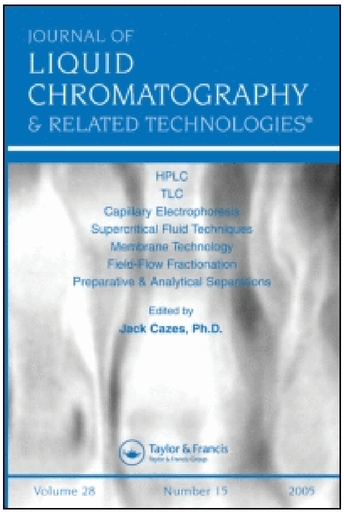

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Direct Determination of Anionic Surfactants Using Ion Chromatography

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DIRECT DETERMINATION OF ANIONIC SURFACTANTS USING ION CHROMATOGRAPHY

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ABSTRACT

A method for the simultaneous qualitative and quantitative analysis of surfactants in solution via ion chromatography has been developed. This method has the capability of separating linear alkyl anionic surfactants which differ by as little as two carbon atoms in the hydrocarbon chain. In addition, the method can differentiate between surfactants of the same chain length which differ only in the chemical nature of the anionic head group. The ion chromatographic method is much simpler and more accurate than previous techniques of determining surfactant concentration which relied on detecting changes in secondary properties, such as surface tension. The method is also highly flexible and should be applicable to a wide variety of ionic and nonionic surfactants. Use of ion chromatography will greatly simplify studies of surfactant behavior.

INTRODUCTION

Surface active agents, or surfactants, are amphipathic compounds which are composed of a lyophobic portion which has little attraction for the solvent, and a lyophilic portion which has a strong attraction for the solvent. When dissolved in aqueous solution at low concentrations, it is energetically favorable for the surfactant to migrate to any available hydrophobic interface and orient itself with its hydrophobic portion toward the interface and its hydrophilic portion in the aqueous phase(1,2). Surfactants are widely used in many products and processes as indicated by the fact that although they are present at no more than a few percent by weight in any given application, the total production of all types of surfactants in the United States was conservatively projected to be 3.3 million metric tons in 1992(3). Although they are typically associated with soaps and detergents, surfactants also play a crucial role in many other applications such as metal treatments, cosmetic and pharmaceutical formulations, pesticides, detergent motor oils, and sol-gel ceramic particle generation processes. Micellar surfactants have even been used as mobile phases in liquid chromatography(4). In all of these applications the effectiveness of the surfactants is determined by the extent to which they adsorb onto a given surface or interface, and the configuration in which they adsorb. This adsorption is controlled by many factors including the nature of the adsorbing surface, the structure of the surface active materials, properties of the bulk fluid phase, and the temperature.

In order to determine the extent of surface adsorption, the amount of surfactant adsorbed onto well characterized surfaces such as spherical polystyrene particles can be measured. Knowledge of the surfactant concentration in the fluid phase which is brought into contact with the surface allows the adsorbed surface concentration to be calculated if the bulk fluid phase concentration can be determined following adsorption equilibrium. When surfactant is added to an aqueous suspension of polymer particles, equilibrium is established between surfactant adsorbed at the air-liquid interface, free surfactant in the bulk solution phase, and surfactant adsorbed at the polymer-liquid interface. As more surfactant is added to the system, all of the interfaces become saturated with a monolayer of surfactant(2,5). When surfactant is added beyond this point, the free surfactant molecules become associated in organized aggregates called micelles. The concentration at which micellization occurs is called the critical micelle concentration (CMC), and is marked by abrupt changes in several physical properties, including surface tension(1,2,6). Maron *et al.*(5) developed a method for determining surface area and particle size of synthetic latexes via the soap titration technique. The titration endpoint can be used to calculate the total amount of surfactant adsorbed on the latex surface at saturation, but cannot distinguish between surfactant species. Use of the soap titration method to obtain adsorption data at surfactant concentrations below saturation is also possible(7,8). However, the soap titration method is tedious, requiring nearly 30 minutes to obtain a single point on the titration curve. In addition, the titration endpoint is rarely well defined leading to large uncertainties in the results. It is much more efficient to determine these concentrations directly. It is also desirable that the analysis be capable of differentiating between multiple surfactants since most practical applications involve the use of two or more surface active species present in the same fluid phase. This investigation introduces one of the newest methods for direct determination of surfactant concentration, ion chromatography.

