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SURFACTANT CHARACTERIZATION BY REVERSED-PHASE ION PAIR CHROMATOGRAPHY

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SUMMARY

Alkylbenzenesulfonates are separated according to the length and structure of the alkyl chain using reversed-phase ion pair high-performance liquid chromatography (HPLC). The separation is controlled by pH, counter ion concentration, and mobile phase polarity. Optimization of these parameters resulted in a calibration curve for retention time *versus* alkyl chain carbon number. This curve provides a quick means for the determination of the sulfonate alkyl chain distribution. The analysis is applicable to synthetic and petroleum sulfonates as well as ethoxylated alkyl sulfates and ethoxylated alkyl carboxylates.

INTRODUCTION

High-performance liquid chromatography (HPLC) provides an excellent means for the analysis of surfactants such as alkylbenzenesulfonates. Procedures have been reported for the separation of sulfonates according to the degree of sulfonation by ion-exchange chromatography[1–3] (hydrophilic end separation). However, the anion-exchange methods do not offer sufficient selectivity to separate sulfonates by the differences in structure of the species carrying the sulfonate group(s) (hydrophobic part separation).

Recently, reversed-phase ion pair chromatography has been applied to the separation of ionic species[4–8]. In reversed-phase ion pair chromatography, the addition of an appropriate ion-pairing reagent to the mobile phase suppresses the ionic nature of the sample while introducing some charge to the non-polar surface of the stationary phase[7–8]. The retention of the resulting ion pair is then controlled by manipulation of the ionic equilibrium of the sample and the ionic strength of the mobile phase.

The reversed-phase ion pair chromatographic methods were used to separate alkylbenzenesulfonates according to their alkyl chain lengths[9–13]. These methods were limited to the isocratic separation of sulfonates with a narrow molecular weight distribution, an alkyl carbon number of C_9–C_{15}. A gradient method was recently reported that separated alkylbenzenesulfonates with alkyl chain lengths ranging between C_3 and C_{18} (ref. 14). The gradient separation was shown to be useful in evaluating the purity of monoisomeric surfactants and analyzing surfactant blends with a narrow distribution.

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Petroleum sulfonates, used as surfactants in chemical enhanced oil recovery (EOR) processes, are highly complex mixtures of alkylarylsulfonates with broad molecular weight distributions. These sulfonate mixtures may encompass diverse aromatic structures that may be mono-, di- and polysulfonated. The length of the alkyl chains and their point(s) of attachment on the aromatic ring may also vary. Synthetic sulfonates and sulfates are also frequently encountered in EOR applications. These latter surfactants are derived from well-defined and reproducible narrow cut refinery streams and usually have narrower molecular weight distributions than petroleum sulfonates. Synthetic surfactants are often added to petroleum sulfonates to modify the molecular weight distribution of the mixture to alter surfactant performance. Common types of synthetic surfactants are alkylbenzenesulfonates, ethoxyalkylsulfonates and ethoxyalkylsulfates. Besides the sulfonated and sulfated surfactants, ethoxyalkylcarboxylates have recently been considered for oil recovery applications. Industry's wide experience has shown that a relationship exists between oil recovery efficiency and the distribution of molecular species within the surfactant system. Consequently, considerable effort is devoted to developing reliable techniques to more fully characterize the molecules present in these mixtures.

For the analysis of complex mixtures of surfactants, we report the development of a reversed-phase ion pair chromatographic method that allows high-resolution separation of alkylbenzenesulfonates according to the length and structure of the alkyl chain. The influence of separation parameters, *i.e.*, pH, counter ion concentration and mobile phase polarity on sulfonate retention was evaluated. Optimization of these parameters resulted in a calibration curve for retention time *versus* alkyl chain carbon number. This curve provides a quick means for the determination of the sulfonate alkyl chain length distribution. The analysis provided the characterization of a wide variety of synthetic and petroleum sulfonates as well as ethoxylated alkyl- and alkylbenzene-sulfates and carboxylates.

EXPERIMENTAL

Apparatus

A DuPont 8850 high-performance liquid chromatograph with a four solvent gradient controller and a heated column compartment was used. The column compartment contained a sample injection valve (Valco No. 851086-901) with a 20-μl sample injection loop, a guard column (Alltech RSIL prep C_{18}, 32 × 4.6 mm I.D.), and an octadecylsilanized silica gel analytical column (DuPont Zorbax 10 μm C_{18}, 250 × 4.6 mm I.D.). A Hewlett-Packard 1040A diode array UV spectrophotometric detector was used for detection. Fast atom bombardment-mass spectral (FAB-MS) analyses were carried out on a VG model 70EQ mass spectrometer equipped with a VG 11-250 data system and an Ion-Tech saddle field atom gun. The mass spectrometer was operated at 6 keV full accelerating voltage, 1000 revolving power, field mode, with a scan rate of 10 s/decade. FAB was accomplished using glycerol (99.5% Aldrich) as the matrix, a stainless-steel target, and with the atom gun operated at 8 keV and 1 mA.

