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UNIVERSAL DETECTION AND QUANTITATION OF SURFACTANTS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY BY MEANS OF THE EVAPORATIVE LIGHT-SCATTERING DETECTOR

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SUMMARY

The evaporative light-scattering (ELS) detector was evaluated for the quantitation of various types of surfactant. High-performance liquid chromatography techniques coupled with the ELS detector were developed for the quantitative analyses of commercially prepared ethoxylated alcohols, alkyl ether sulfates, and alkyl sulfonates, alkylbenzene sulfonates, and petroleum sulfonates. These analyses demonstrate the first direct techniques for separation and universal detection of a wide range of surfactants with a common detector. The ELS detector was ideal for the detection and quantitation of all species including those which do not contain chromophores. The detector provides an equal and linear response factor for each class of surfactant that is independent of molecular weight. The detection limits are in the low nmole range. The standard deviation of all the analyses was less than 1%.

INTRODUCTION

Surfactants are widely used for a variety of purposes including surface wetting agents, detergents, emulsifiers, lubricants, gasoline additives and enhanced oil recovery agents. The type of surfactant selected for a particular application often depends on the chemical and physical properties required and on economics or other considerations such as environmental concerns. To meet these requirements a typical surfactant formulation may contain blends of a variety of commercial products, which could include ionic and non-ionic ethoxylated surfactants, alkyl- and alkylarylsulfonates (synthetic sulfonates) and petroleum sulfonates.

Commercial surfactants contain mixtures of isomers and homologues, and may also contain variable amounts of unreacted starting material or extraneous oil that is added as a diluent or thinning agent. Variable amounts of water and inorganic salts are commonly present in these products. In order to maintain quality assurance, considerable effort must be devoted to developing reliable quantitative techniques for characterizing components present in these surfactants. Several publications and lit-

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erature reviews are available that describe techniques developed for surfactant analysis[1–6].

Difficulties are often encountered in many analytical methods due to the complex nature of the mixture and the lack of adequate detection capabilities, thus leading to poor quantitation techniques. For routine separation of a broad range of surfactants, high-performance liquid chromatography (HPLC) appears to be most promising[7–18]. UV and fluorescence detectors are commonly used in HPLC analysis of surfactants because of their compatibility with separation schemes requiring gradient elution. However, these detectors have two inherent limitations: (1) the detector response is dependent on molecular structure, *i.e.* the degree of aromaticity and type of substitution, and (2) only species with a chromophore can be detected. To overcome these limitations, post-column reaction detectors, based on extraction of fluorescent ion-pairs, were introduced for on-line detection of alkylsulfonates in HPLC[19–22]. However, the ion-pair formation and extraction efficiency were still dependent on the molecular structure and could not easily be used for quantitation.

Recently, the evaporative light-scattering (ELS) detector, also known as the mass detector, was introduced as a universal detector for non-volatile compounds in liquid streams[23–25]. The detector measures light refracted by the non-volatile particles after the effluent from the HPLC column is nebulized and the carrier solvent is evaporated. The amount of refracted light is proportional to the concentration of the analyte species. The ELS detector has been used to detect proteins[26], polymers[27], coal derivatives[28] and petroleum fractions[29] in HPLC separations. This paper reports the first direct techniques for separation and quantitation of surfactants by HPLC by means of the ELS detector for universal detection. The following surfactants were examined in this study: (a) non-ionic ethoxylated alcohols; (b) alkyl ether sulfates; and (c) synthetic and petroleum sulfonates.

EXPERIMENTAL

Apparatus

HPLC was performed with a Hewlett-Packard 1090 chromatograph (Hewlett-Packard, Atlanta, GA, U.S.A.) equipped with a ternary solvent delivery system, an auto-injector with a 0–25-μl injection loop, an oven compartment, and a diode-array UV detector. An ELS detector (Applied Chromatography Systems, Luton, U.K.) was connected in series to the UV detector. Signals from both detectors were processed with a VG 11-250 Multichrom chromatography data system (VG Instruments, Manchester, U.K.).

Reagents

All solvents were of HPLC-reagent grade (Burdick & Jackson Labs., Muskegon, MI, U.S.A.) and were filtered through a 0.45-μm glass fiber filter (Gelman Sciences, Ann Arbor, MI, U.S.A.). Hexane, 2-propanol and water were used for the analysis of non ionic ethoxylated surfactants. Water and tetrahydrofuran (THF) were used for the analysis of anionic surfactants.

