Ion-Chromatographic Characterization of Ethoxylated Anionic Surfactants

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ABSTRACT: Alkyl ether sulfates (AES), analyzed by nonsuppressed or single-column ion chromatography with conductivity detection, generate profiles that are characteristic of the ethoxylate content. Identification of ethoxylation content was accomplished by calculating the slope of the log of the peak area for each homologue vs. the number of ethoxyl groups in the homologue. Quantitation of ethylene oxide content as well as quantitation of mixed alkyl sulfates in the presence of AES in mixed surfactant systems is possible. Raw materials require only dilution in mobile phase, while finished products must be subjected to a solid-phase extraction by means of a reverse-phase cartridge and an ion-pair reagent. The chromatogram of the anionic surfactant yields the moles of ethoxylation and the characterization of the ethoxyl chain distribution. Anionic surfactant mixtures in products are identified and quantitated by reference to AES raw materials with a similar slope.
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KEY WORDS: Alkyl ether sulfate, anionic surfactants, ethoxylation, ion chromatography.

Anionic alkyl sulfates (AS) and alkyl ether sulfates (AES) are probably the most widely used detergents in the personal-care industry and are found in all of the market leader shampoos (1). AS and AES are manufactured from fatty alcohols and fatty alcohol ethoxylates. They are either used individually or blended together to customize viscosity, detergency, foaming and mildness properties of shampoos. Ethoxylation of a fatty alcohol to a fatty alcohol ethoxylate is either acid- or base-catalyzed as follows:

$$ROH + \underset{\diagdown\!\diagup}{\overset{H_2C-CH_2}{O}} \rightarrow RO(CH_2CH_2O)_nH \qquad [1]$$

The product of Equation 1 is a mixture of fatty alcohols and homologues of fatty alcohol ethoxylates, where the degree of polymerization (n) and distribution of homologues varies with reaction conditions and concentrations. Farkas *et al.* (2) attempted to compare the concentration distribution of the ethoxylated homologues under different reaction conditions to a variety of theoretical distributions. Weibull and Törnquist (3) used the log-normal distribution to calculate the mole fraction of each homologue. Moles of ethoxylation can be approximated by using the total hydroxyl value (HV) in mg KOH/g according to the following:

$$\text{moles EO} = [(1000 \cdot 56.1/HV) - MW_{\text{fatty alcohol}}]/44.0 \qquad [2]$$

where 56.1 and 44.0 are the molecular weights of KOH and ethylene oxide (EO), respectively. For example, a common commercially available 1-mole fatty alcohol ethoxylate (AE-1), made from a fatty alcohol with chainlength distribution from C_{10} to C_{16}, which has an average molecular weight of 200 and a hydroxyl value of 235, contains 0.88 moles of EO. It is common for manufacturers to use the term AE-1 for alcohol ethoxylat. with HV from 217 to 240 and corresponding moles of EO from 0.8–1.3. The designations -1, -2, -3, etc., for alcohol ethoxylates represent the moles of EO rounded to the nearest whole number.

Sulfation of fatty alcohols and fatty alcohol ethoxylates to AS and AES occurs either by sulfur trioxide or chlorosulfonic acid:

$$RO(CH_2CH_2O)_nH + SO_3 \rightarrow RO(CH_2CH_2O)_nSO_3^-H^+ \qquad [3]$$

$$RO(CH_2CH_2O)_nH + ClSO_3H \rightarrow RO(CH_2CH_2O)_nSO_3^-H^+ + HCl \qquad [4]$$

followed by neutralization by an appropriate base:

$$RO(CH_2CH_2O)_nSO_3^-H^+ + NH_4OH$$

$$\rightarrow RO(CH_2CH_2O)_nSO_3^-NH_4^+ + H_2O \qquad [5]$$

As indicated by Equations 3–5, the sulfation reaction of the nonionic alcohols and nonionic alcohol ethers results in surfactants with anionic character. AES are commercially available in a variety of moles of ethoxylation, but the one- to three-mole varieties are the most common detergents used in shampoos. The terminology AES-1, AES-2, etc., seems to be based on the EO content of the starting alcohol ethoxylates (AE-1, AE-2, etc.) as described above and not on the EO content of the alcohol ether sulfate. A simple molecular weight ratio can transform one into the other.

