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# Separation of anionic surfactants on anion exchangers

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#### Abstract

Two anion-exchange columns, PRP-X100 and IonPac AS11, that differ in anion-exchange capacity and porous properties are evaluated for applications in the separation of anionic surfactants such as alkane sulfonates, alkyl sulfates, and linear alkylbenzene sulfonates. Retention of the anionic surfactants on the anion exchangers is due to both anion-exchange processes and interactions between the anionic surfactant and exchanger polymeric matrix. The effects of mobile phase solvent composition and counter-anion, counter-anion concentration, and mobile phase cation are evaluated. Isocratic baseline separation of alkane sulfonates and alkyl sulfates in the carbon number range of C<sub>6</sub> to C<sub>12</sub> are possible on the IonPac AS11 anion-exchange column using a 40:60 acetonitrile-water, LiOH eluent with post-column suppression and conductivity detection. Typical detection limits for alkane sulfonates and alkyl sulfates are about 14 pmol. Linear alkylbenzene sulfonate (LAS) homologs can be separated and partial separation of LAS positional isomers is also possible.

#### 1. Introduction

Over half of the surfactants consumed in commercial and industrial products and processes are anionic surfactants. Of the various available forms of anionic surfactants those most used as the acids or their salts are the linear alkylbenzene sulfonates (LAS), which are biodegraded in an aerobic condition, the alkane sulfonates (RSO $_3^-$ ), the alkyl sulfates (ROSO $_4^-$ ), and the alkyl ether sulfates. In most applications and formulations the anionic surfactants are a mixture of homologs. While the carbon number can range from  $C_6$  to  $C_{18}$  most industrial mixtures are composed of a narrower range of homologs and their mixtures are often expressed in terms of average C number. For the LAS surfactants the mixtures can be even more complex because the position of the benzene sul-

Establishing a simple and reliable method for the analysis of anionic surfactants is essential for quality control in anionic surfactant manufacturing and in commercial applications or in the study of the environmental fate of the anionic surfactants since they are often discharged into the environment. Procedures that do not difsurfactant ferentiate among the anionic homologs are limited in their application. For this reason and because detection limits are also favorable separation techniques such as thinlayer chromatography [1,2], gas chromatography (GC) [3-8], capillary electrophoresis (CE) [9-12], and liquid chromatography (LC) [13-32] are widely employed in anionic surfactant analysis. GC and LC are particularly valuable since each can be interfaced with mass spectrometry

fonate ring on the alkyl chain for a given alkylbenzene sulfonate can vary depending on the alkyl chain length and the manufacturing process.

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[4,5,8,25] which allows sensitive identification of individual separated homologs.

LC anionic surfactant separations are based on one of three general approaches and each takes advantage of either the hydrophobic or the anionic property of the surfactant. In one LC strategy anionic surfactants are retained on reversed stationary phases because of the hydrophobic property of the surfactant and resolution of the anionic surfactant homologs comes about because of differences in hydrophobicity of the homologs [13-21]. A second LC strategy is based on retention of the anionic surfactants on anion exchangers. In this case separation occurs because of differential ionic interactions between the surfactant anionic group for each of the homologs and the ionogenic groups of opposite charge on the anion exchanger [22-24]. Both silica bonded phase and organic polymer-based anion exchangers are useful for these kinds of separations although the latter is usually preferred because of the pH limitations of the silicabased anion exchangers. In the third LC strategy a pairing ion or ion interaction reagent, such as a quaternary ammonium salt, is included in the mobile phase and retention and resolution are due to a differential interaction between the reversed stationary phase, the ion interaction reagent, and the anionic surfactant analyte [25-33].

The three LC separation strategies can be used to isolate and/or concentrate trace quantities of anionic surfactants in a precolumn or solid-phase extraction strategy. This kind of application is particularly beneficial with reversed stationary phases and anion exchangers and each of these has been successfully employed in the analysis of anionic surfactants in environmental samples [13,17,19,29].

Each of the LC anionic surfactant separation strategies is subject to specific factors which can be manipulated to enhance retention, resolution, and even detection. For example, in the reversed-phase LC separation of anionic surfactants retention of the surfactant is enhanced as eluent ionic strength is increased and the extent of the enhancement is cation-dependent when different electrolytes are used as the ionic

strength electrolyte [14,21]. Column efficiency depending on the ionic strength and the cation is also increased which increases resolution significantly. These improved chromatographic characteristics were attributed to association between the mobile phase cation and the anionic surfactant. In the LC separation of the anionic surfactants in the presence of an ion interaction reagent resolution can be improved by employing a more hydrophobic ion interaction reagent, varying the mobile phase organic solvent content or ionic strength, and/or by selecting different types of ion interaction reagents [25-33]. The ion interaction reagent, if detector-active, can also provide the basis for the indirect detection of the anionic surfactants [30-33]. In the anionexchange separation of anionic surfactants detection can be improved when RSO<sub>3</sub>, ROSO<sub>3</sub>, or alkyl ether sulfates are being separated by elution with an eluent chromophoric counter-anion, such as phthalate, sulfosalicylate, m-sulfobenzoate, or naphthalene disulfonate. This type of eluent also allows anionic surfactants to be detected by an indirect absorbance detection strategy at a wavelength where the eluent counter-anion absorbs [22,23].

