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Journal of Chromatography A, 752 (1996) 155–165

JOURNAL OF
CHROMATOGRAPHY A

High-performance liquid chromatographic analysis of polydisperse ethoxylated non-ionic surfactants in aqueous samples

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Received 14 March 1996; revised 1 May 1996; accepted 13 May 1996

Abstract

An adsorption HPLC method using traditionally reversed-phase solvents and a hybrid column/precursor has been developed for the quantitative separation and analysis of ethoxylated non-ionic surfactants on the basis of the number of ethoxylate (EO) groups per molecule. This method is demonstrated to separate ethoxylated homologues of broadly distributed linear alcohol ethoxylates and alkylphenol ethoxylates, with numbers of EO groups ranging from 3 to 50 or greater. This method presents a significant advance in non-ionic surfactant analysis because it permits direct injection of aqueous samples, eliminating the need for extensive sample preparation. The method discussed here is optimized for use with an evaporative light scattering detector (ELSD), but works equally well with UV absorbance or fluorescence detectors for the analysis of surfactants with chromophores. ELSD and UV detector operating conditions and calibration methods are discussed.

Keywords: Surfactants; Polydisperse ethoxylated non-ionic surfactants; Evaporative light-scattering detection; Ethoxylated dodecyl alcohols

1. Introduction

The ability to quantitatively analyze aqueous ethoxylated non-ionic surfactant samples is becoming increasingly important in many environmental research applications, including studies of the fate and transport of surfactants in the environment and the design of new aquifer remediation and soil-washing technologies (e.g., [1–5]). Until recently, however, work with many ethoxylated non-ionic surfactants has been difficult, due to the cumbersome techniques that have been required for their analyses. This has forced many researchers to ignore one of the fundamental properties of commercial ethoxylated non-ionic surfactants: the fact that they are nearly always broadly distributed mixtures of homologous ethoxylated components. In addition, experimental difficulties likely have been responsible for the disproportionately large number of studies that have been conducted with ethoxylated alkylphenol surfactants (which can be detected readily with a standard UV absorbance detector); other more difficult-to-analyze, and, perhaps, in many cases, more relevant non-ionic surfactants have been largely neglected.

The advent of the evaporative light scattering detector (ELSD) in recent years has provided a means of quantitatively analyzing by high-performance liquid chromatography (HPLC) many non-ionic surfactants that were previously difficult to analyze

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due to the lack of chromophores. The ELSD is not plagued by many of the problems associated with refractive index detectors, such as baseline drift when solvent gradients are used, and it is significantly more sensitive. However, as will be discussed below, the use of an ELSD presents other issues that must be considered, such as the strong non-linearity of the detector response and the possibility of interference from non-volatile compounds in the eluents or sample matrix.

This paper presents an adsorption HPLC method that permits the separation and analysis of the individual ethoxylated non-ionic surfactant components in aqueous samples. This method is optimized for use with ELSDs and is applicable directly to environmental surfactant research and to analysis of many natural waters or wastewaters. This method has been applied successfully for over two years in our laboratories to the study of mixed surfactant sorption to aquifer materials [6].

The surfactants discussed in this paper are linear alcohol ethoxylates and alkylphenol ethoxylates. Linear alcohol ethoxylate surfactants are very widely used because of their high degree of biodegradability [7]. Alkylphenol ethoxylate surfactants, although no longer as widely used, are of interest because of the large number of studies that have been conducted with them in the past and because the toxicity of some of their biodegradation products may be of concern in wastewaters [7,8]. It is anticipated that the method described here could be applied to analysis of other classes of ethoxylated surfactants without significant modification.

1.1. Analysis of non-ionic surfactants

Methods used for the quantitative analysis of non-ionic surfactants can be grouped into two classes; those that measure bulk surfactant concentration and those that separate and analyze the surfactant on the basis of either its hydrophobe or the number of ethoxylate groups per molecule.

For bulk analysis of non-ionic surfactants, a number of techniques have been used. When chromophores are present, as in the case of ethoxylated alkylphenol surfactants, UV absorbance or fluorescence spectrophotometric analyses can be used [9]. For surfactants without chromophores, such as

ethoxylated linear alcohol surfactants, other methods are necessary. High concentration analyses have been achieved through the use of total organic carbon (TOC) or chemical oxygen demand (COD) analysis and dye solubilization [4]. Lower concentrations are often measured using various precipitation or complexation methods, typically including a preconcentration step and some form of spectrophotometric detection [10,11]. It is important to note that all of these methods require calibration that may be sensitive to changes in the surfactant component distribution; if the composition of surfactant being analyzed differs from that of the standards, these methods may give erroneous values.