Samples

All commercial surfactants used in this study are listed in Table I. No prelimi-

TABLE I

MODEL SURFACTANTS

Surfactant	*Abbreviation*
Nonylphenolethoxyalcohol	
$C_9H_{19}PhO(CH_2\ CH_2O)_{11}H$	NP11
Alkylethoxyalcohols	
$C_{12}H_{25}$–$C_{14}\ H_{29}O(CH_2CH_2O)_5H$	AE5
$C_{12}H_{25}$–$C_{14}\ H_{29}O(CH_2CH_2O)_7H$	AE7
$C_{12}H_{25}$–$C_{14}\ H_{29}O(CH_2CH_2O)_{11}H$	AE11
$C_{12}H_{25}O(CH_2\ CH_2O)_{12}H$	AE12
$C_{13}H_{27}O(CH_2\ CH_2O)_7H$	b-AE7
$C_{13}H_{27}O(CH_2\ CH_2O)_{11}H$	b-AE11
Alkyl ether sulfates	
$C_{12}H_{25}(CH_2\ CH_2O)_6OSO_3Na$	LN-60COS
$C_{12}H_{25}(CH_2\ CH_2O)_8OSO_3Na$	LN-80COS
$C_{12}H_{25}(CH_2\ CH_2O)_{12}OSO_3Na$	LN-120COS
$C_4H_9(C_4H_8O)\ _6(C_2H_4O)_2OSO\ _3Na$	BU-6B2ECOS
$C_4H_9(C_4H_8O)\ _6(C_2H_4O)_7OSO\ _3Na$	BU-6B7ECOS
Alkylsulfonate	
$C_{12}H_{25}SO_3Na$	1-C12
Alkylbenzenesulfonates	
$C_{12}H_{25}PhSO_3Na$	b-PhC12
$C_{16}H_{33}PhSO_3Na$	b-PhC16
Alkylarylsulfonates	
Sodium petroleum sulfonate 1	NaPS-1
Sodium petroleum sulfonate 2	NaPS-2
Calcium petroleum sulfonate 1	CaPS-1
Calcium petroleum sulfonate 2	CaPS-2
Calcium petroleum sulfonate 3	CaPS-3
Calcium petroleum sulfonate 4	CaPS-4

nary sample preparation was needed other than dilution. The non-ionic ethoxylated surfactants were diluted 1:40 (v/v) with hexane. The anionic surfactants (alkyl ether sulfates and synthetic and petroleum sulfonates) were diluted 1:20 (v/v) with water–THF (50:50). The calcium sulfonate surfactants were diluted 1:20 (v/v) with a THF–38% hydrochloric acid solution of pH *ca.* 1. Hydrochloric acid (reagent grade) was required to prevent salt precipitation by converting any excess water-insoluble calcium carbonate into water-soluble calcium chloride. All diluted samples were filtered through a 0.2-μm filter (Gelman Acrodisc CR) directly into the injector vials.

Chromatographic procedures

The non-ionic ethoxylates were separated according to the number of ethylene oxide (EO) groups (n) using normal-phase chromatography. The separation was achieved on an amino column (DuPont Zorbax NH_2, 25 cm × 4.6 cm I.D., 5 μm particle size). A precolumn (Zorbax BP NH_2, 2.5 cm × 0.2 cm I.D.) was connected to

TABLE II

GRADIENT ELUTION PROGRAM FOR NORMAL-PHASE HPLC OF NON-IONIC ETHOXYLATED SURFACTANTS

Time (min)	*Hexane (%)*	*2-Propanol (%)*	*Water (%)*
0	100	0	0
55	37	60	3

the amino column. The solvent system was a gradient of hexane, 2-propanol and water. The 55-min gradient program is summarized in Table II.

Components of the alkyl ether sulfate surfactants were separated into inorganic salt, sulfates and unreacted alchohol using a rapid reversed-phase chromatography. The column used for this separation was a 2.5 cm × 0.2 cm I.D. column packed with 10-μm C_{18}. The solvent system was a 4-min gradient program of water and THF, which is summarized in Table III. The synthetic and petroleum sulfonate components were separated into inorganic salt, sulfonates and unreacted oil by the same reversed-phase chromatographic method.

In all analyses the flow-rate was 1 ml/min and the column compartment was kept at 40°C.

Detection

The diode-array UV and ELS detectors were connected in series. The UV signals were monitored at 230 and 254 nm. The operating conditions of the ELS detector were optimized for maximum detector response and stable baseline. Surfactants with UV absorbance were detected by both detectors, while the UV-transparent surfactants could only be detected by the ELS detector.

The two basic parameters available for optimization of the ELS detector output are the nebulizer gas nitrogen flow-rate and the evaporator tube temperature. During normal-phase chromatography of non-ionic ethoxylates, the nitrogen pressure was 45 p.s.i. and the evaporator tube temperature was *ca.* 35°C. For the reversed-phase chromatography of alkyl ether sulfates and sulfonate surfactants, the nitrogen pressure was 20 p.s.i. and the evaporator tube temperature was *ca.* 50°C.

TABLE III

GRADIENT ELUTION PROGRAM FOR REVERSED-PHASE HPLC OF ALKYL ETHER SULFATE AND SYNTHETIC AND PETROLEUM SULFONATE SURFACTANTS

Time (min)	*Water (%)*	*THF (%)*	*Mode of operation*
0.0	90	10	Normal flow
0.5	90	10	Normal flow
1.0	40	60	Normal flow
2.5	40	60	Normal flow
2.6	0	100	Backflush
4.0	90	10	Backflush

RESULTS AND DISCUSSION

The ELS detector

In the ELS detector operation, the eluent from HPLC column is introduced into the top of a heated evaporator tube where it is nebulized by a stream of nitrogen. Droplets formed at the nebulizer pass through the heated tube. The solvent is vaporized and an aerosol is formed from the non-volatile solute particles contained in the eluent. The particles pass through a light path and the light scattered is detected at a fixed angle. The amount of scattered light is proportional to concentration.

The detector has many desirable features. It is inexpensive, stable and easy to operate. Most important, the detector is not subject to solvent interference and is insensitive to the chemical composition of detected species. The characteristics of the ELS detector in terms of nebulization and light-scattering theories have been studied in detail[25]. It has been shown that detector linearity and detection limits are directly related to the size, shape and number of particles formed in the evaporator tube. Under fixed nebulization and evaporation conditions, the detector response is dependent on the density and refractive index of the aerosol particles. For samples with similar densities and refractive indexes, the response is proportional to the mass of material present in each sample and independent of molecular weight. These characteristics allowed the ELS detector to be used as a universal detector for surfactants.