Ion chromatography is a term which encompasses many modes of the chromatographic separation of ions including conventional ion exchange chromatography and ion-pairing chromatography. Ion-pairing chromatography uses a neutral nonpolar stationary phase together with a mobile phase containing a lipophilic electrolyte called the ion interaction reagent(9), or the ion-pair reagent(10). The structure of the stationary phase dictates the type of ion-pair chromatography being used. Porous inert particles such as silica are used for size-exclusion chromatography which retains the shorter ion pairs longer due to the physical difficulties of moving through the porous regions of the stationary phase. Non-porous hydrophobic particles can also be used, in which case separation occurs based upon the hydrophobic character of the ion pair. Hydrophobic ion-pair chromatography is well-suited for surfactant systems because the ion pair includes the hydrophobic tail group of the surfactant ion, allowing for ideal separation conditions using the hydrophobic stationary phase while allowing control of the retention time and the peak width through the variation of the hydrophobic character of the mobile phase.

In this study, ion chromatography was proven capable of clearly separating closely related surfactant species according to both basic type and chain length, and quantitatively analyzing the relative amounts of the surfactant species present. Ion chromatography is the only technique, to date, which has demonstrated this ability, although capillary electrophoresis systems which may be able to accomplish this task have recently been introduced. The introduction of ion chromatography for the separation and quantitative detection of surface active species offers a simplified and more accurate approach to the determination of adsorption isotherms. As a result, it is possible to accurately assess the concentration of various individual species on an adsorbing surface using a relatively simple analytical method.

EXPERIMENTAL

Instrumentation

The analysis of surfactants in the bulk fluid phase in equilibrium with a model surface was carried out using a Dionex series **4000i** ion chromatograph equipped with an advanced computer interface (ACI) for controlling the system from the **AI-450** version 3.1, Microsoft^{R} **Windows**^{TM} 3.0 compatible software (available from Dionex Corporation, Sunnyvale, California). The chromatograph was also equipped with an eluant gradient pump, an auto sampler with a 25 μL sample loop, the **AMMS-MPIC** micromembrane anion suppressor, and all teflon tubing and fittings. The **IonPac NS1-5μm** hydrophobic separator column was used in series with the **IonPac NG1-GUARD** guard column (all from Dionex). These columns separate analytes on the basis of hydrophobic character, and an eluant gradient was utilized to maximize the separation obtained while minimizing the total run-time required.

The method employed the use of three eluants which were combined in varying ratios through the gradient pump and mixed in the **GM-2** turbulent gradient mixer (Dionex). The mixed eluant stream was passed through the sample valve at a flow rate of 1 mL/minute, and into the guard and separator columns. The sample stream then continued through the suppressor column and into the conductivity cell for detection as shown schematically in Figure 1.

Eluants, Reagents, and Surfactants

Deionized (DI) water of not less than 17 Mohm-cm resistivity was obtained from a **Nanopure** high-purity deionization and filtration system (Barnstead/Thermolyne Corporation, Dubuque, Iowa), and used unaltered as one eluant (E1). Reagent grade acetonitrile and 30%