Separation of non-ionic surfactants on the basis of the distribution of hydrophobic chains has been achieved primarily through reversed-phase HPLC with a variety of detection methods [10,12–14]. Separation on the basis of the number of ethoxylate groups per molecule is often of greater interest, however, because of the significantly greater variation in the properties of the surfactant molecules attributable to the distribution of head groups. Separation and quantitative analysis of ethoxylated non-ionic surfactants on the basis of the number of ethoxylate groups per molecule has been achieved by a number of methods, including gas chromatography and high-performance liquid chromatography (HPLC). Because ethoxylated non-ionic surfactants are non-volatile, however, they are not well suited to analysis by gas chromatography. Typically, only the lowest molecular mass surfactant components can be analyzed by gas chromatography and even these usually require high column temperatures [10]. The volatility of the surfactant components can be increased by derivatization, improving their separation and permitting higher molecular mass components to be analyzed; however, even with derivatization, gas chromatography typically cannot be used to separate components with greater than approximately ten EO groups [10].

HPLC analysis, on the other hand, is well suited to the separation of a wide range of ethoxylated components and a number of methods have been developed for this purpose [8,9,12–26]. These methods vary in the quality of the separation they achieve, with some producing excellent results. Many of these methods are not ideally suited for rapid analysis of

aqueous samples, however, because they are either normal-phase or adsorption methods which make use of non-polar solvents that are immiscible with water; thus, aqueous samples must be extracted into a non-polar solvent before analysis. While extraction does permit preconcentration of the sample for increased sensitivity during analysis as well as possible removal of substances that may interfere with the analysis, it is labor-intensive and may influence the observed surfactant distribution, if components partition into the extraction solvent to different extents. In addition, many available methods make use of derivatization to facilitate UV detection. Derivatization (which typically requires the surfactant to be extracted before it can be derivatized) is labor-intensive, potentially hazardous and may skew the measured surfactant distribution through differing reactivities of the components. Of the methods available that make use of traditionally reversed-phase solvents, few exhibit the same quality of separation achieved with the normal-phase methods or demonstrate the ability to work with large direct injections of aqueous samples.

The adsorption HPLC method described here permits separation and analysis of ethoxylated non-ionic surfactants on the basis of the number of ethoxylate groups per molecule. It utilizes traditionally reversed-phase solvents and a hybrid column/precolumn to permit large injection volumes from aqueous samples, and is optimized for use with ELSD detection.

2. Experimental

2.1. Reagents

Pure-hydrophobe polydisperse ethoxylated dodecyl alcohol surfactants [$C_{12}H_{25}(OCH_2CH_2)_n-OH$, or $C_{12}E_n$] were synthesized and donated by Witco (Chicago, IL, USA). Commercial surfactants used were Brij 35 (ICI Americas, Wilmington, DE, USA), an ethoxylated alcohol surfactant ($C_{12}E_{23}$) and the Tergitol NP series (Union Carbide, Danbury, CT, USA), ethoxylated nonylphenol surfactants [$C_9H_{19}(C_6H_4)(OCH_2CH_2)_nOH$, or NPE_n]. Mono-disperse ethoxylated dodecyl alcohol surfactants were purchased from Nikko Chemicals (Tokyo,

Japan) and were used for identification of peaks in chromatograms of the Witco pure-hydrophobe surfactants. Identification of peaks in ethoxylated nonylphenol surfactants was achieved through fitting the UV chromatograms to theoretical molar distributions calculated from the Poisson distribution. All values given for the average number of EO groups for surfactant distributions are number averages, based on the surfactant molar distribution. Conversion from molar distributions to mass distributions is achieved by scaling each component's molar concentration by its molecular mass and then normalizing the resulting values so that their sum is equal to one.

Eluents used for all analyses were HPLC-grade acetonitrile (Mallinckrodt, Paris, KY, USA) and Milli-Q water (Millipore, Bedford, MA, USA). All eluents were sparged thoroughly with helium before use.

2.2. Equipment

HPLC analyses were conducted using a Hewlett Packard (Palo Alto, CA, USA) 1050 Chemstation with a 100-position autosampler (0–100 μ l loop) and a quaternary gradient pump. Detection was performed by a Sedere (Richard Scientific, Novato, CA, USA) SEDEX 55 ELSD operated at 40°C and a Waters (Milford, MA, USA) Model 480 UV spectrophotometric detector operated at a wavelength of 220 nm. A Hewlett Packard 1046A programmable fluorescence detector was used for fluorescence measurements. It was operated with an excitation wavelength of 202 nm and an emission wavelength of 311 nm. Detector signals were stored and integrated on a Hewlett Packard Chemstation via a Hewlett Packard 35 900 interface.

Analytical columns used to produce the chromatograms presented here were Apex I silica columns (Jones Chromatography, Lakewood, CO, USA). All columns used were packed with 5 μ m particles and had a 4.6-mm I.D. and 250 mm length. Except where otherwise noted, Hypersil ODS (C_{18}) precolumns were used (Shandon Scientific, UK). These were packed with 5 μ m C_{18} -coated silica particles and had a 4.6 mm I.D. and 7.5 mm length. Additional columns tested and discussed in the text include an Alltech Associates (Deerfield, IL, USA) Econosphere 3 μ m silica column with a 4.6 mm I.D. and 150 mm

length, and an Exmere (UK) Exsil 100 silica column with a 4.6 mm I.D. and 250 mm length.