Analysis of non-ionic ethoxylates

Aliphatic and aromatic non-ionic ethoxylated surfactants, $RO(CH_2CH_2O)_nH$, were analyzed to determine the distribution of the ethoxylate oligomers. Oligomers with different numbers of EO groups were separated by normal-phase HPLC method as summarized in Table II. The separated components were monitored by both the ELS and UV detectors. Signals obtained by both detectors were compared, and normalized peak areas were used to calculate the percent composition of each oligomer.

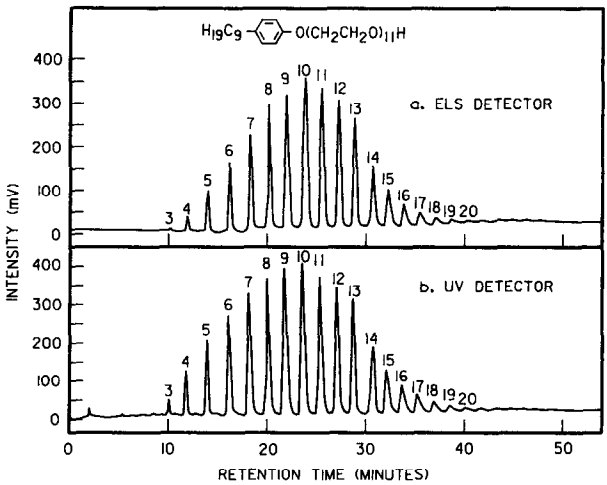

Fig. 1. HPLC analysis of nonylphenolethoxyalcohol oligomers: (a) ELS detector; (b) UV detector.

TABLE IV

QUANTITATIVE ANALYSIS OF NP11 OLIGOMERS WITH THE UV AND ELS DETECTORS

Number of EO groups, n	*Composition (%)*	
	UV	*ELS*
3	0.83	0.01
4	2.30	0.71
5	4.16	2.16
6	6.24	4.25
7	8.54	7.27
8	10.51	10.65
9	11.76	12.78
10	11.91	13.72
11	11.05	13.07
12	9.46	11.30
13	7.66	8.95
14	5.84	6.19
15	4.02	3.92
16	2.60	2.39
17	1.60	1.38
18	0.95	0.80
19	0.56	0.40

An example is shown in Fig. 1. The figure shows the high resolution of components in a nonylphenolethoxyalcohol, NP11, revealing a range of oligomers from n = 3 to 20. Quantitation of NP11 oligomers from these data is shown in Table IV. Comparison of signals obtained by both detectors (Fig. 1a and b) shows that the sensitivity of the ELS detector is comparable to that of a UV detector. Although the distribution profiles obtained by both detectors appeared similar, careful examination of the figures shows that the UV detector gives a higher response for lower-molecular-weight components, *i.e.* for components with $n \leqslant 7$. As shown in Table IV, the difference between the UV and the ELS response is large for $n = 3$, but decreases as n increases. This is due to the change in UV absorbance as a function of molecular structure. At the monitored wavelength (230 nm), the shorter the EO chain, the higher the absorbance[13]. As shown below, the ELS detector was found to provide a uniform linear response for ethoxylates, independent of n.

An especially important feature of the ELS detector was that it could be used for the detection and quantitation of ethoxylates not amenable to UV detection. Fig. 2 shows the distribution profiles of linear alkylethoxyalcohols AE5, AE7, and AE11. The general formula for these alcohol surfactants is $RO(CH_2CH_2O)_nH$, where R is $C_{12}H_{25}$ or $C_{14}H_{29}$ and the average value for n (mean, or $\bar{n}$) is 5 for AE5, 7 for AE7 and 11 for AE11. Using this technique it was possible to separate components of each product according to n. For example, in Fig. 2a, the AE5 components are separated into groups according to n, 1–10. Within each group, components are further separated according to the length of the alkyl chain, *i.e.* C_{12} and C_{14}. A similar separation is shown in Fig. 2b for AE7 and in Fig. 2c for AE11, where the n distribution ranged from 3–11 and 6–16, respectively.