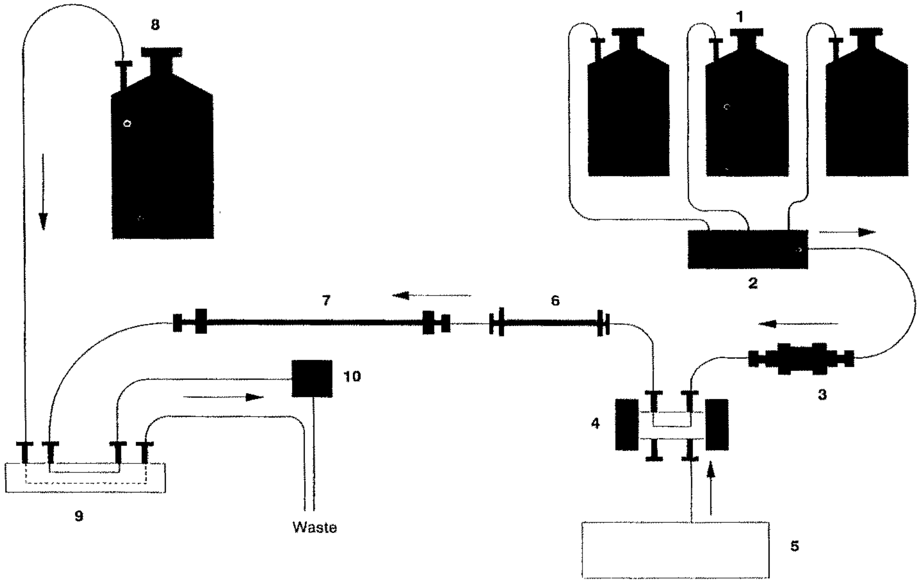

FIGURE 1: Schematic representation of the ion chromatograph system: 1 - eluant reservoirs, 2 - gradient pump, 3 - eluant mixer, 4 - sample valve, 5 - automated sampler, 6 - guard column, 7 - separator column, 8 - acid regenerant reservoir, 9 - suppressor column, 10 - conductivity cell.

ammonium hydroxide (both from J. T. Baker, Inc., Pittsburgh, Pennsylvania) diluted to 30% CH_3CN (v/v) and 10 mM NH_4OH with DI water was used as eluant two (E2) where the low concentration ammonium hydroxide was used as the ion-pair reagent. While most ion-pair applications utilize tetrabutylammonium hydroxide (TBAOH) as the ion-pair reagent, preliminary work indicated that the use of an interaction agent with a highly hydrophobic character resulted in greatly increased elution times for surfactant analytes. Ammonium hydroxide at a concentration of 10 mM offered the best separation and peak resolution within a reasonable analysis period. A 90% (v/v) solution of acetonitrile in DI water was used as the third eluant (E3). All eluants were degassed with helium for 20 minutes prior to use, and pressurized to 10 psi with helium during the analysis. A solution of approximately 5 mM sulfuric acid was used as the regenerant for the ion exchange membranes within the suppressor. The regenerant was pressurized to 10 psi with nitrogen during the analysis. A list of the surfactants used in this investigation and their level of purity is given in Table 1. A series of standard solutions of each surfactant was prepared at concentrations of 50, 100, 500, 1000, and 5000 mg/L in DI water (the saturation point of sodium lauryl sulfonate is around 3000 mg/L, therefore only 50 - 1000 mg/L solutions of SLSN were prepared).

Procedure

The chromatographic method involved a 15 minute gradient and analysis time beginning with a three minute initial purge period during which the mobile phase was maintained as a mixture of 33% eluant 1 (E1: DI water) and 67% eluant 2 (E2: 30% CH_3CN, 10 mM NH_4OH). The purpose of this initial phase was to purge any mobile contaminants from the column and to allow the baseline conductivity to recover following any previous run. Following the first phase, the 25 μL sample loop was introduced into the system for one minute to allow the sample to be completely flushed from the loop. The third phase involved a linear gradient, three minutes in duration, from the initial eluant mixture (33% E1, 67% E2) to a mixture of 83% eluant 2 and

TABLE 1. Surfactants used for ion chromatographic analysis

Surfactant	Acronym	n[a]	MW	Supplier	Purity
Sodium Octyl Sulfate	SOS	8	232.27	Aldrich	99%
Sodium Decyl Sulfate	SDS	10	260.32	Kodak	95%
Sodium Lauryl Sulfate	SLS	12	288.38	Aldrich	98%
Sodium Octyl Sulfonate	SOSN	8	216.28	Aldrich	98%
Sodium Decyl Sulfonate	SDSN	10	244.33	Aldrich	98%
Sodium Lauryl Sulfonate	SLSN	12	272.38	Pfaltz & Bauer	99%

