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Reversed phase liquid chromatographic separation of linear alkylbenzenesulfonates
Effect of mobile phase ionic strength

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Abstract

Linear alkylbenzenesulfonate (LAS) homologues and positional isomers are separated on C_{18} and polystyrene–divinylbenzene reversed stationary phases using an acetonitrile–water + sodium chloride mobile phase. Retention of the LAS surfactants and separation selectivity, efficiency, and resolution are enhanced according to the mobile phase ionic strength and the ionic strength electrolyte cation. The enhanced column performance is due to Stern–Gouy–Chapman double layer interactions at the reversed stationary phase surface. The optimum mobile phase cations of those studied are Na^+, Mg^{2+} and Ba^{2+}. Isocratic or gradient elution can be used with detection by either UV absorbance (2.5 pmol detection limit at signal-to-noise ratio of 3) or by conductance following postcolumn anionic micromembrane suppression (130 pmol detection limit at signal-to-noise ratio of 3). Resolution of the LAS positional isomers is most favorable by using a gradient where acetonitrile increases and sodium chloride decreases simultaneously in an acetonitrile–water + sodium chloride mobile phase.

1. Introduction

Anionic surfactants, such as branched and linear alkylbenzenesulfonates (LASs), alkane-sulfonates (RSO_3^-) and alkyl sulfates ($ROSO_3^-$) are used industrially and in consumer products in large quantities because of their detergent action. Thus, sensitive analytical procedures for their determination are essential to these applications. In addition the anionic surfactants are often discharged into the environment and there is growing concern about their residue levels in plants, foods, and river and waste water. Identification and determination of anionic surfactants in these samples are particularly difficult because the surfactants are present at trace levels in a complex sample matrix.

Traditional methods [1] for the determination of anionic surfactants, such as precipitation and color formation and quenching procedures, are not applicable to these more complex samples for two major reasons. First, the sample matrix causes significant interference. And second, these methods provide poor selectivity. That is, they will not distinguish between different types of anionic surfactants, between members of a homologous series of a surfactant family, or between isomeric anionic surfactants. Modern separation techniques, such as gas chromatography (GC), high-performance liquid chromatography (LC), and capillary electrophoresis (CE), are powerful discriminating techniques for

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separating anionic surfactants. They often provide low detection limits and permit anionic surfactants to be determined and identified at a trace level in a complex sample matrix. This is particularly true when the separation procedure can be combined with mass spectrometric (MS) detection.

Anionic surfactants have low volatility and GC procedures require surfactants to be converted into volatile hydrocarbons through desulfonation [2,3] or conversion into volatile compounds, such as sulfonyl chlorides, sulfonyl fluorides or methyl esters [4–10]. Interfacing GC with MS significantly enhances identification of anionic surfactants particularly in complex matrices [5,6,11].

LC has been widely used to separate RSO_3^-, $ROSO_3^-$, LASs and related anionic surfactants. LC procedures for the separation and determination of RSO_3^- and $ROSO_3^-$ surfactants, which are reviewed elsewhere [12–14], do not require precolumn derivatization, however, postcolumn derivatization, postcolumn anionic suppression, or indirect detection strategies are required to obtain the lowest detection limits. Since LAS surfactants contain a benzene chromophore, they are readily detected at favorable detection limits by UV absorption and fluorescence.

LAS surfactants are commonly used as mixtures of alkyl homologues and alkyl phenyl positional isomers over the alkyl chain length range of C_9 to C_{14}, although in some applications the chain length can be extended to C_{24}. LC procedures for the separation and determination of LAS surfactants employ reversed-phase chromatography usually with C_8 or C_{18} columns and organic–water mobile phases often containing an electrolyte [12,14–26], anion exchangers [27], or reversed stationary phases in combination with mobile phases containing ion interaction reagents such as quaternary ammonium salts [28–34]. Solid-phase extraction, for example by a reversed stationary phase [12,18,19] or an anion exchanger [12,23], to isolate and concentrate LAS surfactants prior to LC separation has been successfully used for environmental type samples, particularly for waste, river and treated water. Mobile phase conditions are optimized in most studies to yield resolution of LAS homologues, however, partial resolution of isomeric LAS surfactants is possible by reversed-phase chromatography, particularly when an electrolyte [15–19] or an ion interaction reagent [28–31,34], are in the mobile phase. Interfacing LC to MS for LAS surfactant identification and analyses has also been successful [33].