Fig. 3 shows the distribution profiles obtained for the branched alkylethoxyal-

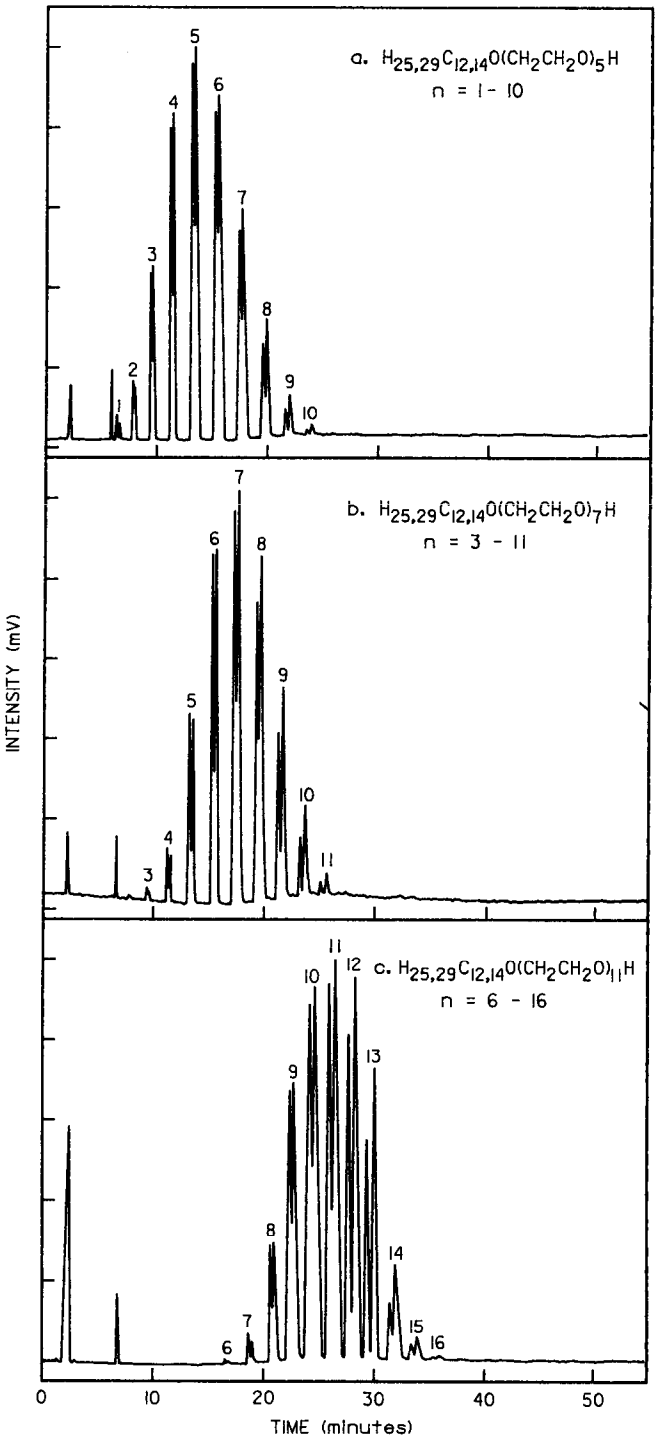

Fig. 2. HPLC analysis of linear alkylethoxyalcohol oligomers: (a) AE5; (b) AE7; (c) AE11.

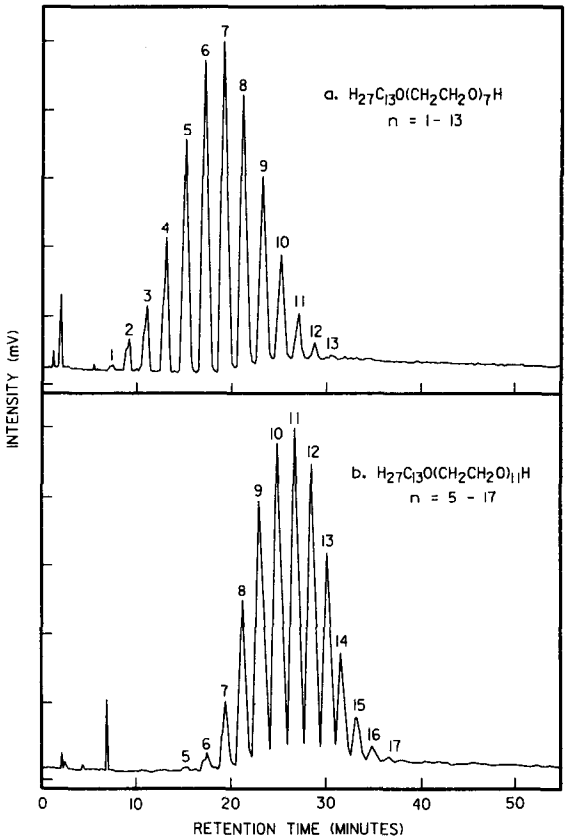

Fig. 3. HPLC analysis of branched alkylethoxyalcohol oligomers: (a) b-AE7; (b) b-AE11.

TABLE V

COMPARISON OF RESULTS OBTAINED BY THE HPLC–ELS METHOD WITH THE MANUFACTURER'S SPECIFICATIONS FOR THE QUANTITATIVE ANALYSIS OF AE11 OLIGOMERS

Number of EO groups, n	*Composition (%)*	
	Manufact. spec.	*ELS detector*
7	1.8	0.8
8	5.0	5.1
9	11.5	12.9
10	19.1	20.0
11	22.4	22.5
12	19.3	19.2
13	12.5	12.5
14	6.2	5.7
15	2.1	1.3

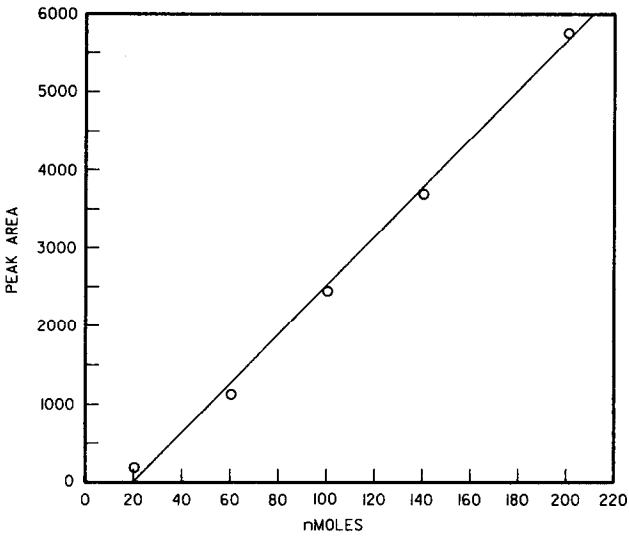

Fig. 4. Calibration curve of alkylethoxyalcohol surfactant, $C_{12}H_{25}O(CH_2CH_2O)_8H$.

cohols $C_{13}H_{27}O(CH_2CH_2O)_nH$, b-AE7 and b-AE11. The EO distribution is shown to be between 1 and 13 with $n = 7$ for b-AE7, and between 5 and 17 with $n = 11$ for b-AE11. In comparison with the linear ethoxylated alcohols shown in Fig. 2, the retention times were longer and peaks were broader due to the alkyl chain branching.