[a] General chemical structure of linear alkyl sulfates: $CH_3(CH_2)_{n-1}OSO_3Na$
General chemical structure of linear alkyl sulfonates: $CH_3(CH_2)_{n-1}SO_3Na$

17% eluant 3 (E3: 90% CH_3CN). The effect of the change to a higher volume fraction of acetonitrile is to increase the hydrophobic nature of the mobile phase in order to elute the more hydrophobic species, long chain surfactants such as sodium lauryl sulfate (SLS), from the separator column more rapidly than would otherwise be possible. This has been found to significantly reduce the analysis time while simultaneously maintaining good peak resolution. This eluant mixture (83% E2, 17% E3) was maintained for six minutes, then a 30 second linear gradient returned the eluant mixture to the initial volumetric ratio (33% E1, 67% E2) where it was maintained for an additional 90 seconds.

The Dionex **4000i** ion chromatograph was calibrated using the concentration standard solutions prepared from the surfactant samples which were to be used for the adsorption experiments. The relationship between concentration and detector response (peak area) was determined to be linear over the defined concentration range of 0 to 5000 mg/L (0 to 1000 mg/L in the case of SLSN), with correlation coefficients of not less than 0.9977. The ion chromatograph required recalibration following any refilling or refreshing of any of the eluants. Slight variations in eluant concentration were found to have a significant effect on the reported concentration values (variations of up to 10% in concentration), as well as on the retention time of a given component (variations of up to 20% in retention time). Column ageing was also found to affect calibration results, but only over periods of time on the order of several months.

The amount of surfactant adsorbed onto a model surface (in this case spherical polystyrene particles were prepared and characterized for this purpose) was determined by equilibrating a known quantity of a polymer latex sol with a known concentration of surfactant and analyzing the bulk fluid phase for surfactant concentration to obtain the difference. In this experiment, samples were prepared in 20 mL vials which contained approximately 1% (by volume) of the polymer particles and a known initial quantity of surfactant. The samples were allowed to reach equilibrium over a period of more than 24 hours at room temperature, the polymer and associated adsorbed surfactant was then removed by filtering the sample through a 0.05 μm polycarbonate microfiltration membrane (Nuclepore, Pleasanton, California). Blank sample analysis indicated that no appreciable amount of surfactant was lost on the membrane. Analysis of the filtrate by the ion chromatographic method described above yields the free surfactant concentration evaluated from the peak areas. If the amount adsorbed at the liquid-air interface is neglected(7), the adsorbed amount of surfactant can be determined from:

$$\Gamma = \frac{M_S}{M_L} \tag{1}$$

where Γ is the adsorbed amount reported as a mass fraction and M_L is the mass of latex present. M_S is the mass of adsorbed surfactant which is determined by difference from:

$$M_S = v(C_{S,i} - C_{S,f}) \tag{2}$$

where v is the liquid phase volume of the sample, $C_{S,i}$ is the initial added surfactant concentration (in mg/L), $C_{S,f}$ is the free surfactant concentration (in mg/L) in the filtered bulk solution, and M_S is reported as mg of surfactant. The resulting minimum detection limit was found to be about 5 to 10 mg/L adsorbed surfactant based on the liquid phase volume. In order to minimize the integration error caused by changes in the baseline conductivity due to the eluant gradient, a sample of DI water was run as a standard. The standard DI water baseline was then subtracted from each analysis chromatogram to provide a more level baseline and consequently improve the accuracy of the peak integration by as much as 3% for those species which eluted during the gradient (e.g. SDS, SLS, and SLSN). An example of this process is shown in Figure 2. The reported free surfactant concentrations could then be converted to adsorbed amount and plotted against the bulk surfactant concentration to produce the adsorption isotherms.