2.3. HPLC method

As with typical adsorption HPLC gradient methods, the method described here works by going from a weaker, less polar, solvent (acetonitrile) to a stronger, more polar, solvent (water). The solvent gradient used here, however, is far more polar than the solvent gradients typically employed for separations on uncoated silica columns, where the weaker solvent is often a non-polar solvent such as hexane [27,28]. Gradients involving only acetonitrile and water are more commonly encountered in reversed-phase methods.

Separation of ethoxylated surfactant components is achieved primarily as a result of hydrogen bonding between the surfactant EO groups and protonated silanol groups on the silica surface. When surfactant is injected, the eluent flowing through the column is pure acetonitrile. Because acetonitrile cannot compete effectively with the surfactant EO groups for the silica surface, the surfactant will sorb at the head of the column. When water is gradually introduced into the column, the competition between the mobile-phase and the surfactant for the surface increases. When sufficient water is present to displace a sorbed surfactant component, it will begin to move down the column. Because a gradient is used which introduces successively more water over time, this produces a separation where the surfactant components with fewer EO groups — and thus the least affinity for the surface — are eluted first, while those with greater numbers of EO groups are eluted later.

Two features of this method which contribute to its success are the use of a hydrophobic C_{18} precolumn and a flow gradient. It is well known that injection of a sample from a polar solvent into a less polar mobile-phase can cause noticeable band broadening in adsorption chromatography, as a result of the sample being carried down the column in the injected solvent [28]. For analysis of aqueous samples, this problem is of real concern because of the high polarity and solvent strength of water. Typical solutions to this problem are to either use a very small injection volume or to transfer the sample to a solvent that is less polar than the eluent. By using a

hydrophobic C_{18} precolumn with a silica analytical column, however, it is possible to avoid these measures and inject large volumes from aqueous samples without noticeable band broadening or loss of resolution (when compared with injections from samples prepared in acetonitrile). This is because the C_{18} precolumn effectively extracts the surfactant from the injected water until sufficient acetonitrile is present to cause the surfactant to leave the C_{18} coating and move on to the silica column. The use of a low flow-rate at the start of the run permits this to occur, providing time for the surfactant to partition to the C_{18} coating. It has been found that starting with a flow-rate that is higher than approximately 0.5 ml/min can lead to loss of some low EO surfactant components.

The flow gradient used here provides a low flow-rate at the start of the run for extraction of surfactant from the aqueous injection and in addition provides the higher flow-rates later in the analysis which are needed for baseline separation of components with greater numbers of EO units. It should be noted that excellent separations of many surfactant mixtures, particularly those containing components with fewer than approximately twenty EO units, can be achieved without the use of a flow gradient as long as a sufficiently slow flow-rate is used.

The solvent and flow gradients used to produce the chromatograms in this paper are shown in Fig. 1A Fig. 1B, respectively. At the start of the method, the flow is held constant at 0.3 ml/min for 1 min, with a solvent composition of 100% acetonitrile. At 1 min, a linear flow gradient begins, with the flow reaching 2 ml/min at 37 min. The solvent gradient extends to 35% water–65% acetonitrile at 43 min. At 43 min, the flow-rate is reduced and the solvent mixture returned to 100% acetonitrile to allow the column to equilibrate before the next injection. It should be mentioned that many variations on this method will work; the slopes and duration of the flow and solvent gradients may be modified to optimize this method for other surfactants. Injection volumes of 80 μ l from aqueous samples were used for all chromatograms. Injection volumes as large as 100 μ l were found to work without problems; larger volumes were not tested, due to the lack of an appropriate sample loop.

As previously mentioned, the columns used for

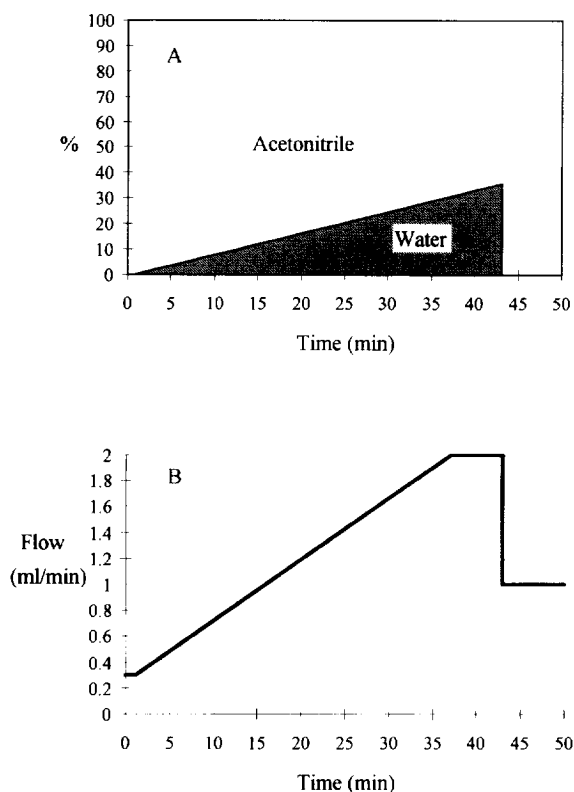


Fig. 1. (A) Solvent gradient and (B) flow gradient used for separation of surfactants.