The percent composition of ethoxylate oligomers obtained with the ELS detector was verified by comparison with product specifications derived from flame ionization detection (FID). An example is shown in Table V for AE11. A similar comparison was obtained for other ethoxylated surfactants indicating close agreement between data obtained with the two detectors. The data illustrate that the ELS detector responds uniformly to these surfactants and is independent of the EO chain length. It also demonstrates the high accuracy of the HPLC–ELS method for quantitating ethoxylated oligomers. In these examples the standard deviation of the HPLC–ELS method was less than 1%.

The linearity and limit of detection of the ELS detector were determined with the ethoxyalcohol $C_{12}H_{25}O(CH_2CH_2O)_8H$. The calibration curve was linear over the concentration range shown in Fig. 4. The detection limit was found to be 20 nmol.

Analysis of alkyl ether sulfates

Anionic alkyl ether sulfate surfactants are produced by sulfating non-ionic alcohol polyalkyloxylates such as the ethoxylated surfactants discussed above. The sulfated products generally contain variable amounts of unconverted alcohols and even inorganic salts as reaction byproducts. Determination of the ratio of anionic to non-ionic components in surfactant mixtures is frequently desired for quality control and performance evaluation.

An HPLC–ELS method was developed to quantitate the ionic alkyl ether sulfates and unconverted non-ionic alcohol components present in the product mixtures. Separation of the ionic sulfate and non-ionic alcohol components was achieved by the reversed-phase chromatographic method summarized in Table III. This method com-

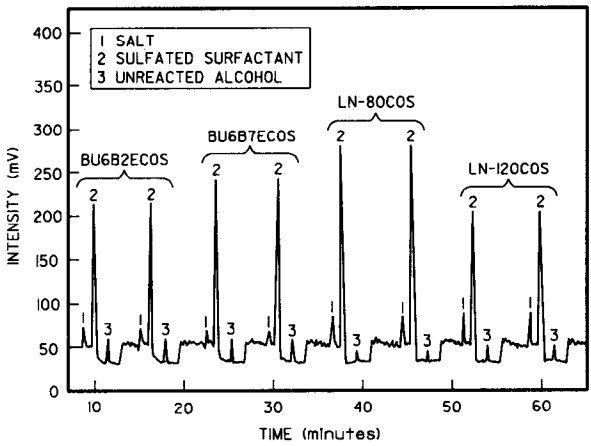

Fig. 5. HPLC analysis of (1) inorganic salt, (2) sulfated surfactant, and (3) unreacted alcohol in alkyl ether sulfate surfactants.

bined with ELS detection provided a fast and accurate technique for on-line separation and quantitation of the ionic and non-ionic alkyloxylate surfactant species.

Analysis of four alkyl ether sulfate surfactants is shown in Fig. 5. This figure shows the separation of each sample into three components, using two injections per sample. The first component is inorganic salt eluted with 90% water and 10% THF (Peak 1). As the THF concentration increases to 60%, the ionic sulfate surfactant components are eluted (Peak 2). After elution of these ionics, the non-ionic components are backflushed with 100% THF (Peak 3). All peaks are sharp and well resolved. The analysis time is 4 min per sample.

The ELS detector response was slightly higher for the non-ionic than for the ionic components. Fig. 6 shows the calibration curves obtained for the linear alkylethoxysulfate standard LN-80COS and the corresponding alkylethoxyalcohol LN-80. Both curves are linear with detection limits of *ca.* 20 nmol for the ionics and

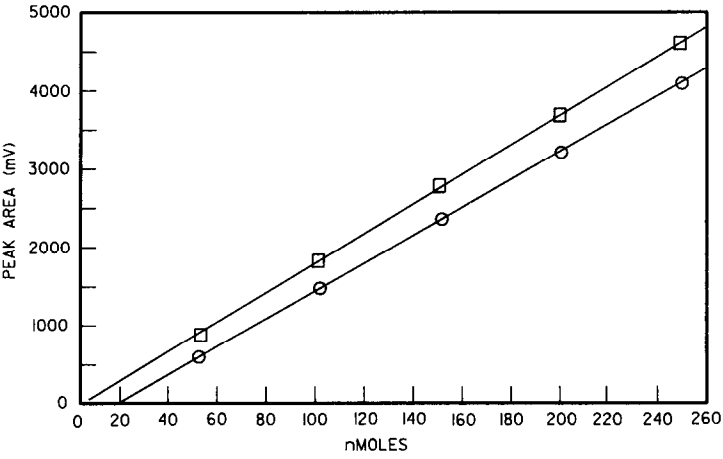

Fig. 6. Calibration curves of alkylethoxysulfate, LN-80COS (○) and alkylethoxyalcohol, LN-80 (□).

ca. 5 nmol for the non-ionics. Similar to the non-ionic ethoxylated surfactants discussed above, the detector response for the ionics was independent of the alkyl and ethoxy or butoxy chain lengths. The concentrations of ionic sulfates and non-ionic alcohols in the mixtures can be calculated directly from peak areas and the calibration curves.