LAS homologues can be separated rapidly and with high efficiency by CE strategies [35–37]. CE separations with an acetonitrile–aqueous boric acid-borate, pH 9 buffer were compared to micellar electrokinetic chromatography (MEKC) by including sodium dodecyl sulfate in the buffer [36]. When different mono- and divalent cations (Mg^{2+} is optimum) are added to a pH 7 phosphate buffer the CE resolution of the LAS surfactant homologues is significantly enhanced because the cation decreases the electroosmotic flow [37]. However, resolution of LAS structural isomers by CE is not improved [36,37] even in the presence of the cation electroosmotic flow modifier and MEKC [36] appears to be the better strategy for separating LAS positional isomers.

Recent studies [13] demonstrated that a high mobile phase ionic strength and the ionic strength and the ionic strength electrolyte cation (Li^+ and Mg^{2+} are optimum) significantly enhance the retention, column efficiency, and resolution for the reversed-phase separation of RSO_3^- and $ROSO_3^-$ surfactants. By using a postcolumn anionic micromembrane suppressor and a conductance detector the detection limit was 0.3 nmol of injected anionic surfactant. For a mobile phase gradient where CH_3CN concentration increases and the LiOH ionic strength electrolyte concentration decreases in the CH_3CN–water mobile phase solvent, multicomponent mixtures of even-numbered RSO_3^- and $ROSO_3^-$ surfactants from C_2 to C_{18} are baseline resolved. This report establishes how mobile phase ionic strength and the ionic strength electrolyte cation influences retention of LAS surfactants on reversed stationary phases. When these parameters and mobile phase solvent composition are optimized, resolution of complex mixtures of LAS surfactant homologues and positional isomers is significantly improved.

2. Experimental

2.1. Reagents and instrumentation

Sodium salts of 2-nonyl-, 2-decyl-, 2-tetradecyl- and 2-pentadecyl-benzenesulfonate were obtained as pure samples from Procter & Gamble. The absence of other positional isomers was verified by LC and the samples were used as standards. The C_{12} and C_{13} LAS surfactants were obtained from Chem Service and Aldrich and were shown to contain positional isomers by LC. These samples were used as received. Commercial LAS mixtures composed of C_{10} to C_{14} homologues and positional isomers were supplied by Procter & Gamble, Vista Chemical, and Pilot Co. and were used as received. Acetonitrile (EM Science) was LC grade and all inorganic salts and acids were analytical-reagent grade. LC water was obtained by passing water distilled in our laboratory through a Millipore Milli-Q Plus water-treatment system. All reversed stationary phases were purchased as prepacked columns. PRP-1, a polystyrene–divinylbenzene copolymer stationary phase, was obtained from Hamilton as a 10 μm, 150 mm × 4.1 mm column while Zorbax ODS, a silica-bonded phase, was obtained from Mac Mod Analytical, as 6 μm, 150 mm or 250 mm × 4.6 mm columns.

The LC system consisted of two Beckman 110A pumps, a Beckman 332 gradient controller, a Rheodyne 7125 injector with a 20-μl fixed sample loop, and either a Spectra-Physics Model SP 8450 variable-wavelength detector or a Dionex AMMS-12 anionic micromembrane suppressor coupled to a Waters 430 conductivity detector. Chromatograms and all related data were collected and handled with a Spectra-Physics 4270 integrator and computer loaded with Spectra-Physics WINner chromatographic software.

2.2. Procedures

Analyte solutions of LAS standards were prepared by dissolving a known quantity of LAS in LC water at a concentration of 0.01 to 0.1 mg/ml. Known mixtures of LAS homologues were similarly prepared to contain each analyte within this range. Mobile phases were made by combining known volumes of CH_3CN and LC water with a known mass of electrolyte and diluting to volume with solvent mixture to yield the desired composition. Solvent composition is expressed in % (v/v). All mobile phases were degassed by water aspiration for about 5 min prior to use. Columns were conditioned by passing 100 to 150 ml of the mobile phase prior to sample injection. Sample aliquots of 5 to 10 μl were injected with a 10-μl syringe. Column performance was determined during the study with a benzene and toluene test sample and a CH_3CN–water (9:1) mobile phase. A new column was used when column efficiency and capacity factor for the two analytes deteriorated with respect to manufacture certification and our initial column evaluation.