RESULTS AND DISCUSSION

The Dionex series **4000i** ion chromatograph was calibrated for quantitative analysis using a six point linear calibration fit for each of the six anionic surfactants. Detector response (peak area) was recorded for the surfactant standard solutions following the baseline adjustment procedure outlined above, and was plotted against the concentration of the standard sample. A sample calibration curve is shown in Figure 3, and the calibration results for each surfactant are tabulated in Table 2. Each point on the calibration curve was calculated from three repeat samples which were found to be within ±10 mg/L (absolute standard deviation - ASD) of each other. Replicate calibration curve indicated no significant variation except when one or more of the eluants was replenished as previously noted. The intercept (*b*) on the linear fits could not be set to zero in the **AI-450** version 3.1 software, therefore the inherent weighting of the data points involved in the least squares calculation resulted in non-zero values for the intercept. Repeat analyses of the samples demonstrated that the instrumental precision was about ±5 mg/L (ASD), while the calibration was determined to be accurate to within approximately 10 mg/L (ASD). Forcing a zero intercept on the calibration curve resulted in slightly improved accuracy at low concentrations (±5 mg/L, ASD), while sacrificing some accuracy at concentrations above 1000 mg/L (±12 mg/L, ASD). However, these changes were relatively small and did not justify the amount of extra effort that would have been involved in external calibrations and concentration determinations. Newer versions of the **AI-450** software, which are now available, do offer the option to force a zero intercept for linear calibrations. All of the data collected in this experiment were based on calibrations with non-zero intercepts as shown in Table 2.

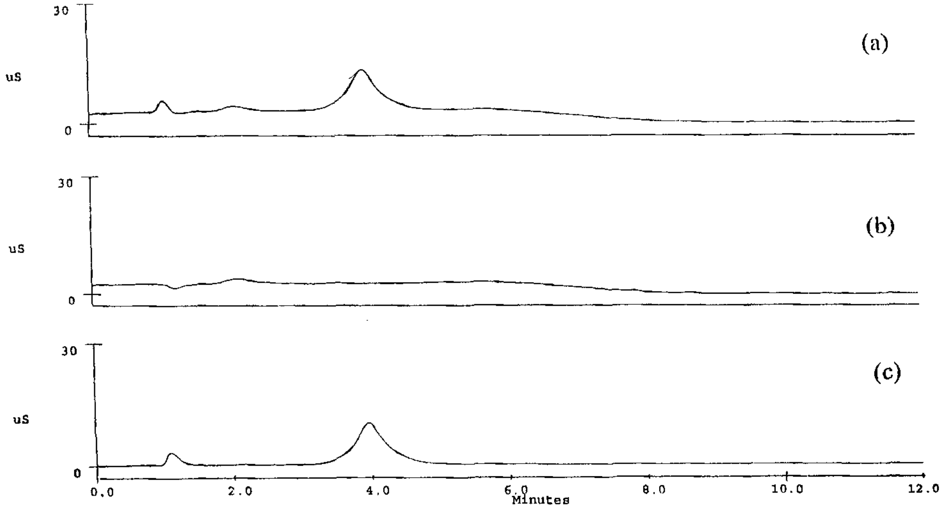

FIGURE 2: Example of the baseline adjustment process showing (a) the original chromatogram of sodium decyl sulfonate (SDSN), (b) the baseline chromatogram of deionized water, and (c) the resulting SDSN chromatogram obtained when the baseline chromatogram (b) is subtracted from the raw data chromatogram (a).

The retention times of the various surfactant species given in Table 2 are spaced in such a way that separation of all six species has been possible (although only at concentrations below 500 mg/L in the case of SOS and SOSN). This chromatographic technique can, therefore, differentiate between linear alkyl sulfates differing by only two carbon atoms in the alkyl chain, as well as distinguishing between sulfates and sulfonates of the same alkyl chain length. The separation of several closely related surfactants, as shown in Figure 4, is not only qualitative, but also quantitative in nature. Table 3 demonstrates that for the separation indicated in Figure 4 the ion chromatographic method accurately determines the concentration of each species to within 10 mg/L. This reliability is representative of the results acquired throughout the experimental investigation.