Table VI lists the concentrations of alkyl ether sulfate samples obtained by HPLC–ELS and the standard mixed-indicator two-phase titration methods[30]. A comparison of the results shows good agreement between the two methods except for the highly water-soluble surfactants, BU-6B7ECOS and LN-120COS. The lower concentrations reported by the two-phase titration can be attributed to incomplete titration of these highly water soluble surfactants[30], a limitation of the titration method. Therefore, concentrations calculated from the ELS detector response for BU-6B7ECOS and LN-120COS are believed to be more accurate.

TABLE VI

QUANTITATION OF IONIC ALKYL ETHER SULFATE SURFACTANTS BY THE HPLC–ELS AND TWO-PHASE TITRATION METHODS

Surfactant	*Two-phase titration (mmol)*	*ELS detector (mmol)*
LN-60COS	9.9	10.0
LN-80COS	9.6	9.1
LN-120COS	7.1	8.6
BU-6B2ECOS	7.3	7.5
BU-6B7ECOS	6.6	8.0

Analysis of synthetic and petroleum sulfonates

Synthetic and petroleum sulfonates were analysed by the reversed-phase chromatographic procedure established for the analysis of alkyl ether sulfate surfactants (Table III). Similar to alkyl ether sulfates, the sulfonate mixtures were separated into three fractions: (1) inorganic salt; (2) sulfonates; and (3) unreacted oil. The ELS detector was used for the detection of the separated fractions and for the quantitation of sulfonates. The results were compared with those obtained by the standard titration methods[30,31].

Results from the HPLC–ELS analysis of a linear sodium alkylsulfonate standard, $C_{12}H_{25}SO_3Na$, are shown in Fig. 7. The response shown in Fig. 7 resulted from various injection volumes of 0.017 *M* C_{12} alkylsulfonate solution, *i.e.* 25 to 2 μl. The analyses of two branched sodium alkylbenzenesulfonate standards, $C_{12}H_{25}PhSO_3Na$ and $C_{16}H_{33}PhSO_3Na$, are shown in Fig. 8. The alkylbenzenesulfonate standards were at concentrations of 0.01 *M*, and the injection volumes ranged from 25 to 4μl. As shown in the chromatograms, all standard solutions contained only sulfonate; no salt or oil was present.

Fig. 9 shows the linear calibration curve obtained for alkylsulfonate and alkylbenzenesulfonate standards. As shown, the sulfonate detection limit is *ca.* 25 nmol and the ELS detector response factor is essentially the same for all the three sulfonate

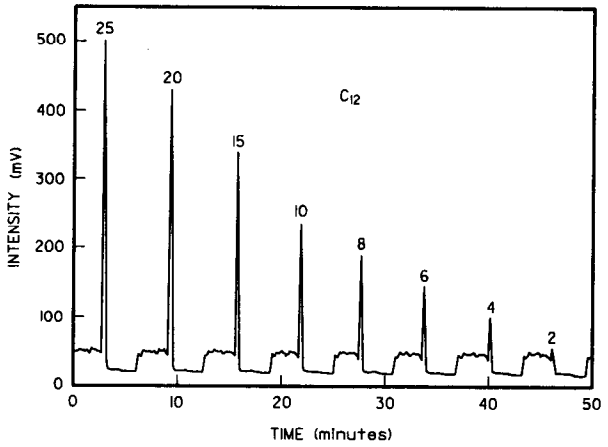

Fig. 7. ELS detector response to injections of 25–2 μl of 0.017 *M* linear sodium alkylsulfonate $C_{12}H_{25}SO_3Na$.

standards. Thus, the response is the same for both aliphatic and aromatic sulfonates and independent of the alkyl chain length.

The analyses of two petroleum sulfonates, NaPS-1 and NaPS-2, are shown in Fig. 10. The response to five injection volumes ranging from 25 to 5 μl for each surfactant is shown. Good separation was achieved between the inorganic salt and the sulfonated components. The oil present in NaPS-1 and NaPS-2 surfactants consisted of low-molecular-weight components, which were totally volatile under the detector operating conditions and, therefore, could not be detected. These two sulfonates are considerably different in molecular structure distribution. Nevertheless, their elution characteristics were the same as those observed for the synthetic single

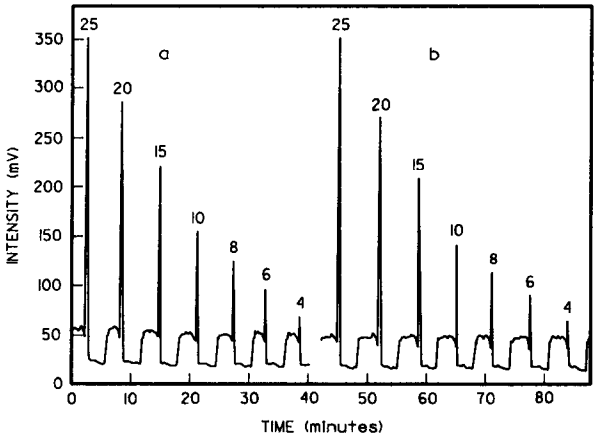

Fig. 8. ELS detector response to injections of 25–4 μl 0.01 *M* branched sodium alkylbenzenesulfonates: (a) $C_{12}H_{25}PhSO_3Na$; (b) $C_{16}H_{33}PhSO_3Na$; (Ph = C_6H_4).

