Characterization of Nonionic Surfactants Using Supercritical Fluid Chromatography and Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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Capillary supercritical fluid chromatography, using a carbon dioxide mobile phase and flame ionization detection, was employed for characterization of nonionic alcohol ethoxylate surfactants. Data from separations was used to calculate average molecular weights, degree of ethoxylation and distribution of telomers. The SFC approach was compared with carbon-13 nuclear magnetic resonance spectroscopy for evaluation of the same samples. The faster chromatographic technique permitted information to be obtained in the presence of materials which interfered with the NMR analysis, and provided a means of identifying the minor components of mixtures. The advantages and disadvantages of the methods are discussed and the complementary nature of the techniques illustrated.

One aspect of the complete characterization of surfactant-based consumer products and commercial detergents is determination of degree of ethoxylation and distribution of the ethylene oxide (EO) chain in nonionic surfactants. Numerous methods have been described for obtaining such information (1-7), but none are ideal. Two common problems of the methods are nonspecificity (or difficulty in obtaining specificity) and lengthy sample preparation and analysis time. One of the most recent instrumental approaches is carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) (2). Although a high resolution technique, which can be performed with limited sample preparation, acquisition of data can require hours of instrument time to complete. The method also requires reasonably pure, milligram quantities of sample. Common impurities in ethoxylated surfactants, particularly from commercial products, can be difficult or impossible to remove and lead to ambiguous or incorrect results. In particular, poly(ethylene glycols) present in ethoxylated surfactants can lead to inaccurate determinations of the degree of ethoxylation and are difficult to detect without additional separation steps.

Another important parameter for ethoxylated surfactants that many of the methods do not evaluate is the distribution of ethoxylated products in the mixture. Techniques such as NMR and elemental analysis (2,4) only provide data on the average number of moles of EO present on the representative surfactant molecule. Actual distribution of individual telomers is not available using these methods.

The use of a separation-based technique, such as chromatography (1,3), to obtain information on average chain length and distribution overcomes the problems described. However, gas, liquid and thin-layer chromatographic methods are limited by sample preparation time, low resolution and molecular weight constraints (1-7). Capillary supercritical fluid chromatography (SFC) provides a fast, high-resolution chromatographic approach to nonionic surfactant characterization able to analyze complex mixtures of higher molecular weight, low volatility, thermally labile materials (8,9). Although not required, SFC can also be coupled with mass spectrometry (SFC-MS) to further the amount of information available regarding surfactant mixtures (8,10).

This paper describes the application of capillary SFC to the analysis of commercial fatty alcohol ethoxylate mixtures and compares the results of the SFC approach to the use of ^{13}C NMR for the same determinations. Relative advantages and disadvantages of each approach and the complementary nature of the techniques are detailed. Areas for future research efforts are also discussed.

EXPERIMENTAL

Supercritical fluid chromatography was conducted using the Model 602 SFC system from Lee Scientific (Salt Lake City, UT), which is shown schematically in Figure 1. Carbon dioxide (SFC grade, AGL, Clifton, NJ) was used as the supercritical mobile phase, isothermally at 75°C. The chromatographic column was a 10 m by 50 μm I.D. fused silica capillary coated with a 30% biphenyl/70% methyl polysiloxane bonded and crosslinked stationary phase (SB-Biphenyl-30, Lee Scientific) with a Lee Scientific frit restrictor connected to the column terminus using a zero-dead-volume butt connector. A helium-activated Rheodyne HPLC injection valve (Model 7526, Rheodyne, Cotati, CA), with a 0.5 μl internal volume, operated at ambient temperature, was used for sample introduction. The system also required use of an injection splitter operated at a split ratio of approximately 20:1. The Model 602 system was equipped with a GC-type flame ionization

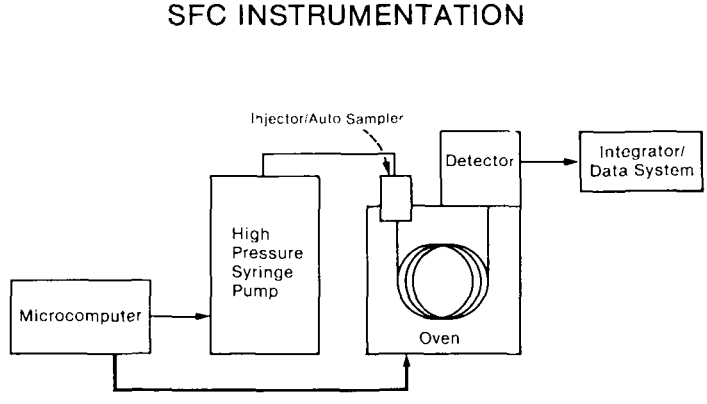

FIG. 1. Schematic diagram of the equipment used for computer-controlled capillary column supercritical fluid chromatography.