Retention time, capacity factor, and other column performance data determined in the presence of the electrolyte were the average of three or more measurements. Retention order and peak identity were established by comparison of unknown retention times to those for the injection of single, known LAS standards except where noted. Calibration curve data were obtained by using samples prepared by dilution of a standard LAS solution. Peak areas were determined and an average of at least three measurements were used to establish each data point. Linear regression was performed with Slide Write software. Flow-rate was 1.0 ml/min, ambient temperature was 25°C, inlet pressure was 700 to 900 p.s.i. (1 p.s.i. = 6894.76 Pa), and column void volume (determined by a KNO_3 sample) was 0.9 to 1.0 ml depending on the column and mobile phase. Absorbance detection was at 225 nm. For conductivity detection the anion micromembrane suppressor was regenerated with 25 m*M* H_2SO_4 at 1.0 ml/min.

3. Results and discussion

3.1. Effect of solvent

LAS surfactants, which contain both a hydrophobic and an anionic center, are retained on both reversed-phase and anion exchange columns. Retention on the former follows reversed-phase interactions in that the LAS surfactant retention decreases as the mobile phase organic modifier concentration increases and increases as the hydrophobicity or the alkyl chain length in the LAS homologue increases. This is illustrated in Fig. 1 where the capacity factor for the retention of 2-positional C_9 and C_{10} LAS standards on a Zorbax ODS column is plotted as a function of the CH_3CN–water mobile phase composition.

3.2. Effect of ionic strength electrolyte

The $-SO_3^-$ group reduces LAS retention on a reversed stationary phase compared to the corresponding hydrocarbon and also causes LAS retention to be sensitive to mobile phase ionic strength [13,38]. This is illustrated in Fig. 2 where capacity factors for 2-positional C_9 and C_{10} LAS standards are shown to increase as NaCl concentration increases in a CH_3CN–water (35:65) mobile phase. The effect of ionic strength is consistent with a double-layer-type interaction [38,39].

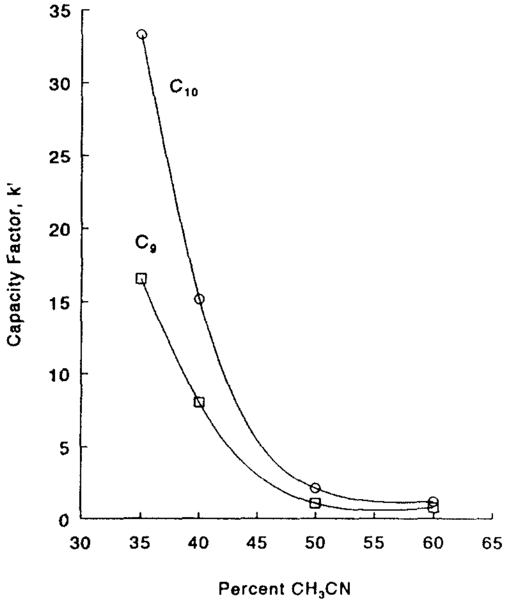

Fig. 1. Effect of CH_3CN–water composition on the retention of LAS surfactants on a Zorbax ODS column.

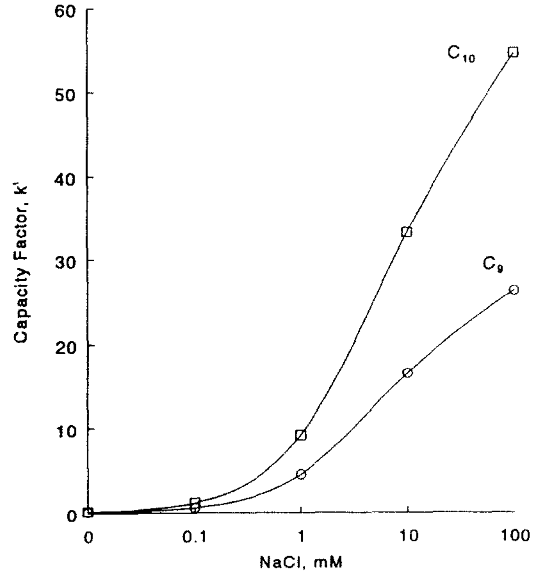

Fig. 2. Effect of mobile phase electrolyte concentration on the retention of LAS surfactants on a Zorbax ODS column. A CH_3CN–water (35:65) + NaCl mobile phase at 1.0 ml/min.