Characterization of the chainlength, amount and distribution of EO homologues in AES is important to understanding

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the performance of a shampoo because they affect the physical properties of the surfactant. A good review of the affect of alkyl chainlength and EO content on the performance of alkyl ether sulfates has been published by Cox (4). His results indicate that increasing EO level increases water solubility; a lauryl chain containing 1 mole of EO is best at lowering surface tension; salt-thickening increases with increasing alkyl chainlength and decreases with increasing EO content; foam volume decreases with increasing EO chainlength; optimum detergency is obtained with 2–3 moles of EO and a 12–16 carbon chainlength; viscosity increases with increasing levels of EO and with increasing alkyl chainlength. Smith (5) has emphasized the rheological changes in sodium dodecyl ether sulfate as a function of EO distribution. Using the same total EO content but differing EO distribution, he was able to explain large differences in viscosity as a function of salt concentration. It is apparent, therefore, that analytical methods to characterize chainlength and ethoxylation distribution of AES and AS are vital toward controlling the behavior of a finished product.

Because of the anionic nature of AES, two-phase titrations with a cationic surfactant as the titrant, have been used extensively for the rapid quantitation of these anionic surfactants in raw materials and products (6). Titrations, however, cannot differentiate individual surfactants in a mixture or characterize differences in homologue distribution. Lee and Puttnam (7) used gas chromatography of AS and AES after iodination with glutamic acid to measure their alkyl chainlengths. Suppressed and nonsuppressed ion-chromatographic (IC) techniques are available for the analysis of individual anionic surfactants with low-capacity, high-efficiency columns, along with ion-pairing techniques (8–18). This paper describes a nonsuppressed IC technique with conductivity detection to characterize and quantitate both the chainlength and ethoxylation content of a variety of alkyl and alkyl ether sulfates. An ultraviolet (UV) detector was also used to simultaneously quantitate aromatic sulfates in raw materials, raw material blends and finished product shampoos.

EXPERIMENTAL PROCEDURES

Reagents. Ammonium acetate and tetramethyl ammonium hydroxide pentahydrate ($TMAOH \cdot 5H_2O$) were reagent-grade; water was purified with a Millipore (Milford, MA) milli-Q system; methanol and acetonitrile were high-performance liquid chromatography-grade.

Sample preparation. Raw materials were simply diluted in mobile phase and filtered through a 0.2μ acrodisc before analysis. Shampoo, containing 45–60 mg of anionic surfactants, was diluted with 15 mL water and filtered through a 0.2μ acrodisc. A Dionex On-Guard R/P cartridge (Dionex Corporation, Sunnyvale, CA) was used for solid-phase extraction and sample clean-up. The On-Guard R/P cartridge was attached to the end of a 10 mL disposable syringe and conditioned with 5 mL methanol, followed by 10 mL water. The packing material was then ion-paired with 5 mL of 0.5 M $TMAOH \cdot 5H_2O$. The shampoo solution was passed slowly through the cartridge to ion-pair with the $TMAOH \cdot 5H_2O$. The retained surfactants were then eluted from the cartridge with 10 mL of 90:10 mobile phase/acetonitrile. The sample size for the ethoxylation analysis was limited to a concentration of 1–3 mg/mL anionic surfactant.

IC analysis. A Dionex 2000i Ion Chromatograph equipped with a Dionex autosampler and a CDM conductivity detector was used to separate ethoxylated homologues from the unethoxylated chains and to determine the ethoxylate distribution and moles of ethoxylation. A Dionex UV detector was used in series with the conductivity detector to characterize aromatic surfactants. Dionex AutoIon 450 chromatography software was used to obtain and process data. The mobile phase was 45:55 (methanol/water) containing 17.5 mg/L ammonium acetate. The surfactant C8 separator column, 5μ, 250 × 4.6 mm (length × i.d.) were obtained from Alltech Associates (Deerfield, IL). The flow rate was 1.0 mL/min at ambient temperature. The conductivity detector was set at 3 μS.