Chemicals and sample preparation

All solvents were reagent grade obtained from Burdick & Jackson Labs. The ion-pairing reagent tetrabutylammonium hydrogen sulfate ($TBAHSO_4$) was obtained from Aldrich. Model compounds, listed with their respective suppliers in Table I, were dissolved in either water or methanol to yield approximately 0.01 *M* solutions. Petroleum and synthetic sulfonates were deoiled prior to analysis using solid phase extraction (SPE). The J. T. Baker SPE apparatus and columns were used for the SPE procedure. A homogeneous aliquot, 50–100 μl, of the sample was deposited on a 3-ml silica gel SPE column which had been conditioned in chloroform. First the oil was extracted by washing the column with four successive 500-μl portions of chloroform. Then the sulfonate was removed from the column by the application of four successive 500-μl portions of methanol. The methanol fraction was evaporated to remove any chloroform which may have been carried over and the oil-free sulfonate redissolved in either water or methanol.

Chromatographic procedure

The mobile phase consisted of an aqueous solution of 0.1 *M* $TBAHSO_4$ (pH 5)–water–acetonitrile. The pH of $TBAHSO_4$ solution was adjusted using sodium hydroxide. The solvent flow-rate was 2.00 ml/min and the column compartment was held at 35°C throughout the analysis. The linear gradient program used for the analysis is summarized in Table II. The analysis started with a solvent composition of 0.1 *M* $TBAHSO_4$–water–acetonitrile (10:50:40). During the first 30 min, the concentration of the ion-pairing reagent $TBAHSO_4$ was kept constant, the water concentration decreased to 10% and the acetonitrile concentration increased to 80%. During the following 10 min, the $TBAHSO_4$ concentration was dropped to 0% and the solvent

TABLE I

MODEL COMPOUNDS AND THEIR RESPECTIVE SUPPLIERS

Model compounds	*Supplier*
Toluenesulfonate	Aldrich Chemical
tert.-Butylbenzenesulfonate	Aldrich Chemical
Octylbenzenesulfonate	Texaco Chemical
Nonylbenzenesulfonate	Texaco Chemical
Decylbenzenesulfonate	Texaco Chemical
Dodecylbenzenesulfonate	University of Texas
Hexadecylbenzenesulfonate	University of Texas
Dodecylbenzenesulfonate Mixture	Pfaultz & Bauer
Aristol A (alkylbenzenesulfonate mixture)	Pilot Chemical
Aristol B (alkylbenzenesulfonate mixture)	Pilot Chemical
Aristol D (alkylbenzenesulfonate mixture)	Pilot Chemical
Aristol E (alkylbenzenesulfonate mixture)	Pilot Chemical
Dihexylbenzenesulfonate	Texaco Chemical
Dioctylbenzenesulfonate	Texaco Chemical
NP-EO4 ethoxyalkylbenzenecarboxylate	Texaco Chemical
NO-EO6 ethoxyalkylbenzenecarboxylate	Texaco Chemical
Alipal CO436 ethoxyalkylbenzenesulfate	G.A.F.
C_{12-14} Alcohol–EO6 ethoxyalkylcarboxylate	Texaco Chemical

TABLE II

MOBILE PHASE GRADIENT PROGRAM

Operational mode	*Segment*	*Time (min)*	*$TBAHSO_4$ 0.1 M at pH 5 (%)*	*Water (%)*	*Acetonitrile (%)*
Analysis	1	30.0	10.0	50.0	40.0
			10.0	10.0	80.0
	2	10.0	10.0	10.0	80.0
			0.0	20.0	80.0
	3	15.0	0.0	20.0	80.0
			0.0	20.0	80.0
Equilibration	4	5.0	0.0	20.0	80.0
			10.0	50.0	40.0
	5	10.0	10.0	50.0	40.0
		10.0	10.0	50.0	80.0

composition changed to water–acetonitrile (20:80). This solvent composition was held constant for another 15 min. At this point, the analysis was completed and the column was re-equilibrated with initial conditions for 15 min.

RESULTS AND DISCUSSION

While the mechanisms responsible for reversed-phase ion pair chromatography are still debatable, most researchers center their discussions around three models. These are: the ion-pair model, the dynamic ion-exhange model, and the ion-interaction model[7]. All three of these mechanisms come into play in the ensuing discussion.

Mobile phase composition effect

Successful separation of surfactant anions by reversed-phase ion pair chromatography is accomplished by carefully controlling the parameters which influence the ion pair formation and subsequent partitioning between the polar mobile phase and non-polar stationary phase. Proper adjustment of the pH controls the degree of ionization of both the surfactant and the pairing reagent or counter ion. This, in turn, permits regulation of the sample retention with maximum retention being realized when both the surfactant and pairing reagent are completely ionized.