these analyses were Jones Chromatography Apex I silica columns. Several other silica columns were tested, with a range of results. Other columns which were found to separate non-ionic surfactants moderately well included the Exmere Exsil 100 silica columns and the Alltech Econosphere columns. The Econosphere column had a $3\text{-}\mu\text{m}$ particle size and provided excellent resolution, but was unable to separate components with greater than approximately 20 EO units. The Exsil column produced excellent separations, but was unusable with an ELSD, due to the high level of dissolved silica it produced (which was picked up by the detector). The Apex I columns were chosen as a result of their excellent separation ability and low silica background on the ELSD. Operating pressures on these columns with this method are typically quite low, always well under 100 bar, suggesting that smaller particle sizes could be used if increased resolution is desired. Interest-

ly, in testing, it was found that ethoxylated linear alcohol surfactant components with as many as 40 EO units could even be separated quite well on a 5-cm long Apex I silica column with a $5\text{-}\mu\text{m}$ particle size, although peaks were broader than those produced by the longer columns and the resolution was not as good; the combination of a short column length with a $3\text{-}\mu\text{m}$ particle size could allow for more rapid analyses than those discussed in this paper.

It is important to note that because the method described here makes use of water with uncoated silica columns, it will tend to be destructive to the columns. As a result, columns will require replacement more often than might be the case with more traditional methods. The low EO components are most sensitive to column deterioration and, as a column ages, the response of these earlier peaks tends to change. It is hypothesized that this change is the result of dissolution of the silica column; to date, the authors have been unable to reverse this process. Nevertheless, experience in our laboratory suggests that this is not a significant problem for routine experimental work as long as standards of known composition are run regularly and calibration is done on a peak by peak basis. Many of the older columns tested in our laboratory still produce excellent separations even after heavy use, although the chromatograms they produce differ from those they produced when new. It should be pointed out that if UV detection is employed, a silica saturation column could be used prior to the injector in order to provide some protection for the column; this would produce an unacceptably high silica background for ELSD detection, however.

3. Results and discussion

Fig. 2A shows HPLC separation of a mixture of two Poisson distributed ethoxylated dodecyl alcohol surfactants (average numbers of EO units of 6.3 and 30.0). The chromatogram demonstrates the wide range of ethoxylated components that can be separated and analyzed using the HPLC method, exhibiting baseline separation of peaks corresponding to surfactant components ranging from approximately 3 to 43 EO units per molecule.

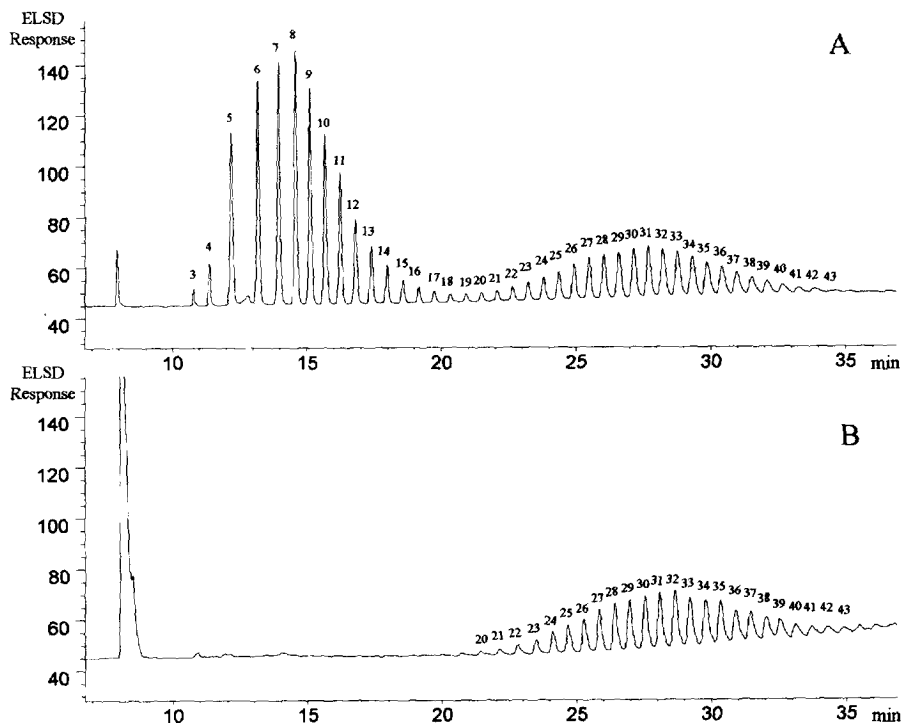


Fig. 2. (A) Separation of a 1:1 mixture (by mass) of Poisson-distributed ethoxylated dodecyl alcohol surfactants with averages of 6.3 and 30.0 EO units (257 mg/l). (B) Same surfactant sample, separated without the Hypersil ODS (C_{18}) precolumn. ELSD detection for both chromatograms. Numbers above peaks correspond to the number of EO units in each separated component.