Data analysis. Chromatograms, plots of peak areas and the calculation of moles of ethoxylation were performed with the QUATTRO PRO™ (Borland International Inc., Scotts Valley, CA) spreadsheet program. Assuming linear response, the average moles of ethoxylation were calculated from the IC data by a mole number weighted average of the adduct peak area. Cluster analysis was performed with STATGRAPHICS PLUS™ (Statistical Graphics Corporation, Rockville, MD).

RESULTS AND DISCUSSION

Several lots of raw material from six different surfactant suppliers were analyzed for ethoxylation by the nonsuppressed IC procedure. For brevity, each surfactant peak is identified by chainlength and number of EO groups. For example, 12:0 represents a C_{12} chainlength with no ethoxyl units, while 12:1 represents a C_{12} chainlength with 1 ethoxyl unit. Figure 1 is a typical separation of ammonium lauryl sulfate (ALS) annotated by the above nomenclature. In addition to the chloride and sulfate anions, the sulfated alcohol peaks are decyl (10:0), dodecyl (lauryl, 12:0), tetradecyl (myristyl, 14:0) and hexadecyl (cetyl, 16:0). They were identified by substituting the conductivity detector with a mass spectrometer with a particle beam interface [liquid chromatography–mass spectrometry (LC–MS)]. Peaks eluting prior to the 10:0 peak were identified using standards of Cl^- and SO_4^{-2}. A typical ALS chainlength distribution of 1:75:20:4 was obtained for the carbon 10:12:14:16 chains (Table 1).

Figure 2 shows typical separations of 1-, 2- and 3-mole ammonium lauryl ether sulfates (ALES-1, ALES-2, ALES-3). A number of peaks are seen eluting between 12:0 and 14:0 and between 14:0 and 16:0. The peaks were identified by LC–MS as being the ethoxylated homologues (n, Equation 5) of 12:0 and 14:0. Table 1 lists typical chainlength distributions, calculated as percent of total peak area for ALES. A decreasing ratio of the 12:0 to 12:1 peak areas as well as a decreasing ratio of the 12:1 to 12:2 peak areas in

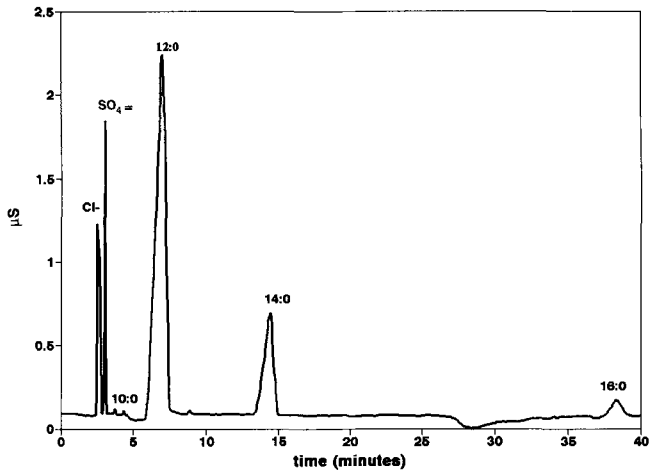

FIG. 1. Chromatogram of ammonium lauryl sulfate with chainlength distribution of C_{10}, C_{12}, C_{14} and C_{16}.