The retention behavior of alkylbenzenesulfonates was investigated as a function of pH. The change in the capacity factor, k', *i.e.* retention, of three alkylbenzenesulfonates over the pH range 2 to 6.2 is shown in Fig. 1. The k' values for all the sulfonates decreased rapidly to minima around pH 4, then leveled off. Since both the sulfonates and $TBAHSO_4$ are strongly acidic compounds with pK_a values <2, the initial decrease in retention with the increase in pH can be attributed to the increase in the SO_4^{2-} concentration in the mobile phase.

$$TBAHSO_4 \rightleftharpoons TBA^+ + HSO_4^- \rightleftharpoons TBA^+ + H^+ + SO_4^{2-} \qquad pK_a = 1.92$$

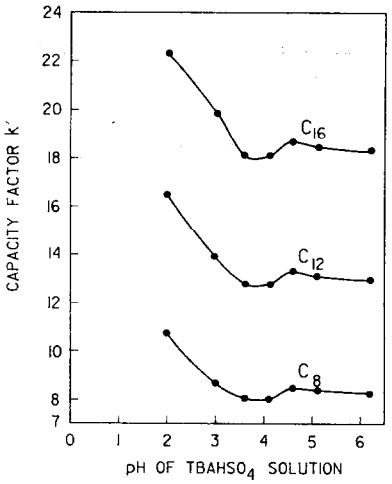

Fig. 1. The effect of pH on the retention of alkylbenzenesulfonates. C_8 = Octylbenzenesulfonate, C_{12} = dodecylbenzenesulfonate, C_{16} = hexadecylbenzenesulfonate.

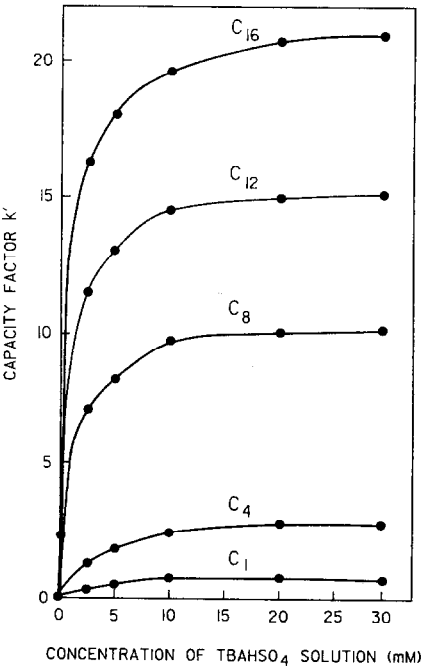

Fig. 2. The effect of $TBAHSO_4$ concentration on the retention of alkylbenzenesulfonate. C_1 = Toluenesulfonate, C_4 = *tert.*-butylbenzenesulfonate, C_8 = octylbenzenesulfonate, C_{12} = dodecylbenzenesulfonate, C_{16} = hexadecylbenzenesulfonate.

The SO_4^{2-} can then act as a competing ion with the sulfonate ion for the surface. The negatively charged sulfonate ion in the mobile phase experiences an electrostatic repulsion which tends to keep it away from the stationary phase and, thus, account for the decrease in retention.

A pH of 5 was selected for use in this study. As can be seen by reference to Fig. 1, small deviations in pH at this value will have little or no effect on the retention times for the alkylbenzenesulfonates. At this pH, the sulfonates and pairing reagent are completely ionized as will be the carboxylated surfactants (*vide infra*) whose pK_a values are somewhat higher, somewhere around pK_a 4.

The structure and concentration of the pairing reagent also influences the retention behavior. Increasing the lipophilicity of the pairing reagent increases the retention of the surfactant ion pair by increasing its affinity for the non-polar stationary phase. Increasing the concentration of the pairing agent will lead to greater coverage of the stationary phase surface and, consequently, longer sample retention.

The concentration effect of the ion-pairing reagent $TBAHSO_4$ on the retention of alkylbenzenesulfonates is shown in Fig. 2. For each sulfonate, the retention increased rapidly between 0 and 5 m*M*. Sufficient retention and optimum separation were obtained with the $TBAHSO_4$ concentration between 10 and 30 m*M*. The lower concentration was selected for use in this study to minimize the salt content in the system.

Mobile phase polarity greatly influenced the sulfonate retention. As expected, the capacity factors of alkylbenzenesulfonates decreased with the increase in organic content of the mobile phase. Thus, a proper gradient of water and acetonitrile was necessary to control the anion retention and to provide a good separation. Acetonitrile was chosen as the organic modifier because it provided better retention control than methanol. With methanol, the differences in retention times were much shorter and did not allow adequate resolution of the components. The gradient shown in Table II was found to be optimum.

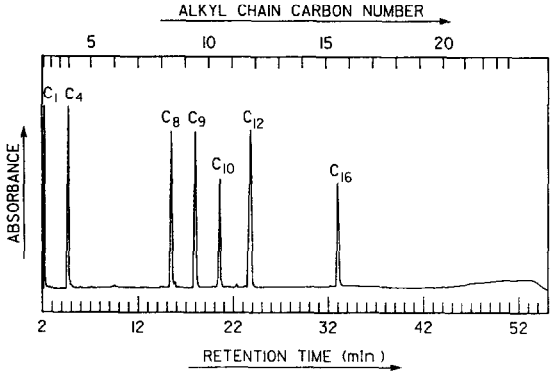

Fig. 3. Separation of model alkylbenzenesulfonate compounds with linear alkyl chains: C_1 = toluenesulfonate, C_8 = octylbenzenesulfonate, C_9 = nonylbenzenesulfonate, C_{10} = decylbenzenesulfonate; with branched alkyl chains: C_4 = *tert.*-butylbenzenesulfonate, C_{12} = dodecylbenzenesulfonate and C_{16} = hexadecylbenzenesulfonate. Stationary phase: Dupont Zorbax C_{18}. Mobile phase: gradient of 0.1 *M* $TBAHSO_4$ at pH 5, water and acetonitrile. UV detection at 225 nm.

