest RSD was found at the ethoxylate with the highest concentration.

Analysis of mixed carbon alcohol ethoxylates. With ethoxylates of single carbon numbered alcohols, the SFC traces are typically similar to the one shown in Figure 3 for 2-ethylhexanol 9 mole ethoxylate. Transferring this type of SFC peak area data into normalized molar percentages is a relatively simple matter. However, the SFC separation of ethoxylates under the conditions of this study is such that peak retention times are not affected by the presence of ether oxygen atoms. Therefore, when the alcohol being ethoxylated is a mixture of alcohols differing by two carbon numbers, peak overlap occurs between ethoxylates of a given carbon-numbered alcohol and the one-lower ethoxylates of the two-higher carbon-numbered alcohol that contain an equal number of total carbon atoms. This makes data treatment considerably more complicated than in the case of single carbon-numbered alcohols. Optimization of the chromatographic

TABLE 1

Comparison of SFC Results With Other Data

Analysis	Alcohol Ethoxylate	N-C ₈ OH			2-Ethylhexanol			Mixed C ₈ OH		
		3EO	6EO	9EO	3EO	6EO	9EO	3EO	6EO	9EO
EO/alc by SFC by NMR		2.82	5.48	8.24	2.98	6.54	9.10	3.14	5.56	8.57
		2.83	5.58	8.37	2.87	6.50	8.89	2.93	5.79	8.49
Mole % free alcohol by SFC by GC		11.8	2.84	0.86	17.3	2.11	0.72	13.7	5.24	1.88
		12.7	2.96	0.92	17.9	2.04	0.72	14.8	4.92	1.93

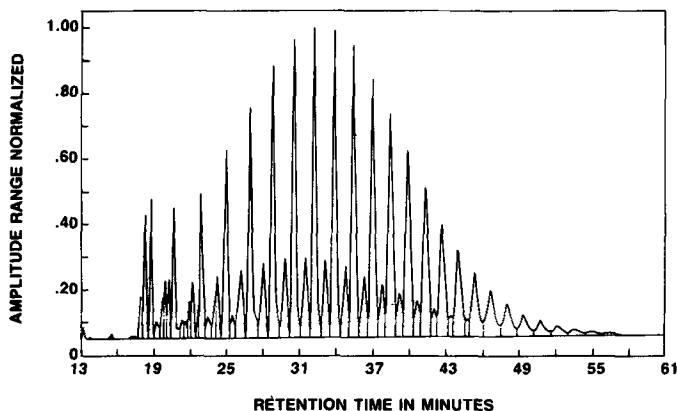
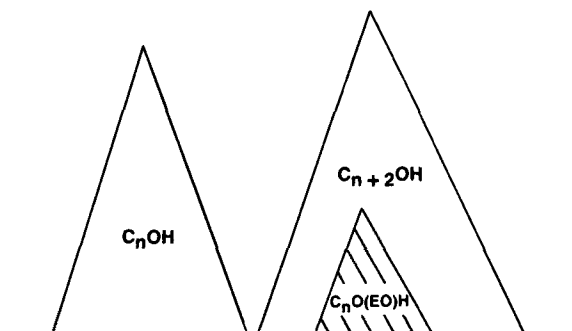


FIG. 4. SFC chromatogram of 7 EO ethoxylate of EXXAL® L1315 Alcohol.

separation by using smaller i.d. columns, different stationary phases, or higher column-oven temperatures would help to some extent to resolve these overlapping peaks, but none were tested during this work.

Figure 4 shows the SFC trace for a 7-mole ethoxylate of such an alcohol mixture, EXXAL® L1315 Alcohol. This is a mixture of C-13 and C-15 linear and α -branched alcohols. The α -branched isomers elute before the corresponding alcohols and ethoxylates. Two distributions, one for the higher-concentrated normal alcohol ethoxylates and another for the 2-alkyl isomer ethoxylates, can be visualized in the trace. However, even though separation between normal and branched ethoxylate peaks is obtained, the above noted overlap between equal total-carbon numbered alcohol ethoxylates is clearly present. Figure 5 summarizes the method that was developed to mathematically deconvolute these overlapped peak areas. Because there is no overlap in the first (unreacted alcohol) peak or set of peaks in mixtures such as EXXAL® L1315 Alcohol, the weight of the lowest carbon-numbered (n) alcohol can be calculated from its response factor. The weight of the unreacted ($n + 2$) alcohol is then calculated based on the molar ratio of the two alcohols in the feed. The area of this unreacted alcohol can then be derived from its response factor and the total area of the overlapped monoethoxylate of the (n) alcohol by difference and then converted to a weight through its response factor. These manipulations are necessary because not only is there overlap between two components, but the overlap is between two components having different response factors. These steps are then repeated in the same sequence until all the ethoxylates have been calculated. The repetitive steps in this calculation are ideally suited for an electronic spreadsheet method of solution, and LOTUS®123 templates have been developed for ease of use.