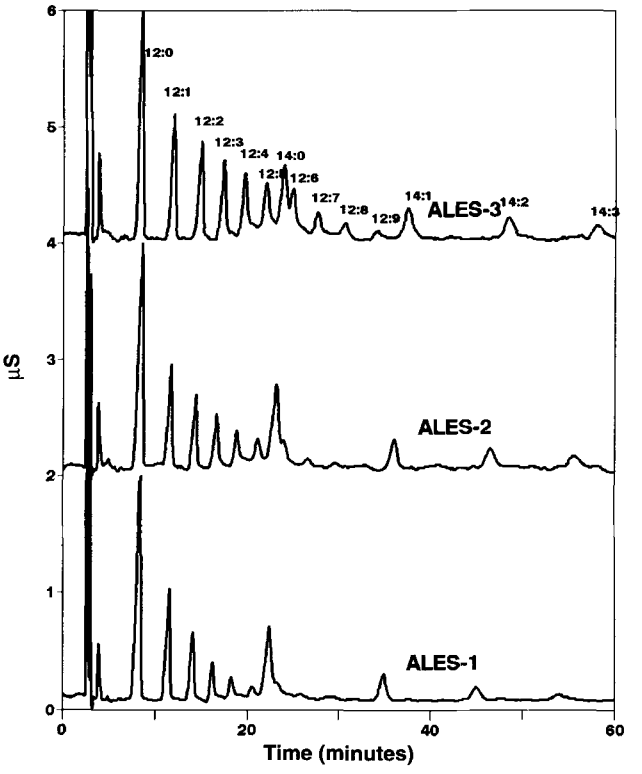

FIG. 2. Chromatograms of ammonium lauryl ether sulfate (ALES) termed 1- to 3-mole by the suppliers.

going from a 1-mole to a 3-mole ALES is apparent. Plots of the log of the peak areas for the 12:1 through 12:5 homologues vs. the number of ethoxyl groups (Fig. 3) generated straight lines for all samples tested. This seemed to indicate that the commercial ethoxylation reaction, practiced by all six suppliers, yields a Weibull and Törnquist (3) log-normal distribution of homologues, at least for the 1- to 3-mole materials. In general, the extrapolation of the slope to the Y-intercept coincided with the point generated by the log of the 12:0 peak area. Several samples of ALES-1, ALES-2 and ALES-3 raw materials have the log of the 12:0 peak area somewhat offset from the Y-intercept extrapolation. Only two possibilities could explain Y-intercept offsets: the efficiency of the ethoxylation process described by Equation 1 or a dilution by excess amounts of 12:0 component, either to meet the HV specification or to create a blended detergent.

The variation of slopes and moles of ethoxylation, detected in 95 lots of ALES-1, ALES-2 and ALES-3 from the six sources, are shown in Figure 4. Four groups were identified by cluster analysis and are designated 1, 2 or 3 for ALES-1, ALES-2 and ALES-3 as per the supplier nomenclature (Fig. 4). Unexpectedly, cluster analysis indicated two groups

TABLE 1
Typical Chainlength Distributions in Percent of Total Peak Area for Ammonium Lauryl and Ammonium Lauryl Ether Sulfates[a]

Carbon chainlength	ALS	ALES-1	ALES-2	ALES-3
C10:0	0.4	3.1	2.6	2.5
C12:0	75.2	40.4	29.5	11.3
C12:1		15.1	12.1	7.1
C12:2		8.1	9.9	7.0
C12:3		4.1	7.7	6.0
C12:4		1.8	4.6	4.2
C12:5		1.3	3.7	3.9
C12:6		0.6	1.9	1.8
C12:7		0.3		
C12:8		0.2		
C14:0	20.4	12.5	12.1	14.3
C14:1		4.9	6.2	10.8
C14:2		2.8	3.9	8.2
C14:3		1.2	2.7	6.6
C14:4		0.6	1.4	5.0
C14:5				3.9
C14:6				3.0
C14:7				2.8
C14:8				1.6
C16:0	4.0	2.9	1.7	

[a]ALS = ammonium lauryl sulfate; ALES-1 = ammonium lauryl ether sulfate with 1 ethylene oxide, etc.