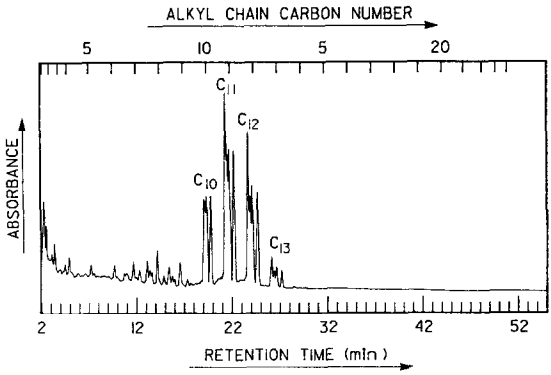

Fig. 4. Separation of commercial dodecylbenzenesulfonate mixture. Conditions as in Fig. 3.

Application to alkylbenzenesulfonates

Typical chromatograms obtained for the separation of model alkylbenzenesulfonates under optimized conditions are shown in Figs. 3–5. Fig. 3 illustrates the separation of linear and branched monoisomeric alkylbenzenesulfonates ranging from C_1 to C_{16} alkyl chain carbon number. Fig. 4 shows the high resolution separation of a commercial "dodecyl" benzenesulfonate mixture. As shown, the mixture

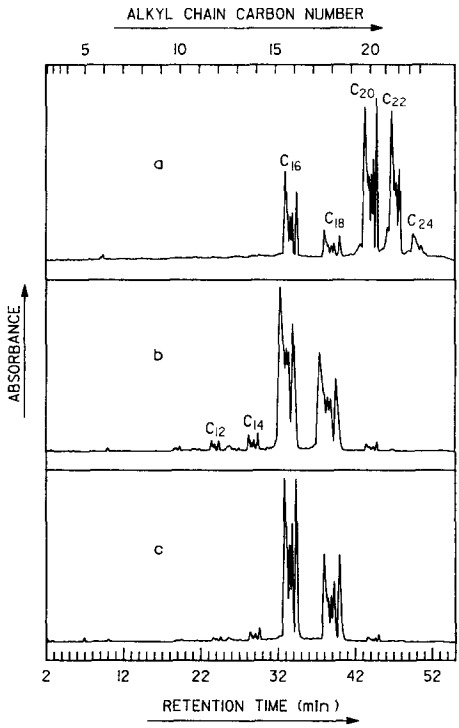

Fig. 5. Separation of alkylbenzenesulfonate mixtures: (a) Aristol A, (b) Aristol B and (c) Aristol D. Conditions as in Fig. 3.

is separated into groups of C_{10}, C_{11}, C_{12} and C_{13} alkyl chain lengths. Within each group, components are further separated according to alkyl chain branching. The linear alkyl chain component has the longest retention time, and as branching increases retention time decreases. A similar type of separation is shown in Fig. 5 for the Aristol sulfonate mixtures. Aristol A, B and D are high equivalent weight alkylbenzenesulfonates. As can be seen, the Aristol mixtures are well resolved into even-carbon-numbered groups of positional isomers with alkyl chain lengths ranging from C_{12} to C_{24}. The alkyl chain length assignments in Figs. 4 and 5 were verified by FAB-MS analysis as shown in Figs. 6 and 7.

From the retention data of these model compounds, a calibration curve of retention time *versus* alkyl chain length was constructed for monoalkylbenzenesulfonates. As shown in Fig. 8, the calibration curve has two linear segments over the range of C_4 to C_{24} with an inflection point at C_{20}. The elution region shown for each alkyl chain length was based on the retention time observed for each of the positional isomers. The average retention time of the positional isomers within each group was used to establish the alkyl chain carbon number scale shown at the top of each figure.

The retention behavior of alkylbenzenesulfonate compounds containing two alkyl chains, *i.e.* dialkylates, was also investigated. An example is shown in Fig. 9 for the separation of di-*n*-hexylbenzenesulfonate and branched dioctylbenzenesulfonate, *i.e.* total alkyl chain carbon numbers of 12 and 16, respectively. The resolution obtained for these dialkyl compounds and their various positional isomers was similar to that for the C_{12} and C_{16} monoalkylbenzenesulfonates. However, the retention times of the dialkyl substituted compounds were slightly shorter than what would have been expected had the effect of disubstitution been additive. For example di-C_6 had a retention time equivalent to mono-C_{10} while di-C_8 was equivalent to mono-C_{14}. This is in line with the observation that branched mono-alkyl isomers have shorter retention times than the linear isomers. This then suggests that steric restraints may be limiting the extent of interaction between the alkyl chains and the stationary phase.

The effect of dialkylation appears to be limited to reducing the retention times

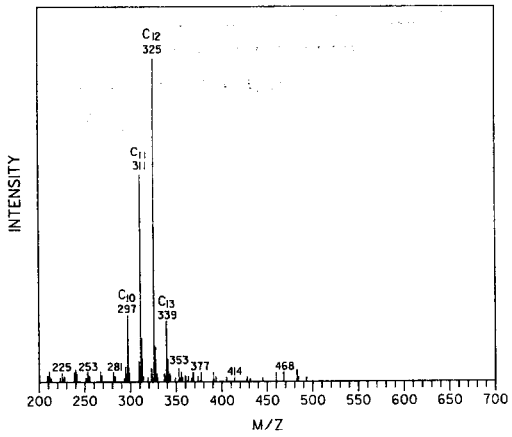

Fig. 6. FAB-MS analysis of commercial dodecylbenzenesulfonate.