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detector (FID), which was heated to 395°C for these experiments. Chromatograms were recorded on a model 3393A integrator (Hewlett-Packard, Avondale, PA).

Surfactant samples were obtained from various commercial sources and prepared in solutions of chloroform or dichloromethane (certified ACS grade, Fisher Scientific, Fair Lawn, NJ). Poly(ethylene glycol) (average molecular weight 400, PEG) was obtained from Aldrich Chemical Co. (Milwaukee, WI) and used in solution in dichloromethane.

The solvating power of a supercritical fluid is controlled through control of density. By increasing fluid density during a chromatographic separation, the solvent character of the mobile phase changes in a manner analagous to gradient elution in HPLC (8–10). This density change is achieved by changing the pressure of the CO_2 under isothermal conditions. The particular program used for these experiments involved increasing the density from 0.203 g/mL (90 bar pressure at 75°C) to 0.660 g/mL (215 bar) at 0.033 g/mL/min (20 bar/min), followed by an increase of 0.007 g/mL/min (4.4 bar/min) to 0.84 g/mL (400 bar), and holding until the sample separation was complete.

Carbon-13 nuclear magnetic resonance spectroscopy was conducted on an IBM Instruments Spectrometer equipped with a Bruker 200 MHz magnet using a 10 mm multinuclear probe head at ambient temperature. Samples, at 10% solution in $CDCl_3$ with chromium (III) acetyl acetonate added as a relaxation reagent, were scanned overnight, acquiring about 14,000 scans. Broad band decoupling and automatic baseline correction were employed for all spectra. Data acquisition and processing were carried out on an ASPECT-3000 computer using ADA KOS (ver. 840615). Spectrometer was operated at an acquisition time of 1.08 sec/scan with a pulse width of 10 (90°) and a sweep width of 15 kHz. Chemical shift data is reported relative to TMS.