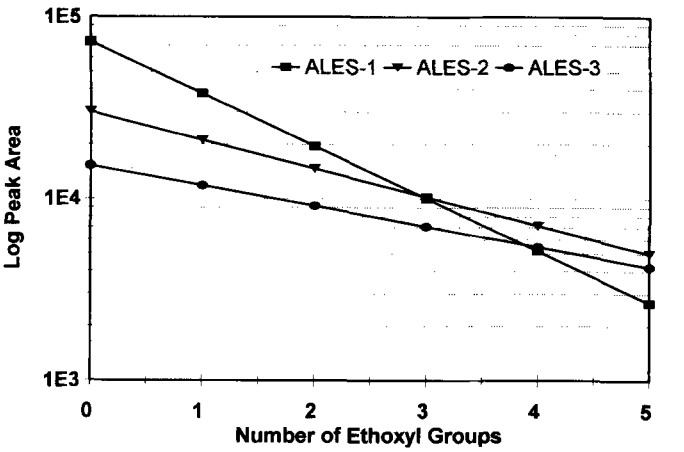

FIG. 3. Plot of log peak area vs. number of ethoxyl groups for three typical alkyl ether sulfates raw materials. See Figure 2 for abbreviation.

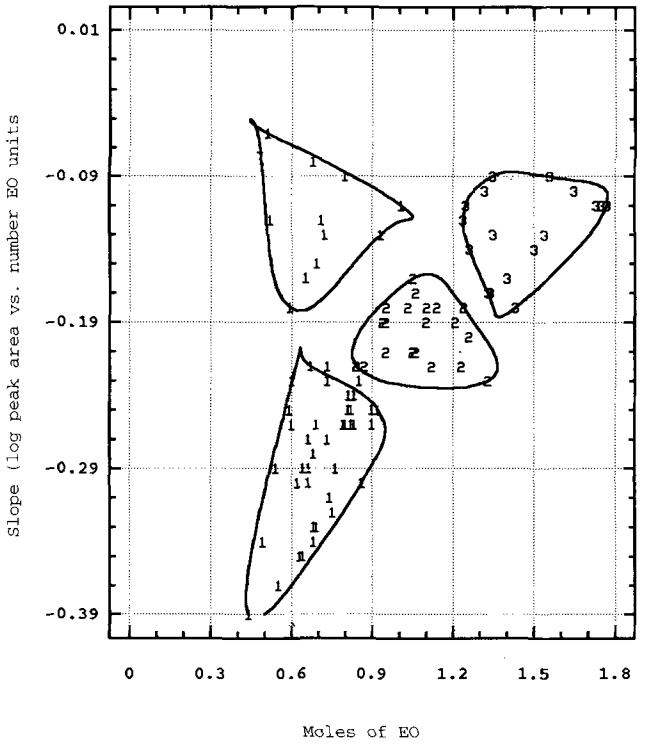

FIG. 4. Cluster analysis plot of moles of ethylene oxide (EO) vs. slope of the peak area for 95 different lots of ammonium lauryl ether sulfates.

for the ALES-1 raw material lots. Table 2 lists the means and standard deviations of the slopes of the log peak area of the first four or five ethoxyl homologues and the moles of ethoxylation of all ethoxylated homologues for the four groups identified by the cluster analysis. The two ALES-1 groups have equal ranges for moles of EO but have quite different slope ranges. It was noted that the group with less negative slopes had log 12:0 peak areas that were much offset from the extrapolated Y intercept, indicating a much larger amount of the 12:0 component than that normally obtained by the ethoxylation reaction (Eq. 1). The less negative slopes for this ALES-1 group are also in the same ranges as the slopes for the ALES-3 group (Table 2, Fig. 4). It was concluded that some suppliers' terminology for AES was based only on the moles of ethoxylation and not on the adduct distribution. More specifically, Figure 4 demonstrates the practice by some suppliers of diluting ALES-3 with ALS to obtain the correct moles of EO to be sold under the nomenclature of ALES-1. Figure 4 also indicates a linear relationship between the slope of the log peak areas and the moles of ethoxylation for one ALES-1 group, and for the ALES-2 and ALES-3 groups, as would be expected with increasing ratios of ethylene oxide to lauryl alcohol, as per Equation 1.