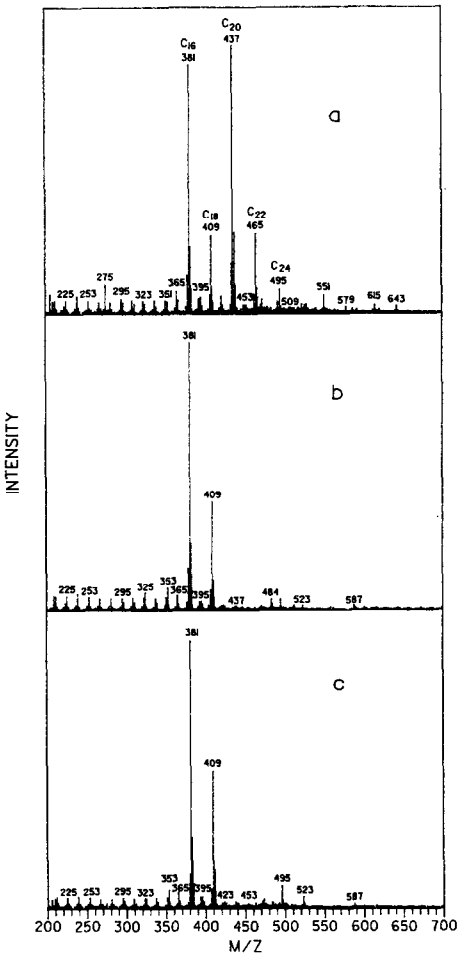

Fig. 7. FAB-MS analysis of alkylbenzenesulfonate mixtures: (a) Aristol A, (b) Aristol B and (c) Aristol D.

only by the equivalent of two carbon number units. Evidence in support of this is shown in Fig. 10 for the separation of a synthetic mixture containing both mono- and dialkylbenzenesulfonates. The chromatogram shows the separation of Aristol E into C_{13}, C_{14}, C_{16}, C_{18} and C_{20} monoalkylbenzenesulfonates and C_{22}, C_{24}, C_{25} and C_{26} dialkylbenzenesulfonates. Alkyl chain carbon number assignments were based on retention data and were confirmed by FAB-MS analysis shown in Fig. 11. As can be seen, increasing the dialkylbenzenesulfonates even up to total alkyl chain lengths of C_{26} only results in decreasing the retention time by the equivalent of two carbon number units on the calibration scale.

Application to other anionic surfactants

This reversed-phase ion pair chromatographic technique was developed and

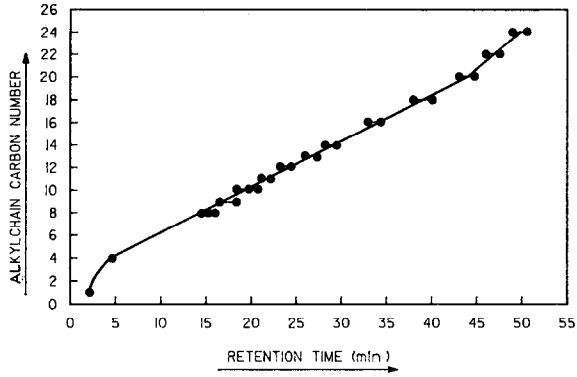

Fig. 8. Calibration curve of alkyl chain carbon number *versus* retention time for alkylbenzenesulfonates.

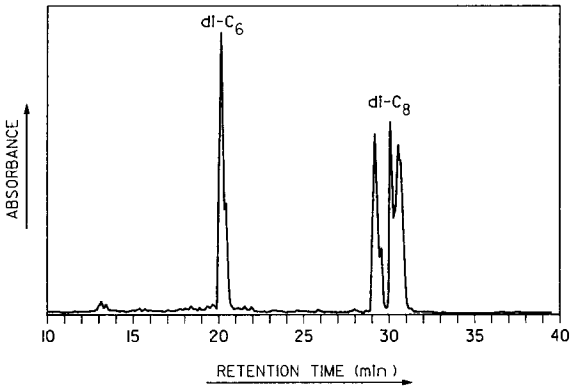

Fig. 9. Separation of di-*n*-hexylbenzenesulfonate and branched dioctylbenzenesulfonates. Conditions as in Fig. 3.

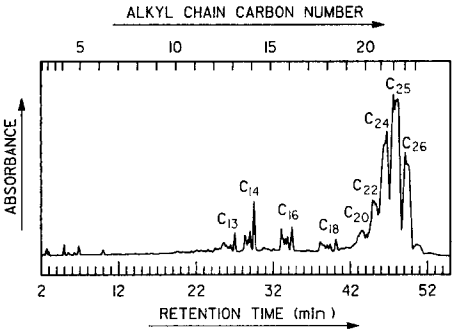

Fig. 10. Separation of alkylbenzenesulfonate mixture Aristol E. Conditions as in Fig. 3.