When electrolytes that differ only in the cation are used in the mobile phase at identical mobile phase ionic strength, LAS retention changes depending on the cation provided by the ionic strength electrolyte. This is illustrated in Table 1 where capacity factors for the 2-positional C_9 and C_{10} LAS standards are listed for both the PRP-1 and Zorbax ODS stationary phases in the presence of monovalent and multivalent charged cations. Ionic strengths of the different mobile phases are identical assuming that the electrolytes are completely dissociated. A similar cation dependence was observed in previous studies using RSO_3^- and $ROSO_3^-$ surfactant analytes [13].

The enhancement in retention on the two reversed stationary phases due to the cation (see Table 1) follows the order: $Al^{3+} > Ba^{2+} > Mg^{2+}$

Table 1
Effect of mobile phase cations on LAS retention on reversed stationary phases

Electrolyte	Capacity factor, k'			
	PRP-1		Zorbax ODS	
	C_9	C_{10}	C_9	C_{10}
LiCl	4.51	7.78	2.87	5.88
NaCl	5.54	9.54	4.49	9.15
NH_4Cl	5.75	9.59	4.67	9.62
$(CH_3)_4NBr$	5.70	9.97	5.52	11.2
$MgCl_2$	6.47	11.1	7.70	15.5
$BaCl_2$	8.02	13.7	7.89	16.0
$AlCl_3$	9.46	16.1	9.64	19.4

CH_3CN–water (35:65) mobile phase containing electrolyte at 0.0010 *M* ionic strength at 1.0 ml/min, 2-positional C_9 and C_{10} LAS standards as analytes, and 150 mm × 4.6 mm Zorbax ODS column.

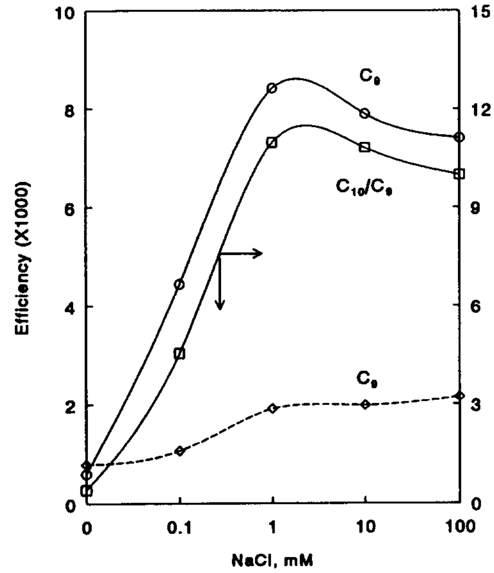

Fig. 3. Effect of mobile phase electrolyte concentration on efficiency and resolution. Conditions as in Fig. 2; solid lines = Zorbax ODS column; dotted line = PRP-1 column; analytes are 2-positional C_9 and C_{10} LAS standards.

$> (CH_3)_4N^+ > NH_4^+ > Na^+ > Li^+$. In general, the trivalent cation has the largest effect while the monovalent cation has the least effect on enhancing LAS retention. The increase in the enhancement correlates linearly to the ratio, cation hydrated radius to cation charge. As this value decreases LAS analyte retention increases according to the equation $k' = -4.72$ (cation hydrated radius/cation charge) + 31.44 with a correlation coefficient of 0.9827.

Enhanced column efficiency, resolution, and selectivity for LAS surfactant retention are also dependent on the mobile phase electrolyte cation and its concentration. As mobile phase NaCl concentration increases, column efficiency increases. This is illustrated in Fig. 3 using a 2-positional C_9 LAS standard and both the Zorbax ODS (solid line) and the PRP-1 (dashed line) columns. The enhanced efficiency, which was also determined with other LAS standards, is much greater on the Zorbax ODS column by a factor of about 3. Selectivity, for example for the separation of a mixture of C_{10}/C_9 2-positional LAS standards, undergoes only a small increase on both columns and does not contribute appreciably to the improved resolution. Thus, the sharp increase in resolution as NaCl concentration increases, which is shown in Fig. 3 only for the separation of a mixture of C_{10}/C_9 2-positional standards and the Zorbax ODS column, occurs because of the significant peak narrowing.

Enhanced column efficiency, resolution, and selectivity are cation dependent. Table 2 surveys

Table 2
Effect of different cations on efficiency, resolution and selectivity for a Zorbax ODS column

Electrolyte[a]	Efficiency[b]	Resolution[c]	Selectivity[c]
None	590	0.41	1.89
LiCl	7040	9.52	2.05
NaCl	8420	11.0	2.04
NH_4Cl	7640	10.8	2.06
$(CH_4)_4NBr$	8370	10.8	2.03
$MgCl_2$	7790	10.7	2.01
$BaCl_2$	7670	10.8	2.03
$AlCl_3$	3940	7.30	2.01

[a] A CH_3CN–water (35:65), 0.0010 *M* ionic strength mobile phase.