Fig. 2B shows the same surfactant sample, analyzed without the hydrophobic Hypersil ODS (C_{18}) precolumn. This figure demonstrates the importance of the hydrophobic precolumn to the performance of the method. Note that components with fewer than approximately 20 EO units appear to be passing rapidly through the column in the solvent peak. The water from the injection is effectively short-circuiting the gradient, making the eluent too polar at the start to allow the column to retain the rapidly eluting low EO components. When the C_{18} precolumn is not used, we have found this effect to distort the observed distribution, even with injection volumes as small as 4 μ l.

Fig. 3A–C shows separation of several different pure-hydrophobe ethoxylated dodecyl alcohol surfactants, again demonstrating the wide range of applicability of this method.

Fig. 4 shows the separation of Brij 35, a commercial lauryl alcohol surfactant with an average of 23 EO units. Note that although separation is primarily

achieved on the basis of the number of ethoxylate groups per molecule, branching or variations in the hydrophobe can cause some peak splitting. This has been observed by others [17]. With modified flow and gradient conditions, it is possible that the components corresponding to the various hydrophobes could be resolved.

Fig. 5A and Fig. 5B show separation of a mixture of Tergitol NP15 and Tergitol NP40, commercial ethoxylated nonylphenol surfactants with an average of 15 and 40 EO units, analyzed on the ELSD and UV absorbance detectors, respectively. The chromatograms shown were generated from the same injection, with the ELSD following the UV detector in series (this explains the slight lag in retention times observed on the ELSD chromatogram compared with those on the UV chromatogram). Separation of nonylphenol surfactants with high numbers of EO units proved to be more difficult than separation of ethoxylated linear alcohol surfactants, possibly as a result of variations in the hydrophobe or

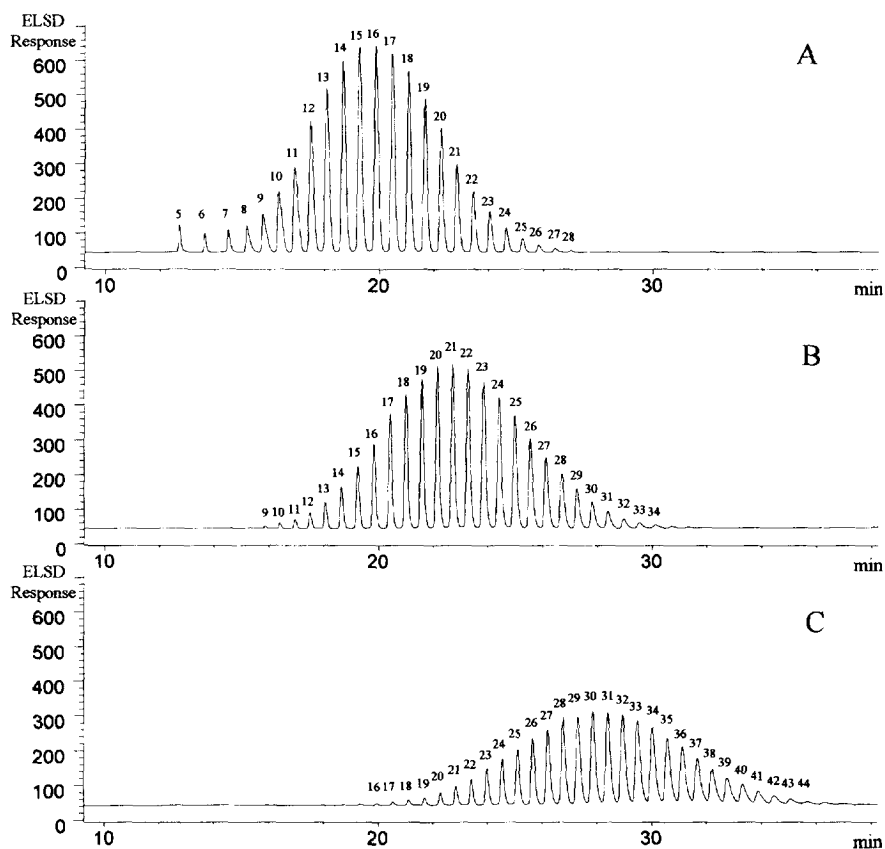


Fig. 3. Separation of pure-hydrophobe ethoxylated dodecyl alcohol surfactants. (A) $C_{12}E_{15.3}$ (867 mg/l), (B) $C_{12}E_{20.6}$ (859 mg/l), (C) $C_{12}E_{30.0}$ (861 mg/l). ELSD detection for all chromatograms.

interactions between the hydrophobe and the silica surface. Nevertheless, near-baseline separation can be achieved for many distributions.