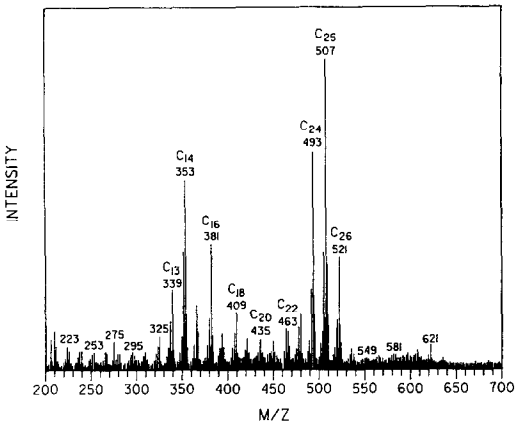

Fig. 11. FAB-MS analysis of alkylbenzenesulfonate mixture Aristol E.

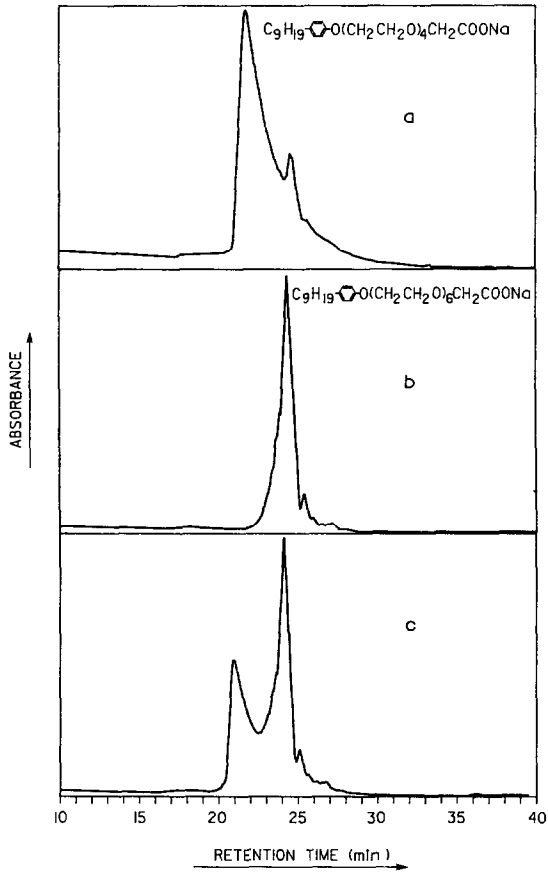

Fig. 12. Chromatogram of ethoxyalkylbenzenesulfonates: (a) NP-EO4, (b) NP-EO6 and (c) mixture of NP-EO4 and NP-EO6. Conditions as in Fig. 3.

optimized using mixtures of alkylbenzenesulfonates. Nevertheless, the same chromatographic conditions can be used to analyze other ionic surfactants such as ethoxylated surfactants and petroleum sulfonates.

Ethoxylated surfactants

Ethoxylated surfactants are synthetic compounds with the general formula $R(OCH_2CH_2)_nOX^-M^+$ where R is an alkyl or alkylaryl group; n is the average number of ethylene oxide (EO) groups; X is a sulfonate, ethyl or propyl sulfonate, or methylcarboxylate function group; and M is a cation such as Na^+, NH_4^+, etc. Fig. 12 shows the chromatograms obtained for two ethoxylated surfactants. The NP-EO4 (Fig. 12a) and NP-EO6 (Fig. 12b) ethoxyalkylbenzenecarboxylates have branched C_9 alkyl chains and average EO numbers of 4 and 6, respectively. The chromatograms shown in this figure illustrate the effect of EO groups on the separation. Compounds having the same alkyl substituent but a different number of EO's are separated with the retention increasing as the number of EO groups increases. Peak width is due to the Poisson distribution of the oligomers centered about 4 and 6 EO groups and is characteristic of ethoxylated surfactants.

An example of an ethoxyalkylbenzenesulfate, Alipal CO436, is shown in Fig. 13. Similar to the ethoxyalkylbenzenecarboxylate NP-EO4, Alipal CO436 has a C_9 alkyl chain and an average EO number of 4. However, Alipal CO436 has a shorter retention than does NP-EO. Similarly, the alkylbenzenesulfonates were observed to elute more rapidly than the alkylbenzenecarboxylates. This difference in retention between the anions may arise from the higher charge density on the carboxylate group relative to the sulfonate and sulfate groups. The higher the charge density, the stronger the interaction between the analyte anion and the stationary phase, and thus the longer the retention.

The analysis was also applied to the separation of ionic and non-ionic components of ethoxylated surfactants. Commercial ethoxylated anionic surfactants generally contain from 10 to 40% unreacted alcohol, *i.e.* starting material $R(OCH_2CH_2)_nOH$. Non-ionic components do not form ion-pairs, so the mechanism for the separation of the alcohols is different than that for the ionic compounds

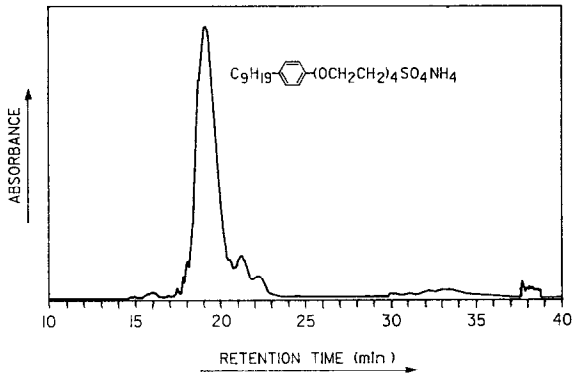

Fig. 13. Chromatogram of ethoxyalkylbenzenesulfate Alipal CO436. Conditions as in Fig. 3.