[b] The analyte was a 2-positional C_9 LAS standard; efficiency is expressed as plates/column.

[c] Data are for separation of 2-positional C_{10}/C_9 LAS standards.

how individual cations enhance these three key column properties for the Zorbax ODS column. In Table 2 the mobile phase solvent is CH_3CN–water (35:65) and each electrolyte as the chloride salt, except for the tetramethylammonium cation which was used as the bromide salt, provides an ionic strength of 0.0010 *M* assuming the electrolytes are completely dissociated. Efficiency data are for a 2-positional C_9 LAS standard and selectivity and resolution data are for the separation of a mixture of C_{10}/C_9 2-positional LAS standards. The mobile phase cation also enhances efficiency, resolution, and selectivity on the PRP-1 column, but to a much lesser extent compared to the Zorbax ODS column. For example, PRP-1 column efficiency was lower by a factor of three to four, resolution was less by two to three, and selectivity was lower by about 10% depending on the cation.

3.3. Role of the cation

Retention of the LAS surfactants on the reversed stationary phase follows the Stern–Gouy–Chapman electric double layer model [38,39]. The LAS anions are retained on the stationary phase surface through a hydrophobic interaction between the alkyl chain of the anionic surfactant and the stationary phase. This creates a negatively charged primary layer at the stationary phase surface and a secondary diffuse layer of cations to maintain electrical neutrality. This is shown in Eq. 1

$$\begin{aligned}&\mathrm{SP} + \text{R–phenyl–SO}_3^- + \mathrm{M}^+ \rightarrow\\&\mathrm{SP}\cdots\text{R–phenyl–SO}_3^-\mathrm{M}^+ \rightarrow\\&\mathrm{SP}\cdots\text{R–phenyl–SO}_3\mathrm{M} \qquad (1)\end{aligned}$$

where SP is the reversed stationary phase. As mobile phase ionic strength increases, the interaction between the cation and the retained LAS increases which decreases the diffuse nature of the cation. This reduces the anionic character of the LAS surfactant anionic group, thus increasing the interaction between the LAS surfactant and the stationary phase.

The influence of different cations provided by the ionic strength electrolyte on anionic surfactant retention and the linear correlation between the hydrated radius of the cation and retention of the LAS surfactant can be explained by considering the change in the surface charge density. Because the hydrated cations have a finite size, they cannot approach the charged surface any closer than the hydrated radius. The plane of closest approach of cations in the double layer is the Outer Helmholz Plane (OHP) (see ref. 39) and the region between the charged surface and the OHP is a compact layer. The compact layer can be treated as a capacitor consisting of the LAS anion and the cation. The surface charge density, σ°, is related to the capacitance, c, of the compact layer by:

$$\sigma^\circ = C(\Psi_0 - \Psi_{\mathrm{OHP}}) \qquad (2)$$

where Ψ_0 is the potential difference between the stationary phase surface and the bulk solution and Ψ_{OHP} is the potential difference between the OHP plane and the bulk solution. As the hydrated radius of the hydrated cation decreases, the capacitance of the compact layer increases, thus σ° increases. Since the surface charge is due to the LAS anions, there would be more LAS anions retained on the stationary phase surface and a longer retention time would occur.

When an inert electrolyte such as NaCl is added to the mobile phase, both surfactant anions and electrolyte anions will be adsorbed on the stationary phase surface as potential determining ions and they are responsible for the potential difference, Ψ_{OHP}, between the stationary phase surface and the bulk solution. Since the concentration of the added electrolyte is high, the electrolyte anions are largely responsible for establishing Ψ_{OHP}. As a result, Ψ_{OHP} is independent of anionic surfactant concentration and the equilibrium constant for the retention of the surfactant anion is constant and a linear adsorption isotherm is obtained. Thus, under these conditions of high ionic strength, chromatographic peaks are more symmetrical and well defined which results in a sharply improved column efficiency and resolution.