Shampoos and other personal-care products that contain anionic surfactants were also analyzed for their ethoxylation content. Quantitation of moles of EO as well as ethoxylated and nonethoxylated ratio for blended detergents was possible with the results obtained from Table 2. Initially, samples were injected directly into the ion chromatograph after dilution with mobile phase. The procedure produced large, broad peaks, which affected quantitation of subsequent samples. Therefore, the clean-up procedure, outlined in the Experimental Procedures section, was developed. A chromatogram of a typical shampoo, cleaned up by this procedure, is shown in Figure 5. This shampoo contains a 2-mole ethoxylate (slope: –0.21, Table 2), which has been diluted with 70% LS as calculated from the 12:0 peak area, the difference between the predicted and actual 12:0 intercept and the total peak area. This sample also contained 5% C10:0 as well as its ethoxylated species. As indicated by Table 1, the average 2-mole ethoxylate should not have more than a 3% C10:0 contribution. Because this sample is a diluted 2-mole ethoxylate, the 5% contribution of C10:0 plus its ethoxylates must indicate the addition of the latter to the shampoo to obtain some desirable physical characteristic. This shampoo then must contain a mixture of three separate raw materials: LS, LES-2 and decyl ether sulfate.

Figure 6 is the chromatogram of a shampoo that contained a 1-mole ethoxylate (slope: –0.29, moles EO: 0.74). The calculated Y-intercept (12:0) was nearly coincident with the actual log (12:0) peak area and indicated that the sample was not blended with LS. This sample also contains the 1% C10:0 and 3% C16:0 chains of a typical ALES-1 (Table 1), as well as a large conductive component, which eluted in the 2–3-

TABLE 2
Means and Standard Deviations of the Slopes of the Log Peak Area of the First Four or Five Ethoxyl Homologues and the Moles of Ethoxylation of All Ethoxylated Homologues for the Four Groups Identified the Cluster Analysis

Group	Slope	Moles EO[a]
ALES-1 (n = 38)	–0.29 ± 0.04	0.70 ± 0.11
ALES-1 (n = 16)	–0.12 ± 0.05	0.65 ± 0.14
ALES-2 (n = 20)	–0.20 ± 0.03	1.04 ± 0.17
ALES-3 (n = 21)	–0.14 ± 0.04	1.37 ± 0.24

[a]EO = ethylene oxide; see Table 1 for other abbreviations.

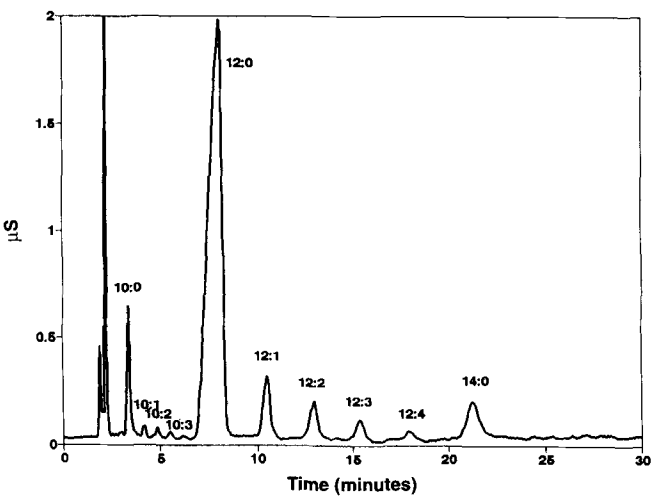

FIG. 5. Chromatogram of a mixture of ammonium lauryl sulfate, a 2-mole ammonium lauryl ether sulfate and a decyl ether sulfate.