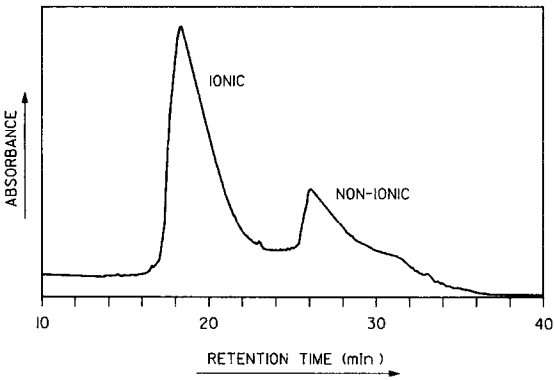

Fig. 14. Separation of ionic and non-ionic components of C_{12-14} alcohol–EO6 ethoxyalkylcarboxylate. Conditions as in Fig. 3. UV detection at 195 nm.

within the sample. In this case, the more lipophylic alcohols will have longer retention times than the ionic components due to their higher affinity for the stationary phase. An example is shown in Fig. 14 where C_{12-14} alcohol–EO6 ethoxyalkylcarboxylate is separated into two peaks, the ionic $C_{12-14}(OCH_2CH_2)_6OCH_2COO^-$ and non-ionic $C_{12-14}(OCH_2CH_2)_6OH$ components. (Since no aryl chromophore is present in these samples, the signal was monitored at 195 nm to allow for the detection of both species.) As in the case of the NP-EO6 ethoxyalkylbenzenecarboxylate, the C_{12-14} alcohol–EO6 surfactant peaks are broad as a result of the Poisson distribution of the EO oligomers. But due to the difference in the hydrophobe structure, the C_{12-14} alcohol–EO6 surfactant had a shorter retention time than the branched aryl NP-EO6 compound.

Petroleum sulfonates

There are three major limitations with the reversed-phase ion pair chromatographic analysis of petroleum sulfonates. The extremely wide variation in the hydrophobe structures in petroleum sulfonates leads to a broad distribution in retention times for the alkylarylsulfonate anions. Studies associated with this investigation demonstrated that the petroleum sulfonates form 1:1 ion-pair complexes regardless of the degree of sulfonation. As a result, the di- and polysulfonate–counterion ion-pairs will have some residual ionic character which will lead to shorter retention times than the equivalent monosulfonated species. Finally, any differences in the UV absorptivities of the alkylaryl species may affect the apparent abundance of one compound relative to another. For all of these reasons, chromatograms obtained for petroleum sulfonates are more complex and less defined than those obtained for synthetic sulfonates.

Chromatograms of several petroleum sulfonates are shown in Figs. 15–17. In spite of the absence of detailed separation, the reversed-phase ion pair chromatographic analysis of petroleum sulfonates will produce distribution profiles that can still be used very effectively for the characterization of EOR surfactants. Industry-wide experience with petroleum sulfonates has shown that the structural distribution of the components within the mixture appears to correlate with EOR performance.

The reversed-phase ion pair chromatographic method can then be used to quickly screen petroleum sulfonates to define the distribution prior to testing as EOR agents. Preliminary screening may allow modification of the petroleum sulfonate by either enrichment with a specific synthetic sulfonate or blending of different petroleum sulfonates to obtain one with the desired distribution.

Chromatograms of two commercial petroleum sulfonates, Witco Chemical Corporation's TRS-40 and TRS-18, are shown in Fig. 15. Fig. 15a shows that TRS-40 has an apparent alkyl chain distribution between C_3 and C_{18} with a broad maxima at approximately C_7–C_9. Meanwhile, the TRS-18 distribution, shown in Fig. 15b, is mainly between C_{10}–C_{28} with a maxima at approximately C_{22}. The difference in TRS-40 and TRS-18 distributions is consistent with the difference in their average equivalent weights. The average equivalent weight of TRS-40 is 340 g/equiv. compared to 520 g/equiv. for TRS-18.

To obtain a petroleum sulfonate with the broad equivalent weight distribution, a blend of low and high equivalent weight surfactants is often needed. A blend of 50:50 TRS-40 and TRS-18 gives the distribution shown in Fig. 15c. As expected, this mixture has a very wide distribution with an even higher relative abundance of alkyl chain lengths over the entire C_6–C_{17} range than shown by TRS-40 or TRS-18 alone.