3.4. Separations

Comparison of the data included here and elsewhere [40] indicates that the Zorbax ODS column provides a significantly improved column performance, particularly in column efficiency, over the PRP-1 column. Since the better detection limit is obtained by UV absorption over postcolumn anionic micromembrane suppression and conductivity detection, a basic mobile phase is not required for the lowest detection limit [13], thus, this also favors the C_{18} column over the PRP-1 column and increases the flexibility in optimizing the mobile phase conditions. For these reasons separation examples shown here focus only on the Zorbax ODS column. No attempt was made to study other C_{18} columns of similar or microbore diameters.

Tables 1, 2 and other data [40] demonstrate that Na^+, Mg^{2+} and Ba^{2+} are the optimum cations of those studied while Figs. 1–3 indicate the optimum mobile phase and cation concentration to use to separate LAS mixtures efficiently and effectively at a reasonable analysis time. Since a potential solubility problem may occur between Mg^{2+} or Ba^{2+} and the higher-alkyl-chain LAS analytes, Na^+ was selected as the optimum cation and NaCl was used as the electrolyte to provide both the cation and the mobile phase ionic strength.

Mixtures of homologous LAS analytes are readily separated by isocratic elution when the benzenesulfonate is located at the same position on the alkyl chain and the alkyl chain covers a small range of carbon chain lengths. Fig. 4 illustrates the separation of 2-positional C_9, C_{10}, C_{14} and C_{15} LAS standards from an isomeric C_{12} LAS sample using an isocratic CH_3CN–water (3:2) + 100 m*M* NaCl mobile phase and a Zorbax ODS column. For the conditions reported in Fig. 4 a linear correlation was found between log *k'* and alkyl chain carbon number for the 2-positional C_9, C_{10}, C_{14} and C_{15}, LAS standards and corresponds to the equation log *k'* = 0.190 (alkyl chain carbon number) − 1.71 with a correlation coefficient of 0.9991. When these chromatographic data for each 2-positional LAS standard were compared to the chromatographic data for the separation of the corresponding isomeric mixture of each LAS, the 2-positional isomer peak occurred at the longest retention time. Based on these studies and others [30] it is concluded that the peak of highest retention in the C_{12} isomeric peak region in Fig. 4 contains or is the 2-positional C_{12} isomer. Other positional LAS standards where not available, however, it is expected that other positional isomer homologues should also yield linear log *k'*–carbon number retention–structure correlations.

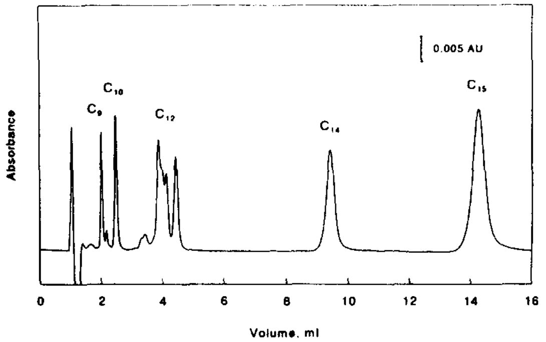

Fig. 4. Isocratic separation of an isomeric mixture of C_{12} LAS and 2-positional C_9, C_{10}, C_{14} and C_{15} LAS standards. CH_3CN–water (3:2) + 100 m*M* NaCl mobile phase at 1.0 ml/min and 150 mm × 4.6 mm Zorbax ODS column.

More complex mixtures of LAS surfactants and/or resolution of isomeric LAS homologues in a favorable analysis time require a gradient elution. Three gradient strategies examined when using the Zorbax ODS column were: (1) a solvent gradient where CH_3CN concentration increases in a CH_3CN–water + constant NaCl mobile phase, (2) an electrolyte gradient where NaCl concentration decreases in a NaCl + constant CH_3CN–water mobile phase, and (3) a combined solvent and electrolyte gradient where CH_3CN increases and NaCl decreases simultaneously in a CH_3CN–water + NaCl mobile phase. Preliminary studies demonstrated that the combined solvent, electrolyte gradient was optimum for the separation of a complex mixture of homologues and positional isomers. In addition the combined gradient provided a minimum absorbance background change during the course of the gradient and this yielded the best detection limit for the LAS peaks. The background changes for the three gradients and the Zorbax ODS column are shown in Fig. 5. For the solvent gradient (Fig. 5A), at fixed NaCl the absorbance increases with an increase in CH_3CN concentration while for the NaCl gradient (Fig. 5C), at fixed CH_3CN–water, absorbance de-