It is interesting to note the difference between the responses of the two detectors, with the components with the higher numbers of ethoxylate groups exhibiting a greater response on the ELSD than on the UV detector. This is because the UV detector is a molar detector, while the ELSD is a mass detector. Because each of the surfactant molecules, regardless of the number of ethoxylate groups, has only one chromophore, the area under each peak on the UV chromatogram is proportional to the number of molecules present. However, the mass of all of the components is not equal; it increases by 44 g/mol for each additional ethoxylate group. Thus, with each successive peak on the chromatogram, the response of the ELSD will increase relative to that of the UV

detector. This is the reason that the lowest EO components that appear on the UV chromatogram (Fig. 5B) are not detected by the ELSD (Fig. 5A), yet the highest EO components detected on the ELSD are not detected on the UV detector.

3.1. Sample considerations

Because this method involves direct injection of aqueous samples, it is best suited to the analysis of relatively clean samples, such as those from research applications, natural waters or from some wastewaters. Excessive levels of solids or other contaminants may clog the HPLC column or injection system and may produce an unacceptable background on either the UV or ELSD detector. Samples do not need to be completely free of contamination, however. For example, although many salts will be

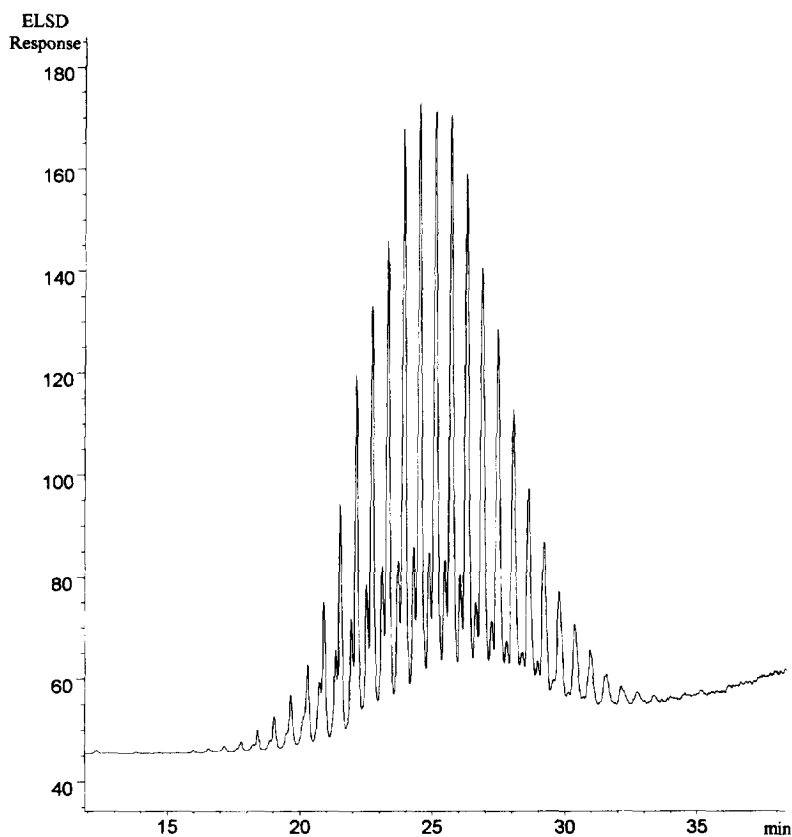


Fig. 4. Separation of Brij 35 commercial surfactant, $C_{12}E_{23}$ (472 mg/l). ELSD detection.

detected on the ELSD and may coelute with surfactant components, their retention times can be modified to some extent by varying the solvent and flow gradients. As a worst case, they may mask one or more of the surfactant peaks. Many other contaminants that would typically cause problems with spectroscopic detection may not interfere with ELSD detection because they may be too volatile to be detected.

3.2. Detection limits, ELSD operation and calibration

Detection limits for the method as described here are in the high $\mu\text{g/l}$ range for individual surfactant components when using the ELSD or UV absorbance detectors. This translates into bulk surfactant concentrations in the low mg/l range, depending on the number of components in the distribution. This level

of sensitivity is quite sufficient for many environmental research applications. If lower detection limits are required for ethoxylated alkylphenol surfactants, fluorescence detection can be employed. Preliminary testing in our laboratory showed that detection limits in the low ng/l range can be achieved for individual ethoxylated alkylphenol components through fluorescence detection.

For all analyses conducted for this paper, the SEDEX 55 ELSD was operated at 40°C . Although the ELSD is largely insensitive to solvent gradients, when operated below 40°C , incompletely evaporated water can produce background noise, particularly at high flow-rates. When the detector is operated above approximately 50°C , however, compounds with fewer than approximately five EO units can no longer be detected, probably as a result of volatilization of these low EO components.