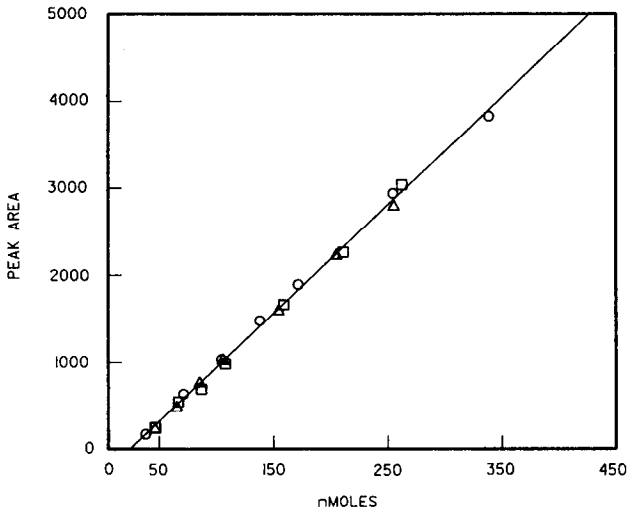

Fig. 9. Calibration curve of synthetic sulfonates, $C_{12}H_{25}SO_3Na$ (○); $C_{12}H_{25}PhSO_3Na$ (△); and $C_{16}H_{33}PhSO_3Na$ (□); (Ph = C_6H_4).

component sulfonates, *i.e.* a single, narrow, well defined peak for the sulfonate constituents. Fig. 11 shows the calibration curve obtained for both NaPS-1 and NaPS-2. This curve is the same as that obtained for C_{12} alkyl sulfonates. Therefore, the ELS detector response was the same for both synthetic and petroleum sulfonates and independent of molecular weight.

The concentrations of synthetic and petroleum sulfonates were calculated directly from peak areas using the sulfonate calibration curve shown in Fig. 9. Table VII summarizes the quantitative results calculated from the ELS detector response

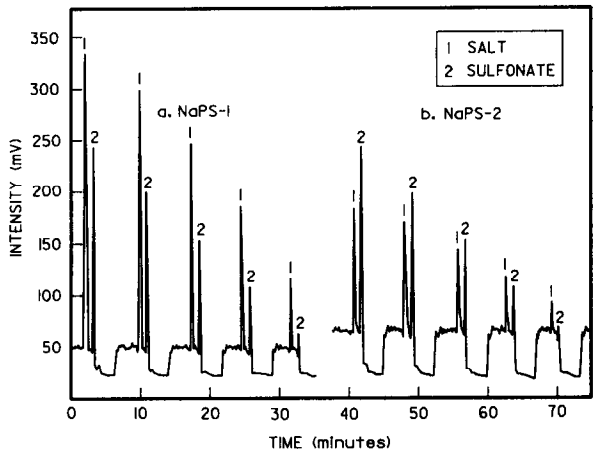

Fig. 10. HPLC analysis of (1) inorganic salt and (2) sulfonates present in sodium petroleum sulfonates: (a) NaPS-1; (b) NaPS-2. Injection volumes: 25, 20, 15, 10 and 5 μl of each.

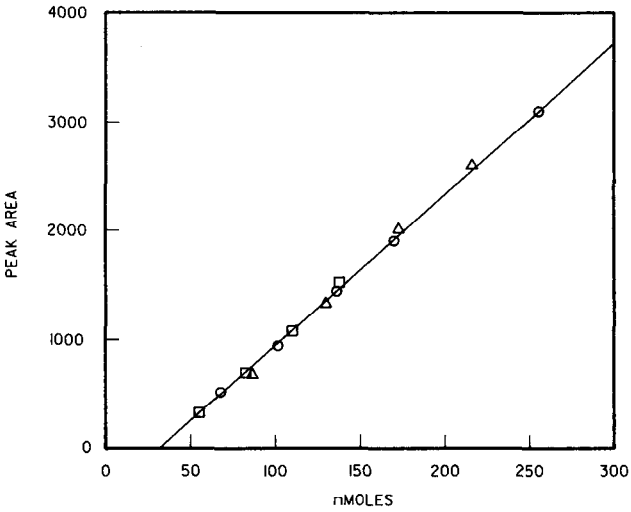

Fig. 11. Calibration curve of synthetic sulfonate $C_{12}H_{25}SO_3Na$ (○) and petroleum sulfonates NaPS-1 (△) and NaPS-2 (□).