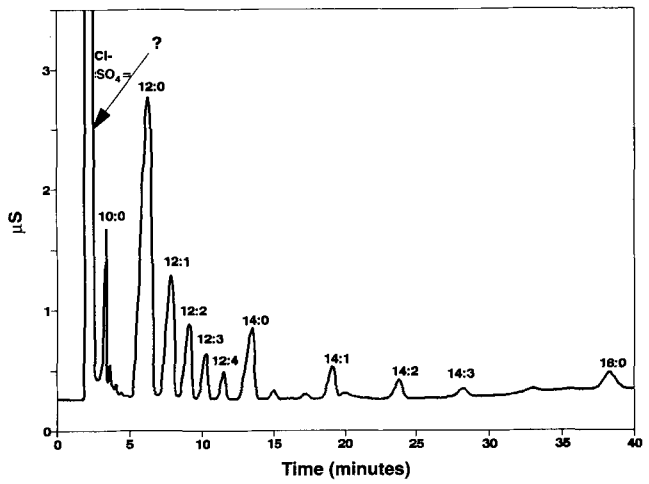

FIG. 6. Chromatogram of a shampoo containing a 1-mole lauryl ether sulfate and an unknown anionic species eluting between 2–3 min.

minute range along with the Cl^- and SO_4^{-2} components. Figure 7 is a chromatogram of the same sample and was obtained by linking an UV detector in series with the conductivity detector to determine whether the anionic component had aromatic character. A now quantifiable separation of ammonium xylene sulfonate (identified by LC–MS) was obtained. Other than ammonium xylene sulfonate, dodecyl benzene sulfonate and sodium lauryl sarcosinate were detected and quantitated by UV detection in series with conductivity detection. Alkyl sulfonates were also detected in shampoos and were quantitated by external standard procedures. A slight modification of the mobile phase, due to the shorter elution time for the sulfonates, was necessary. Similarly, other anionic surfactants, such as myristyl sulfate, could be determined by increasing the level of methanol in the mobile phase.

Nonsuppressed ion chromatography with conductivity detection can measure the level of ethoxylation in various AS and AES raw materials. Dilution of an ethoxylated surfactant with AS can also be determined. The log-normal distribution of the ethoxylation products was used as log plots to better characterize the ethoxylated homologue distribution and to quantitate dilution effects, while peak areas were used to calculate moles of ethoxylation. Large differences in the composition of ethoxylated raw materials from different suppliers have been noted. A clean-up procedure was used to separate anionic surfactants from other compounds in shampoos and other personal-care products. Analysis of numerous shampoos indicated that a wide variation in levels and types of ethoxylation, as well as a wide variation of detergent blending, is used by manufacturers. By coupling conductivity and UV detectors, other surfactants with aromatic character could be identified in products. The mobile phase used for the IC separation can be modified slightly to quantitate other hydrotropes or anionic surfactants in a surfactant mixture of a product.

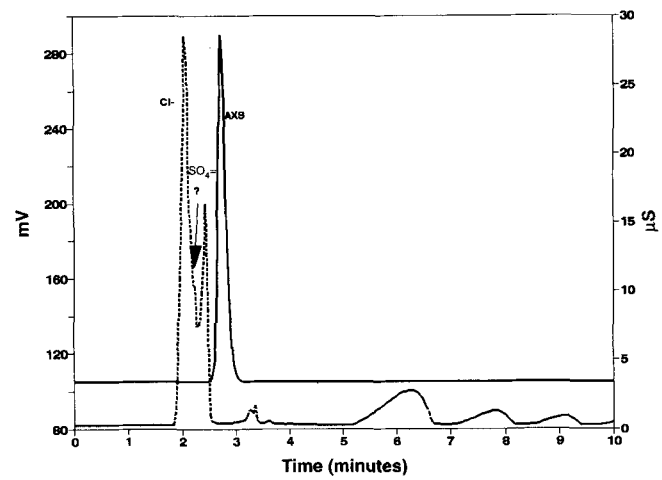

FIG. 7. Chromatogram of the shampoo in Figure 6, taken with an ultraviolet detector (dark line) in series with a conductivity detector (dotted line). AXS = ammonium xylene sulfonate.

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