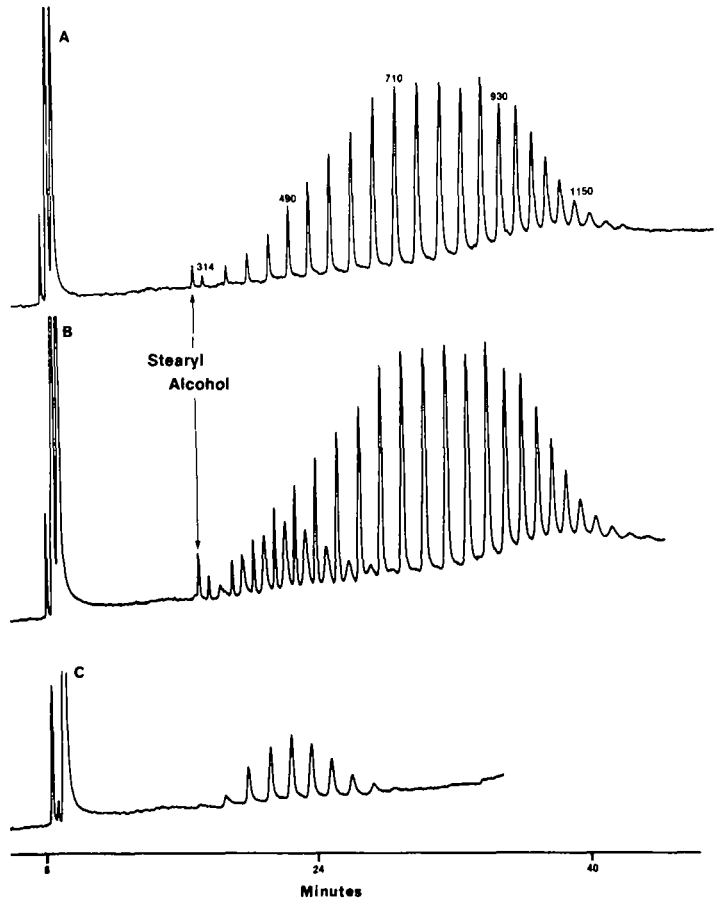

FIG. 2. Chromatograms of the carbon dioxide supercritical fluid separations of a stearyl alcohol ethoxylate sample (A), the same stearyl alcohol ethoxylate with 15% (w/w) poly(ethylene glycol) added (B), and an average molecular weight 400 poly(ethylene glycol) (C). All separations were conducted using the same conditions, as described in the Experimental section.

RESULTS AND DISCUSSION

Supercritical Fluid Chromatography. Figure 2 shows the CO_2 SFC separations of three nonionic ethoxylated mixtures. Figure 2A is the separation of a sample of an ethoxylated stearyl alcohol with an average of ten moles EO (manufacturer's value). The retention time of the first chromatographic peak (17.2 min) corresponds to that of stearyl alcohol (EO=O) verifying the identity of the alkyl chain. The area of this peak can also be used to determine the residual alcohol content of the mixture. The remaining peaks in the chromatogram represent the EO=1 through EO=23 telomers of the surfactant. Identification of the mixture was aided by information supplied by the manufacturer and verified by obtaining chromatograms of standard materials under identical instrumental conditions. In the case of an unknown sample, information may be available from other techniques, such as infrared spectra, chemical class fractionation, GC/MS of low molecular weight components or mass spectrometry of the entire mixture. Supercritical fluid chromatography can also be interfaced with mass spectrometry to verify identification of components in complex mixtures.

The number and weight average molecular weights of surfactant mixtures were calculated using data obtained from the SFC chromatograms and equations (1) and (2):

$$(1)\quad \overline{M_n} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} \qquad (2)\quad \overline{M_w} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

The molecular weight of each individual telomer (M_i) was obtained from the alkyl chain length (alcohol identification) and the chromatographic peak number, corresponding to EO number. The molecular weights of selected stearyl alcohol ethoxylates are given in Figure 2A. The value N_i is related to the number of molecules of each telomer (abundance), and is proportional to chromatographic peak area. Although response factors for the FID may differ for each telomer (3), response factors were not calculated for this study. This may produce skewed values for average molecular weights, but the calculation of weight average molecular weight accounts for the greater contribution of higher molecular weight materials to the determination. A more detailed study of SFC for average molecu-

lar weight determinations for surfactants, including evaluation of response factors, is in progress.

Number average molecular weight of the mixture shown in Figure 2A was calculated to be 795.3 g/mol, corresponding to 11.9 EO and the weight average molecular weight of 836.4 g/mol corresponds to 12.9 EO. These values correlate well with the anticipated value of about 10 EO for the sample. For the calculations, the contribution from residual stearyl alcohol was included as this component will affect the physical and chemical properties of the mixture. In contrast to other methods (3), the high chromatographic resolution of SFC permits the calculation without estimating contributions from co-eluting materials.

The time required to separate this mixture was approximately 45 minutes, with negligible time required for sample preparation (the time needed to weigh the sample and add solvent). With the aid of an algebraic computer program, average molecular weights were calculated in less than five minutes (time required to enter values into the program). Total analysis time, on a functional chromatographic system, was less than one hour per sample. Although reproducibility, precision and accuracy studies have been conducted on our system, the discussion of reproducibility in capillary SFC is beyond the scope of the present work and is discussed in greater detail elsewhere (9). The number and weight average molecular weights given were found to have percent standard deviations of less than one percent (0.65% and 0.88%, respectively) for the data from eight separations.

Information regarding the distribution of telomers in the mixture, which has value when comparing chemical and physical properties of different surfactant mixtures, was available from the separation. One measure of distribution is the polydispersity index (PI), the ratio of weight average to number average molecular weights (M_w/M_n). Polydispersity indices for the samples in Figures 2A and 2B were 1.07 amd 1.08, respectively.