This deconvolution assumes that the molar rates for the respective propagation to the initiation ethoxylation steps are unaffected by chain length at these carbon numbers (these ratios and not absolute rates determine the EO/alcohol distributions in ethoxylated alcohols) and that the ratios of normal to branched alcohols in the feed are roughly equal for each of the alcohols. Studies with normal alcohols with different chain lengths showing the validity of the first of these assumptions with respect to



CALCULATION METHODOLOGY

- 1) CALCULATE WEIGHT C_nOH VIA ITS RESPONSE FACTOR
- 2) WT $C_nOH \rightarrow$ WT $C_{n+2}OH$ VIA MOLAR CONCENTRATIONS AND MOLECULAR WEIGHTS
- 3) WT $C_{n+2}OH \rightarrow$ AREA $C_{n+2}OH$ VIA ITS RESPONSE FACTOR
- 4) AREA OF $C_nO(EO)_H =$ TOTAL $-C_{n+2}OH$
- 5) AREA $C_nO(EO)_H \rightarrow$ WT $C_nO(EO)_H$ VIA ITS RESPONSE FACTOR
- 6) REPEAT ABOVE STEPS IN SEQUENCE UNTIL ALL ETHOXYLATES ARE CALCULATED

FIG. 5. Mathematical deconvolution of overlapping ethoxylate peaks.

resulting EO distributions have been completed and will be the subject of a future paper. The second assumption was verified by GC analysis of the feed alcohol. The accuracy of this method was demonstrated by calculating a SFC EO/alcohol ratio of 12.9 for an EXXAL® L1315 Alcohol ethoxylate for which material balance across its synthesis and NMR analysis showed a ratio of 13.0. This procedure also has been applied successfully to ethoxylates of mixed n , $n + 1$, $n + 2$ and $n + 3$ alcohols by treating them as a combination of two mixed alcohol systems, for example, C12/C14 and C13/C15 for a C-12 to C-15 alcohol mixture. The validity of these deconvolution methods has been demonstrated by comparisons similar to those shown in Table 1. For example, an analysis of a 5-mole ethoxylate of EXXAL® L1315 Alcohol shows average EO/alcohol ratios of 4.60 and 4.58, by SFC and NMR, respectively.

Comparison of SFC and theoretical EO distributions. SFC data can easily be converted into normalized molar percentages. These can be compared with theoretical distributions derived from Weibull-Nycander kinetics (17-19), based on the assumption that the rate constant for initial ethoxylation is slower than those of the succeeding propagation ethoxylation steps and that the rate constants for all the propagation steps are equivalent. As an example, a comparison was made for the nine-mole ethoxylate of normal octanol discussed above. A value of 3.2 for the ratio of the propagation to initiation ethoxylation rate constants was found to best match the

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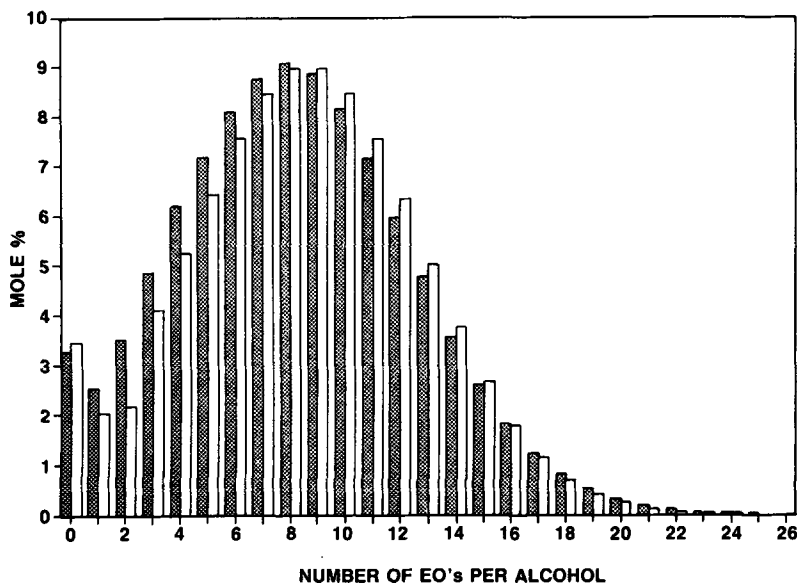


FIG. 6. Comparison of theoretical Weibull-Nycander and SFC experimental EO distributions for 9 EO normal octanol ethoxylate (shaded bars, SFC data; open bars, theoretical values using 3.2 for ratio of propagation to initiation ethoxylation rate constants).

percent unreacted alcohol derived from such theoretical Weibull-Nycander kinetics with SFC data. The theoretical EO distribution using this ratio is compared in Figure 6 with the experimental distribution based on the same SFC data. As can be seen, agreement between the two distributions is good. Work is currently under way in our laboratories to improve the agreement by calculating individual rate constants for each propagation step from these and other SFC data. The results and findings of this work will be presented in a subsequent paper to be published in the near future.

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