When analyzing mixtures with as many as forty

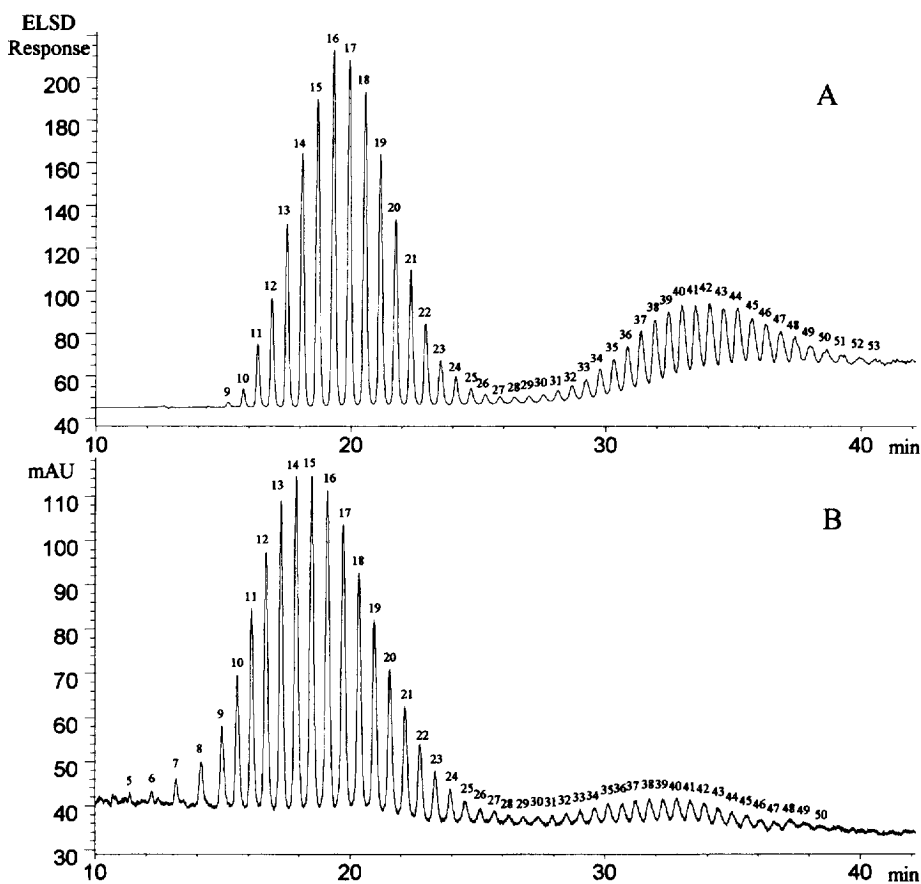


Fig. 5. Tergitol commercial surfactants. Separation of a 1:1 mixture (by mass) of NP15 and NP40 (567 mg/l). Detection by (A) ELSD and (B) UV absorbance detector.

components, quantitative calibration can present a problem, because it is often not possible to run a standard curve for each component and the distribution of the mixture to be analyzed may not be known. In the case of UV detection, where the response is typically linear on a molar basis, special techniques are not generally required and distributions can be determined from chromatograms with reasonable accuracy in many cases. Analysis with the ELSD is more difficult, however. Fig. 6 shows a typical standard curve for an individual component analyzed on an ELSD. Although this curve is fit to peak height, the same trend can be observed when standard curves are fit to peak area; a linear or quadratic log–log fit will usually describe the data well. The non-linear response of the ELSD has many implications for calibration of multi-component sam-

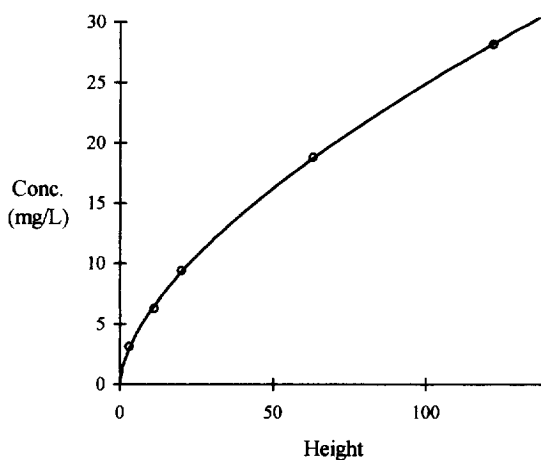


Fig. 6. Typical ELSD standard curve. A curve for monodisperse $C_{12}E_8$ is shown.

ples. First, although the ELSD produces a similar response for many different compounds, because the response is non-linear, peak area is not linearly related to mass or peak height; thus, two peaks of the same area will only correspond to the same mass if their peak shape is the same. Because broadening of peaks increases with retention time in HPLC, it is quite reasonable to expect that different peaks in a surfactant chromatogram will not have the same shape for a given mass and thus will not produce the same ELSD response. In addition, if a baseline shift is observed during a run, as the result of a buffer or dissolving silica from the column, peaks that elute when the baseline is high will not fit the same standard curve that they would fit if the shift were not present, due to the additional mass passing through the detector. As a result, linear baseline subtraction will not work on an ELSD. Compounding these problems is the fact that a component may produce a different ELSD response when being eluted in different solvent mixtures. For example, surfactant components eluted in water appear to produce a greater response than the same components eluted in acetonitrile (this can be observed when injections are made without an analytical column). This phenomenon is examined in some detail in Ref. [21].