Figure 2B is the separation of the same stearyl alcohol ethoxylate used for Figure 2A with 15% (w/w) poly(ethylene glycol), average molecular weight 400, added. The SFC method was clearly able to separate the ethoxylate components from the PEG with no loss of chromatographic efficiency. Broader peak widths for PEG components compared with ethoxylate materials (0.26 min FWHH vs 0.15 min FWHH) result from the more polar nature of PEG and the greater interaction with the polarizable Biphenyl SFC stationary phase, relative to the surfactant.

Average molecular weight values calculated for the ethoxylate-PEG mixture (Fig. 2B, M_n = 795.7, 11.9 EO, M_w = 841.7, 12.9 EO) indicate the PEG did not affect the determination of the values. The same type of information was available for the PEG, which agreed well with the manufacturer's values (M_n = 385.7, M_w = 398.7). To complete the comparison, the CO_2 SFC separation of the PEG-400 is shown in Figure 2C.

In situations where the PEG may not be chromatographically resolved from the surfactant by SFC, SFC-MS could be used to distinguish PEG from ethoxylate components. Mass spectrometry could differentiate between materials contributing to chromatographic peaks based on molecular weight and the data used to quantitate the relative contribution of each component (10).

The particular temperature-density program used for the separations in Figure 2 was employed for separation of alcohol ethoxylate mixtures up to $\overline{EO}$=30 on stearyl alcohol with comparably good results. Other types of hydrophobe, such as alkyl phenols and secondary alcohols, also gave good results. Coupled with other efforts (8-10) on the analysis of high molecular weight materials, these results indicate SFC is not limited by the molecular weight of components in surfactant mixtures.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Figure 3 shows the ^{13}C NMR spectra of the stearyl alcohol ethoxylate (no PEG, Fig. 3A) used for Figure 2A and the ethoxylate-PEG mixture (Fig. 3B) separated in Figure 2B. The current work was not designed to demonstrate the distinct advantages of the NMR approach for surfactant analysis (2), but to compare the SFC method to a "standard" technique. To obtain average EO values using NMR spectra, the integrated signal area for the α methylene carbon on the surfactant (δ ~ 61 ppm) is compared to the integrated signal area for the ε-methylene carbons (δ ~ 70 ppm) in the ethoxylate chain.

$$\underset{\omega}{R - CHR_1} - \underset{\varepsilon}{CH_2O(CH_2CH_2O)_n}\underset{\beta}{CH_2}\ \underset{\alpha}{CH_2}\ OH$$

The ω-methylene signal (δ ~ 71 ppm) is influenced by the nature of R_1 (2), which, in these experiments, is always a proton, and is used to obtain information on the parent alcohol. Other signals from the R group are found between 13 and 33 ppm (not shown).

For the "pure" stearyl alcohol ethoxylate (Fig. 3A) the average EO was determined to be 12.7, in agreement with the value determined from SFC data. The value calculated from NMR data for the ethoxylate-PEG mixture (Fig. 3B) was $\overline{EO}$=7, significantly lower than that found by SFC. As the true nature of the sample was not available to the individual obtaining the NMR spectrum (as can be the case for samples obtained through chemical class fractionation), this average EO value appeared completely reasonable. Even closer examination of the NMR spectrum to identify signals arising from PEG (2) did not indicate the presence of any other material in the sample. The only difference in the spectra (Fig. 3A vs Fig. 3B) is the slightly lower relative abundance of the signal arising from the ω-methylene carbon, which would require a second spectrum of the sample to verify.

Also to be noted in the comparison is the time required to obtain the spectra. Sample preparation for both SFC and NMR can be the same, so the difference in acquisition (or analysis) time should be compared. Although no more than three hours is usually required to obtain NMR data, it is often more practical to acquire data overnight. This is particularly true when the NMR instrument cannot be dedicated to ethoxylate determination. The three hours is still substantially longer than the time required for the chromatographic method. If it is believed additional components might be present in a mixture, a duplicate NMR spectrum or further separation and sample clean-up may be required. Information regarding additional compo-