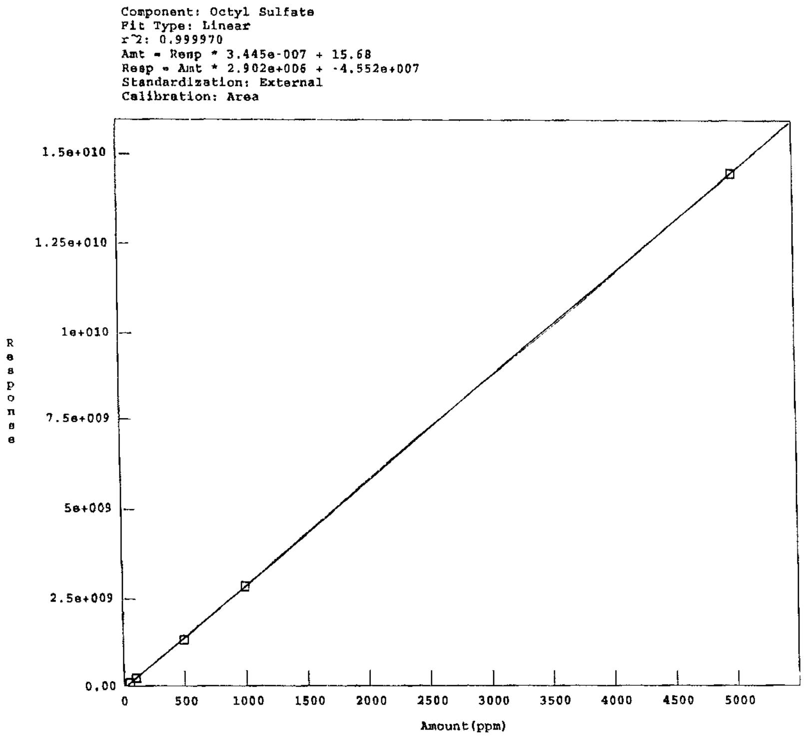

FIGURE 3: Ion chromatograph calibration curve of sodium octyl sulfate showing detector response versus concentration relationship and least squares fit results.

TABLE 2. Ion chromatograph example calibration results (linear fit)
Concentration = Response × a + b

Surfactant	Retention Time (min)	*a*	*b*	r^2
SOS	2.65	3.445×10^{-7}	15.68	1.0000
SDS	6.00	3.366×10^{-7}	-27.39	0.9977
SLS	7.95	3.766×10^{-7}	-6.03	0.9996
SOSN	2.40	2.573×10^{-7}	-39.89	0.9991
SDSN	4.25	2.794×10^{-7}	-23.49	0.9998
SLSN	7.35	3.984×10^{-7}	-6.15	0.9996

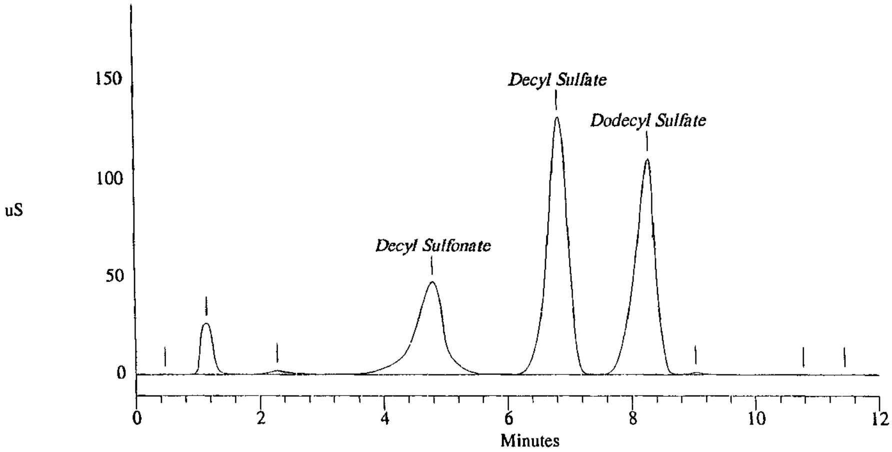

FIGURE 4: Separation of C_{10} and C_{12} alkyl sulfates and C_{10} alkyl sulfonate obtained using ion chromatography.