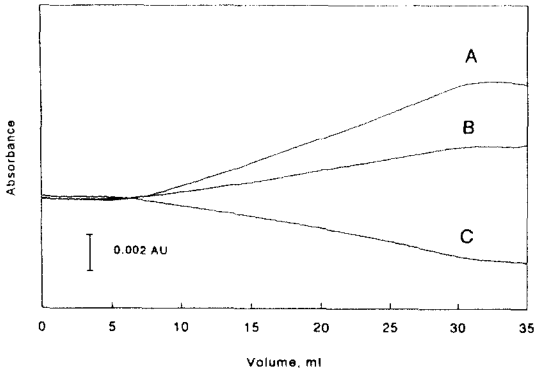

Fig. 5. Effect of gradient change on absorbance background. A = A solvent gradient where solvent 2 of CH_3CN–water (60:40) is added to solvent 1 of CH_3CN–water (40:60). B = A solvent and electrolyte gradient where solvent 2 of CH_3CN–water (60:40) is added to solvent 2 of CH_3CN–water (40:60) + 100 m*M* NaCl. C = An electrolyte gradient where solvent 2 of CH_3CN–water (40:60) is added to solvent 1 of CH_3CN–water (40:60) + 100 m*M* NaCl. In all cases the gradient is 0 to 90% solvent 2 in 25 min at 1.0 ml/min and a 150 mm × 4.6 mm Zorbax ODS column was used.

creases as the NaCl concentration decreases. When the combined NaCl + solvent gradient was employed with the UV detector used in these studies, the two opposing effects partially cancel and provide a more favorable, small background absorbance change (see Fig. 5B).

Several industrial-grade LAS mixtures were separated on the more efficient Zorbax ODS column. Fig. 6 illustrates the effectiveness of adding an electrolyte to the mobile phase. In the absence of the electrolyte and elution by a CH_3CN–water mobile phase (Fig. 6A), bands are broader, resolution is less complete, and positional isomers are poorly resolved. In the presence of NaCl and elution by a combined solvent and electrolyte gradient similar to that used in Fig. 5B, retention, efficiency and resolution of the LAS homologues and positional isomers are significantly improved as shown in Fig. 6B. Fig. 7 illustrates the separation of two other industrial LAS surfactant mixtures that differ in homologue ratio on the 150 mm × 4.6 mm Zorbax ODS column. In Fig. 7A the longer alkyl chain homologues are in the majority while in Fig. 7B the shorter homologues dominate. A combined solvent and electrolyte gradient was used for both separations in Fig. 7. For Fig. 7A the gradient was the same as Fig. 5B while for Fig. 7B the gradient change to 85% solvent 2 occurred over 30 min. The peaks for the C_{10}, C_{12} and C_{14} LASs were identified by comparison to

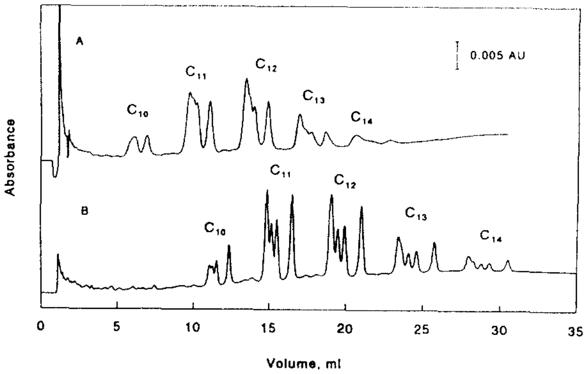

Fig. 6. Effect of mobile phase electrolyte on resolution of a commercial LAS mixture. In (A) the gradient free of electrolyte listed in Fig. 5A was used while for (B) the gradient listed in Fig. 5B was used. Flow-rate was 1.0 ml/min and a 150 mm × 4.6 mm Zorbax column was used.