TABLE VII

QUANTITATION OF SYNTHETIC AND PETROLEUM SULFONATES BY THE HPLC–ELS AND TWO-PHASE TITRATION METHODS

Surfactant	*Two-phase titration (mmol)*	*ELS detector (mmol)*
1-C_{12}	16.9	17.0
b-PhC_{12}	10.2	10.0
b-PhC_{16}	10.5	10.7
NaPS-1	8.5	8.6
NaPS-2	5.8	5.5

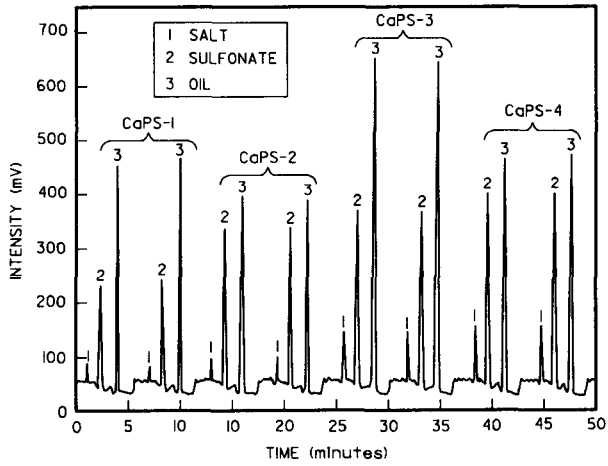

Fig. 12. HPLC analysis of (1) inorganic salt, (2) sulfonates, and (3) oil present in calcium petroleum sulfonates CaPS-1, CaPS-2, CaPS-3 and CaPS-4.

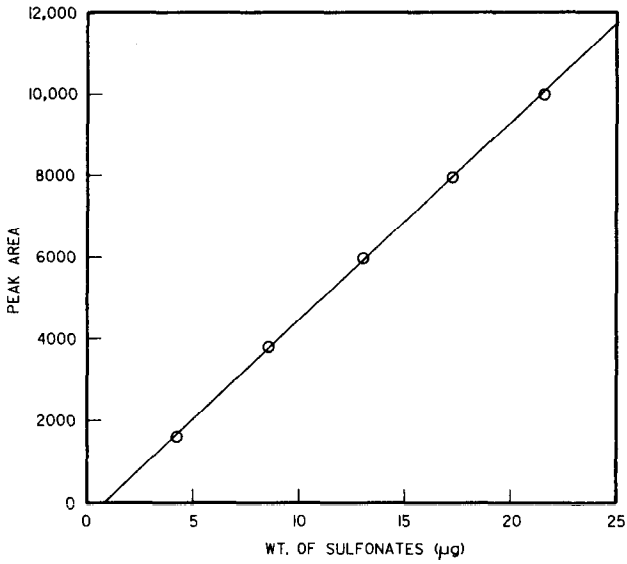

Fig. 13. Calibration curve of calcium petroleum sulfonate CaPS-1.

and those obtained by the two-phase titration method. Excellent agreement was found between results from the two methods (correlation coefficient = 0.9999). This agreement demonstrates the high accuracy of the HPLC–ELS method.

The analyses of four calcium petroleum sulfonate surfactants, CaPS-1, CaPS-2, CaPS-3, and CaPS-4, which are used as lubricating oil additives, are presented in Fig. 12. As shown, the surfactant components are separated into inorganic salt, sulfonated species, and unreacted oil. A baseline separation was obtained for all components and the repeatability was excellent.

The ELS detector response factor was found to be higher for these calcium-based surfactants than for the sodium sulfonates. This is not surprising in view of the structural differences between these two types of surfactant. Calcium-based sulfonates contain two sulfonate moieties per molecule in contrast to only one as in the sodium based compounds. Clearly, this difference in structure affects the properties of

TABLE VIII

QUANTITATION OF CALCIUM PETROLEUM SULFONATE SURFACTANTS BY THE HPLC–ELS AND METHYLENE BLUE TITRATION METHODS

Surfactant	*Activity (%)*	
	MB titration	*ELS detector*
CaPS-1	45.3	45.3
CaPS-2	44.9	45.6
CaPS-3	19.3	18.5
CaPS-4	30.9	30.6

the aerosol particles, *i.e.* size, shape, and number of particles formed in the evaporator tube, resulting in a higher response factor for the calcium-based class of surfactants. Fig. 13 shows the relationship between the injected quantity of CaPS-1 sulfonate and peak area. The response is linear with a detection limit of *ca.* 1 μg and a standard deviation of less than 1%.

The sulfonate peak areas and the calibration curve shown in Fig. 13 were used to calculate the percent activity (sulfonate weight percent) of each surfactant mixture. The calcium petroleum sulfonate activities obtained in this manner are listed in Table VIII, along with the activities obtained by the standard methylene blue titration[31]. Again, the comparison of the two techniques demonstrated a uniform response for the ELS detector and the high accuracy of the HPLC–ELS method.

For all analyses of the sodium and calcium synthetic and for the petroleum sulfonates presented here the standard deviation of the HPLC–ELS method was less than 1%. A correlation coefficient greater than 0.999 was found in comparison with the standard titration methods.

CONCLUSIONS

Examination of a wide range of non-ionic and anionic ethoxylated surfactants, $RO(CH_2CH_2O)_nH$ and $R(CH_2CH_2O)_nOSO_3Na$, where R ranged from C_6 to C_{14} alkyl or alkylbenzene and n varied from 1 to 20, showed no measurable change in detector response with the change in molecular weight. The ELS detector also exhibited an equal response factor for both synthetic and petroleum sulfonates, *i.e.* alkyl-, alkylbenzene- and alkylarylpetroleum sulfonates, that was independent of the alkyl chain length and the degree of aromaticity. The detector provided a uniform linear response for each class of surfactant, with detection limits in the low nmole range.

The HPLC procedures presented here provide effective separation and quantitation of components in commercial surfactant products. In comparison with conventional assays of surfactant activity, HPLC–ELS methods are simple, rapid, accurate, reproducible, and free from interferences.

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