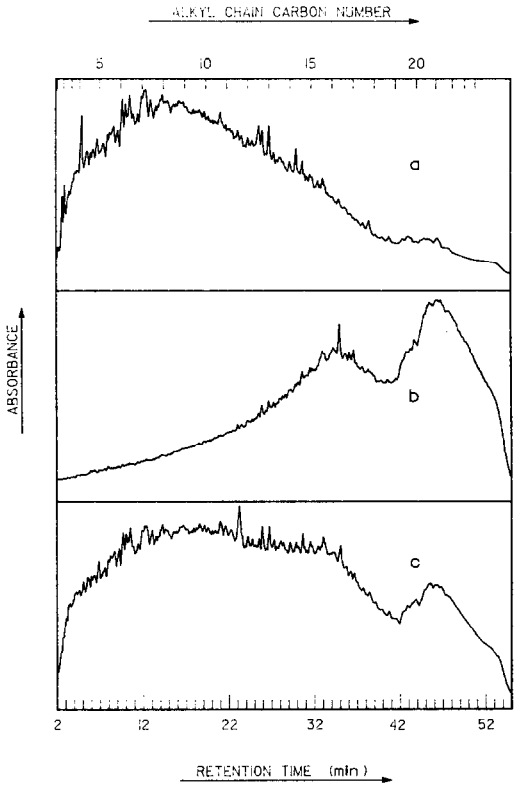

Fig. 15. Chromatograms of Witco petroleum sulfonates: (a) TRS-40, (b) TRS-18 and (c) mixture of 50:50 TRS-40 and TRS-18. Conditions as in Fig. 3.

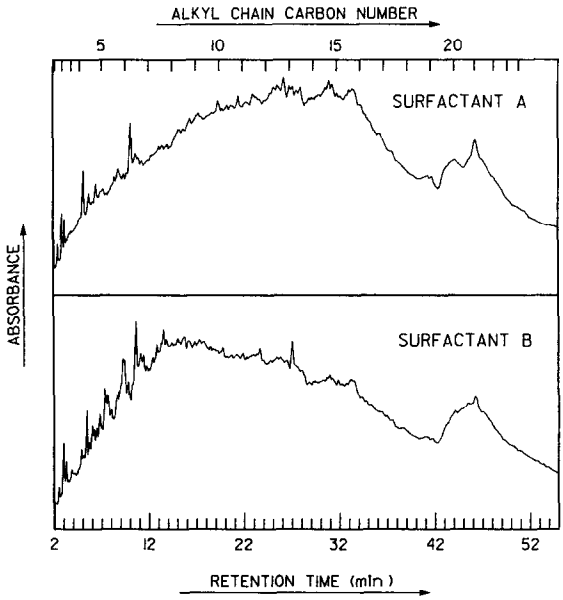

Fig. 16. Chromatograms of petroleum sulfonate A and petroleum sulfonate B. Conditions as in Fig. 3.

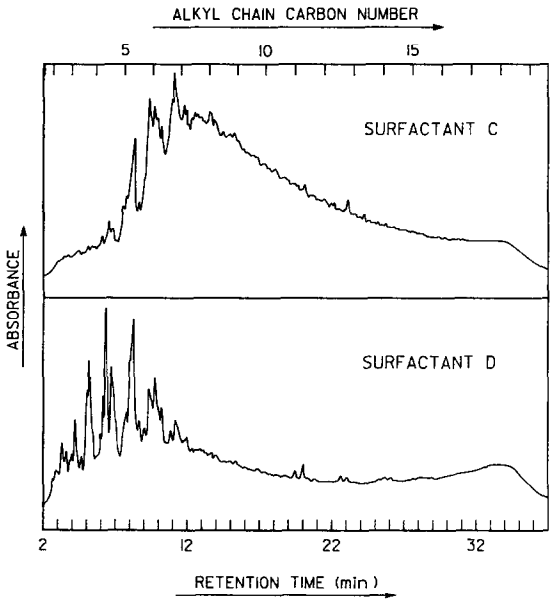

Fig. 17. Chromatograms of petroleum sulfonate C and petroleum sulfonate D. Conditions as in Fig. 3.

Some researchers feel that the best EOR performance is achieved by using a petroleum sulfonate mixture with a broad alkyl aromatic equivalent weight distribution. Examples for the difference in distribution profiles of petroleum sulfonates expected to have high and low potential as oil recovery surfactants are shown in Figs. 16 and 17. Fig. 16 illustrates the distribution profiles of two petroleum sulfonates which would be considered to have high EOR potential. As shown, both sulfonates have broad distributions with broad maxima in the region C_{10}–C_{16} for petroleum sulfonate A and C_7–C_{13} for petroleum sulfonate B. Meanwhile, petroleum sulfonates which would be predicted to show poor EOR performance have relatively narrow distributions with the maxima being around C_6–C_8 for petroleum sulfonate C and C_5–C_6 for petroleum sulfonate D as shown in Fig. 17.

CONCLUSIONS

The reversed-phase ion pair HPLC procedure presented in this paper allows alkylbenzenesulfonates to be separated according to alkyl chain length. Optimization of pH, counter ion concentration, and mobile phase polarity provides a linear relationship between retention time and alkyl chain carbon number. The results suggest that steric restraints may be responsible for the slightly shorter retention times observed for the dialkylbenzenesulfonates as compared to the monoalkylated species.

This reversed-phase ion pair HPLC technique can also be used to separate and characterize more complex surfactants such as ethoxylated sulfates or carboxylates and petroleum sulfonates. While the method does not allow exact assignment of the carbon chain lengths in petroleum sulfonate, it does yield chromatographic fingerprints which, in turn, furnish information pertinent to the surfactants' oil recovery potential.

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