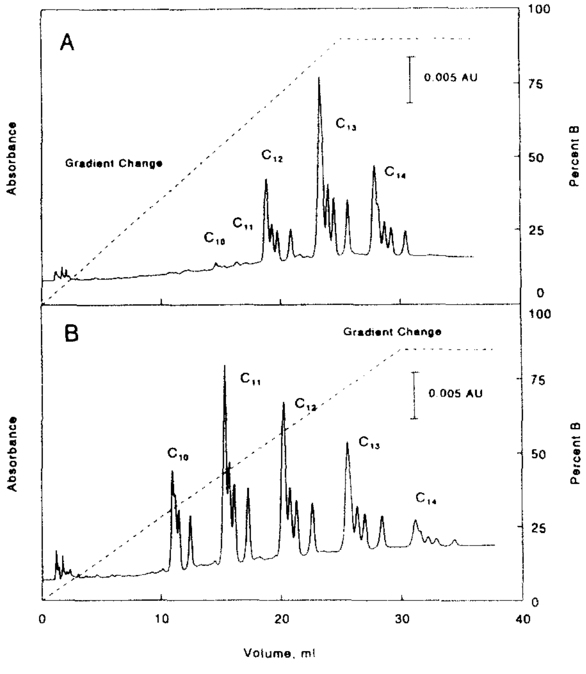

Fig. 7. Separation of two different commercial LAS mixtures. The gradient and column used in A and B are the same as listed in Fig. 5B except in B the change is 0 to 85% solvent 2 in 30 min.

2-positional LAS standards while C_{11} and C_{13} isomeric peaks were predicted based on hydrophobic considerations of the LAS derivatives. In both Figs. 6 and 7 the LAS sample solution was made by dissolving 0.5 mg of the commercial LAS mixture per ml of CH_3CN–water (2:3) and was injected as a 5-μl aliquot. When the column length was increased from 150 mm (see Fig. 6B) to 250 mm (see Fig. 8), resolution of the positional isomers is increased. For these separations the peak of highest retention for each homologue was shown to be the 2-positional isomer by comparison to retention data determined for 2-positional C_9, C_{10}, C_{14} and C_{15} LAS standards. Based on hydrophobic considerations the other homologue isomeric peaks are believed to correspond to shorter retention times as the benzenesulfonate group is positioned towards the center of the alkyl chain. Standards, however, were not available to confirm this prediction.

Calibration curves were prepared for 2-positional C_{10} and C_{14} LAS standards using detection by UV absorbance at 225 nm and by conductance following postcolumn anionic micromembrane suppression. The former, which provides the better detection limit was established using the gradient outlined in Fig. 6B while in the latter the elution was isocratic at a CH_3CN–water (45:55) + 10 mM $Mg(OAc)_2$ mobile phase. The linear calibration curve for the C_{10} LAS standard and the absorbance detection corresponded to the equation peak area $= 1.1 \cdot 10^3$ (pmol LAS) $- 9.8 \cdot 10^2$ with a correlation coefficient of 0.9995 and provided a detection limit (at a signal-to-noise ratio 3) of 2.5 pmol of injected C_{10} LAS standard in a 10-μl aliquot while for conductance detection the linear calibration curve corresponded to peak area $= 1.25 \cdot 10^2$ (pmol LAS) $-$ $5.46 \cdot 10^3$ with a correlation coefficient of 0.9995 and yielded a detection limit of 130 pmol for the same injection and signal-to-noise ratio. Similar results were also obtained with a C_{14} LAS standard.

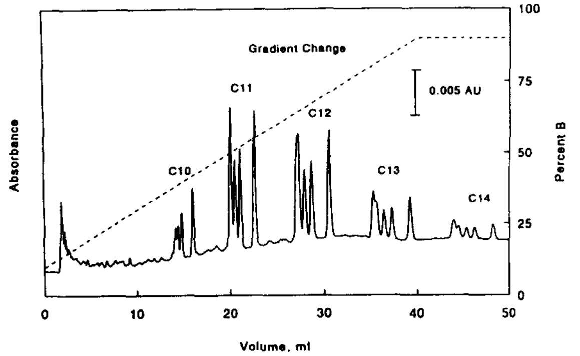

Fig. 8. Separation of a commercial LAS mixture from Fig. 7 on a 250 mm Zorbax column. The gradient is the same as Fig. 5B except the gradient change from 0 to 90% solvent 2 occurred over 40 min.

4. Conclusions

Retention of LAS surfactants increases on reversed stationary phases according to mobile phase ionic strength and ionic strength electrolyte cation. A major improvement in efficiency and resolution is also ionic strength and cation dependent while selectivity is only modestly increased. The optimum mobile phase cations are Na^+, Mg^{2+} and Ba^{2+} with Na^+ being the most convenient to use. LAS homologues are resolved conveniently by isocratic elution while resolution of LAS positional isomers requires a mobile phase gradient. The most favorable gradient is one where the CH_3CN concentration increases and the NaCl concentration decreases simultaneously in a CH_3CN–water solvent mixture.

5. Acknowledgements

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