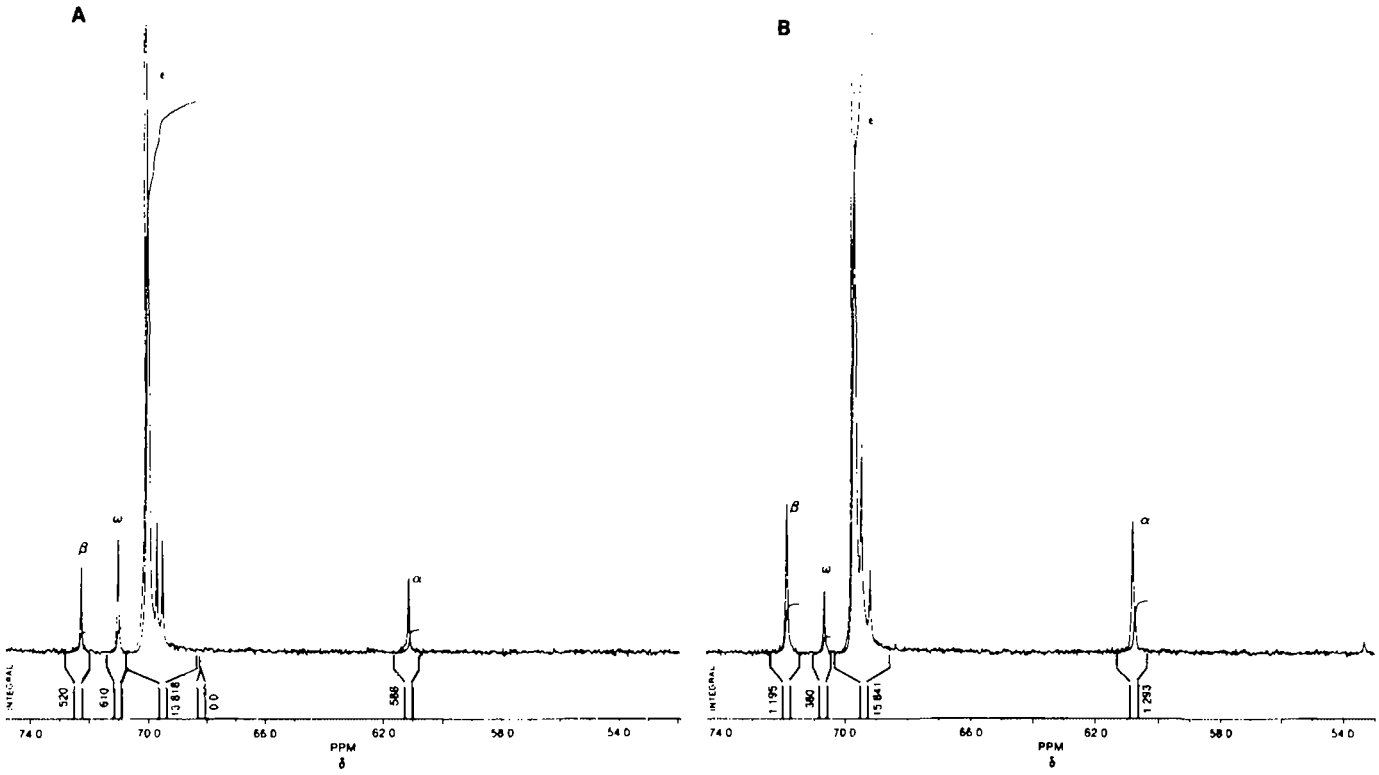

FIG. 3. Portions of the carbon-13 nuclear magnetic resonance spectra of a stearyl alcohol ethoxylate sample (A), and a stearyl alcohol ethoxylate/poly(ethylene glycol) mixture (B), acquired under the same conditions, as described in the Experimental section.

nents is directly available in the initial SFC separation.

Finally, distribution information obtained through separation-based methods is unavailable from NMR data. If complete characterization of surfactant mixtures requires distribution data, an additional method would be necessary. If valuable instrument time is to be dedicated to a single analysis, the analysis should yield a maximum amount of information.

Analysis of an "Unknown" Surfactant Mixture. To demonstrate the complementary nature of SFC and NMR and to illustrate the advantages and disadvantages of both methods for surfactant characterization, an additional sample was considered. Figure 4 shows the CO_2 capillary SFC separation of an alcohol ethoxylate mixture requiring characterization prior to product formulation. The identity of the material as a stearyl alcohol ethoxylate was apparent from the SFC separation and the ethoxylate chain was calculated to be an average of 13 EO. The distribution of the chain indicated a reasonable quantity of residual alcohol and that the material was a blend of low ethoxylate and higher ethoxylate materials (two distinct maxima in the distribution). However, the material was supplied as a 20 $\overline{EO}$ surfactant and had been found to behave unlike other materials of corresponding composition.