TABLE 3. Quantitative results of ion chromatographic separation shown in Figure 4.

Retention Time	Component Name	Sample Concentration	Observed Concentration
4.80	SDSN	500 mg/L	508 mg/L
6.83	SDS	1000 mg/L	993 mg/L
8.28	SLS	1000 mg/L	1002 mg/L

The separation and quantitative precision obtained using this technique is important for future investigations of surfactant adsorption behavior since most practical application's of surface -active agents involve a multi-component system containing two or more unique surfactant species. In addition, minor modifications in the eluant gradient can be made which have been proven to allow extremely hydrophobic (i.e. strongly retained) species to elute in relatively short periods. While most of the work in this investigation was conducted using a method which involved a gradient from 20% (v:v) acetonitrile to 40% CH_3CN, a method using a 40% to 70% CH_3CN gradient was utilized to facilitate the detection of sodium lauryl benzene sulfonate (SLBSN,

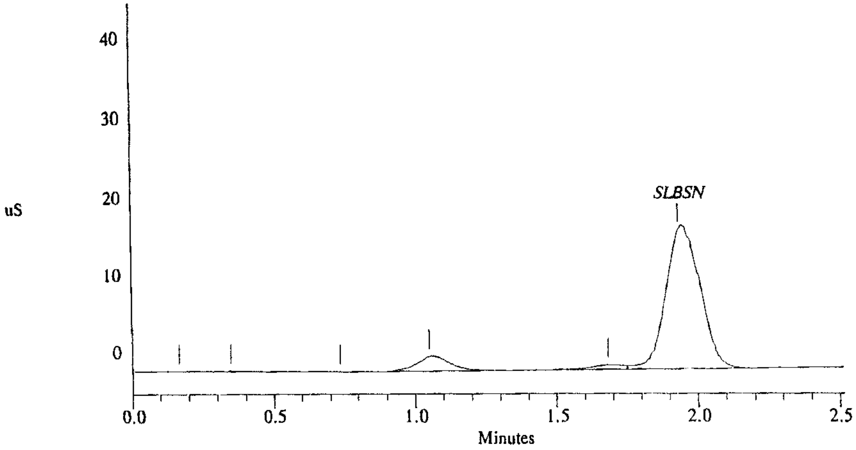

FIGURE 5: Chromatogram of sodium lauryl benzene sulfonate using modified eluant gradient 40-70 (%CH_3CN by volume).

Aldrich) with a minimal analysis time and without any loss of experimental accuracy. This analysis is shown in Figure 5 in which a 50 mg/L SLBSN standard solution was observed to contain 49.7 mg/L SLBSN. Work at this location has recently reported success in obtaining adsorption isotherms for single component systems of anionic surfactants(11). The analysis of multi-component systems of anionic surfactants and a comparison of these adsorption isotherms with those of the individual components is currently in progress. In addition, an investigation of the application of this technique to systems of nonionic and cationic surfactants as well as cosurfactant species such as linear alcohols is planned.

CONCLUSIONS

Today the chromatographic analysis of ionic materials is widely applied and rapidly expanding. The number of species which may be determined continues to grow, as does the number of areas of science and technology where ion chromatography plays an important role. This investigation has indicated that ion chromatography is capable of clearly separating closely related anionic surfactants and reporting quantitatively accurate information regarding the concentration of each of these species. Techniques used for acquiring the same information in previous studies were tedious and inaccurate. In addition, the ion chromatographic technique is highly flexible and can be easily modified to be applicable to a wide variety of surface active materials. The introduction of an ion chromatographic method to directly determine the concentration of surfactant species in a bulk fluid phase greatly simplifies the analysis of surfactant adsorption behavior.

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