Several approaches can be used to calibrate the ELSD for mixed surfactant analysis, depending on the purpose of the analysis and the accuracy required. For qualitative determination of the mass distribution of a surfactant, the fact that the response of the ELSD is nearly linear for large masses can be utilized. If high concentration surfactant samples (of the order of 1 g/l or more, depending on the number of peaks in the distribution) are injected onto a new column, the height or area fractions of the resulting chromatograms should closely approximate the surfactant mass distribution. Fig. 7 shows the theoretical mass distribution for an ethoxylated dodecyl alcohol surfactant with an average of 20.6 EO units and a Poisson distribution in the number of EO groups per molecule, plotted against the ELSD height distribution from the chromatogram shown in Fig. 3B. The excellent agreement between these two plots demonstrates the applicability of this approach. It should be emphasized, however, that this calibration method is not appropriate for all analyses, due to the fact that

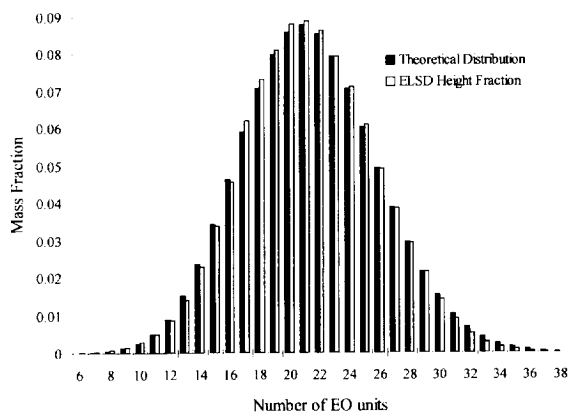


Fig. 7. Height distribution from the chromatogram shown in Fig. 3B ($C_{12}E_{20.6}$), plotted with the theoretical mass distribution for a $C_{12}E_{20.6}$ surfactant with a Poisson distribution in the number of ethoxylate groups per molecule.

it is limited to high concentration samples and does not correct for differences in ELSD response due to the variation in composition of the eluents passing through the detector, so extremely broad distributions may be skewed. In addition, distributions determined by this approach may be sensitive to changes in column performance, so it is best applied with new columns.

For the routine analysis of aqueous surfactant samples with a range of concentrations, excellent results may be achieved by generating a calibration curve for each ethoxylated component. Because monodisperse ethoxylated non-ionic surfactants are typically not available with more than nine or ten ethoxylate groups, this is done by analyzing mixed standards of known composition that contain all the components of interest. (Composition of standards can be determined by the previously discussed approach, or through other chromatographic methods). Quadratic log–log standard curves are generated for all components in the mixture, based on the known component mass in each standard and the corresponding ELSD response. These curves are then used to determine the masses of the individual components in the samples to be analyzed. This is the approach that is used for most measurements in our laboratories. When calibration curves are generated with each sample run, this approach is quite insensitive to changes in column performance over time and produces very consistent results. Draw-

backs to this approach are that it is somewhat computationally difficult to implement and the accuracy of the results will depend on the accuracy with which the mass distribution of the standards is known.

Despite these difficulties, the ELSD provides an excellent method for detecting surfactants that are difficult to detect by other means. With careful calibration, the ELSD and the HPLC method described here can be used for the rapid analysis of mixed surfactants that would otherwise require cumbersome analytical techniques.

4. Conclusions

The HPLC method presented here provides a means of separating and quantifying the individual components of ethoxylated non-ionic surfactants in aqueous samples. The chromatograms shown demonstrate this method's suitability for use with large direct aqueous injections and for separating samples on the basis of the number of EO groups per molecule over a wide range of surfactant distributions. This method is useful as a research tool for the analysis of aqueous non-ionic surfactant samples from a variety of sources.

Acknowledgments

The pure-hydrophobe ethoxylated linear alcohol surfactants discussed here were synthesized, characterized and donated by Witco Corp. We express our appreciation to Ms. Joanne Geils and Mr. Dennis Anderson of Witco for making this possible. Funding for the research was provided by the Great Lakes and Mid-Atlantic Hazardous Substance Research Center under Grant R819605-01 from the Office of Research and Development, U.S. Environmental Protection Agency. Partial funding of the research activities of the Center is also provided by the State of Michigan Department of Natural Resources. The content of this publication does not necessarily represent the views of either agency. This material is based on work supported under a National Science Foundation Graduate Fellowship and a U.S. Environmental Protection Agency Graduate Fellowship.

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