The ^{13}C NMR spectrum of the sample yields an average of 25 EO, but no information on the distribution of telomers. Although the average value obtained from the NMR data more closely conforms to the manufacturer's value, it does not explain the differences in formulation behavior compared with reportedly similar surfactants.

A likely explanation, and one requiring further evaluation to confirm, is that the material is composed of the low $\overline{EO}$ surfactant determined by SFC and a small percentage of very high $\overline{EO}$ material, not detected by SFC. This explanation does not contradict the statement that SFC is not limited by molecular weight, rather the particular SFC program used was designed for evaluation of lower (<30 $\overline{EO}$) alcohol ethoxylates and other conditions are required to evaluate high $\overline{EO}$ materials.

This example illustrates the fact that neither ^{13}C NMR nor SFC always yields complete information in a single analysis but do complement one another in obtaining more complete characterizations of alcohol ethoxylate surfactants. Often the analyst must use many techniques for complete characterization, and SFC expands the arsenal of techniques available for these efforts.

SUMMARY

Capillary supercritical fluid chromatography provides a fast, efficient, separation-based method for characterization of alcohol ethoxylate nonionic surfactants. SFC can, under the proper conditions, provide information on the parent alcohol, degree of ethoxylation and distribution of the ethoxylate chain. The presence of potentially interfering materials can be detected and evaluated using SFC. In coordination with other analytical techniques, ^{13}C NMR in particular, exten-

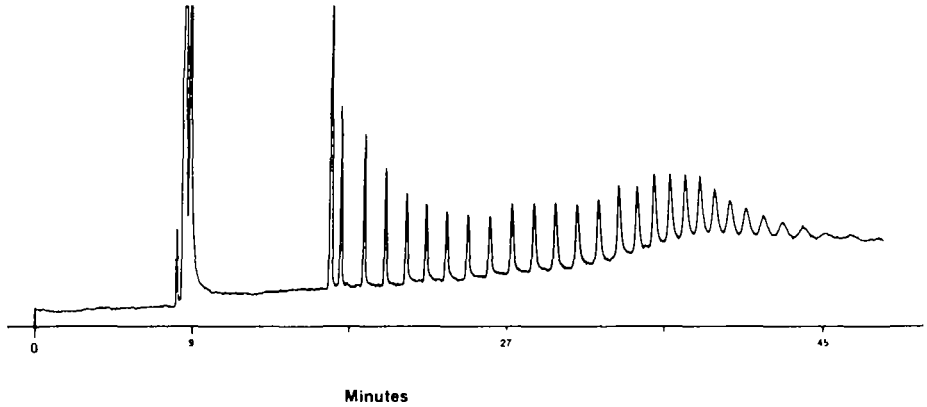

FIG. 4. Chromatogram of the carbon dioxide supercritical fluid capillary column separation of a stearyl alcohol ethoxylate sample reported to contain twenty moles of ethylene oxide. Conditions for the separation are described in the Experimental section.

sive characterization of nonionic surfactants is available.

The approach is not perfect, further effort is required to address the range of nonionic surfactants and mixtures currently in use. Already SFC has been coupled with mass spectrometry to aid in evaluation of complex mixtures. Supercritical solvents have been used for high pressure NMR studies. The ultimate molecular weight of materials amenable to SFC is still being probed and the use of other fluids in SFC is being explored to extend the range of materials addressable by SFC. The concentration at which materials can interfere with ^{13}C NMR evaluations needs to be fully determined, as do detection limits for such materials by capillary SFC. Although not addressed in the current work, packed-column SFC is another versatile technique for mixture characterization.

Complete characterization of surfactant-based materials requires the use of every technique available to the modern analytical chemist and SFC provides another powerful tool in this effort.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. C. Nunn and Mr. M. Hill for supplies of surfactant materials, Mr. L.O. Hargiss with help in devising computer programs and analyzing data and Ms. M.P. Kieselbach for typing the manuscript.

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[Received September 15, 1988; accepted June 13, 1989]
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