This report focuses on our studies on the retention and separation of anionic surfactants on anion exchangers. The importance of anion-exchange capacity, the influence of the anion-exchange matrix on retention, and the effect of eluent cation on anionic surfactant retention on anion exchangers were evaluated. Optimum conditions for the separation of RSO<sub>3</sub>, ROSO<sub>3</sub>, and LAS analytes on anion exchangers are established.

# 2. Experimental

### 2.1. Reagents and instrumentation

Alkane sulfonates and alkyl sulfates were purchased from Chem Service and Eastman Kodak as the sodium salts or free acids. Benzene-, p-toluene-, and p-ethylbenzenesulfonic acids, p-hydroxybenzoic acid (PHBA), potassium acid phthalate (KHP), and trimesic acid

were purchased from Eastman Kodak, Sigma, EM Science, or Aldrich. Commercial mixtures of LAS surfactants and pure samples of sodium salts of 2-nonyl-, 2-decyl-, 2-tetradecyl-, and 2-pentadecylbenzenesulfonate were obtained from Procter and Gamble. The pure samples were shown to be free of other positional isomers by LC [21]. Acetonitrile and methanol (EM Science) were analytical-reagent grade. LC water was freshly prepared by passing in house distilled water through a Millipore Milli-Q Plus water treatment system.

Two commercially available prepacked anion-exchange columns were studied. A macroporous polystyrene–divinylbenzene copolymer-based anion exchanger, PRP-X100, was obtained from Hamilton as a 10- $\mu$ m particle, 150 mm  $\times$  4.6 mm I.D. column with an exchange capacity of 190  $\mu$ equiv. per column. A second pellicular-type polystyrene–divinylbenzene latex-modified anion exchanger, IonPac AS11, was obtained from Dionex as a 13- $\mu$ m particle, 250 mm  $\times$  4.6 mm column with an anion-exchange capacity of 45  $\mu$ equiv. per column.

Beckman Model 110A reciprocating pumps and a Beckman Model 332 gradient controller delivered the eluent while sample injection was by a Rheodyne 7125 injector with a 20-μl sample loop. Detection was by UV absorbance (LAS analytes) with a Spectra Physics SP 8450 or SP100 variable-wavelength detector at 220 or 225 nm or by a Waters M-430 conductivity detector (RSO<sub>3</sub><sup>-</sup>, ROSO<sub>3</sub><sup>-</sup> analytes) following suppression with a Dionex AMMS-1 anion micromembrane suppresser. Chromatographic data were collected on a Spectra Physics 4270 integrator and handled by Spectra Physics WINner chromatographic software.

# 2.2. Procedures

Anion-exchange columns were evaluated periodically with a  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $NO_3$  test sample where each anion was 0.1 mg/ml. An aqueous 4.0 mM p-hydroxybenzoic acid solution at 2.0 ml/min and a 21 mM NaOH solution at 1.0 ml/min were used for the PRP-X100 and

IonPac AS11 columns, respectively, and analytes were detected by conductivity.

Mobile phase solutions were prepared by dilution of a known volume of aqueous salt, acid, or base solution of known concentration which had been determined by titration versus standards. Organic solvent-water eluents (v/v) were degassed for several minutes prior to their use. Analyte solutions of known concentration (0.030 to 0.30 mg/ml) were prepared in deionized water or 1:1 acetonitrile-water. Standard analyte solutions for the calibration curves were prepared by a series of dilutions of standard solutions of the analyte. Sample injection was by Hamilton syringe, eluent flow-rate was 1.00 ml/ min with the IonPac AS11 column and 2.0 ml/ min with the PRP-X100 column, temperature was 25°C, and inlet pressure and void volume, which depended on the column and the eluent, was 500 to 900 p.s.i. and 0.9-1.0 ml, respectively. Aqueous 25 mM H<sub>2</sub>SO<sub>4</sub> at 1.0 ml/min was used to regenerate the anion micromembrane suppresser. Multiple measurements were averaged to establish capacity factors, column efficiency, and calibration curve data. Retention order and peak identity were confirmed by comparison to retention times for known standards except where noted.

#### 3. Results and discussion

### 3.1. Anion exchangers

Analyte anion retention in typical anion-exchange processes is affected by eluent counteranion, counter-anion concentration, solvent composition, and pH, particularly when the analyte anion has a weak base property. Retention is also influenced by anion-exchange capacity and increases as the capacity of the exchanger increases. Two types of anion exchangers, PRP-X100 and IonPac AS11, were investigated. Both are strong base-type anion exchangers containing the quaternary ammonium ionogenic group. The PRP-X100, however, has an anion-exchange capacity of about four times that of the IonPac AS11 and is macro-

porous while the IonPac AS11 is pellicular. Consequently, both anion exchangers have the potential for hydrophobic interactions between the analyte anion and the polymeric exchanger matrix when the analyte anion also contains a hydrophobic center in addition to ordinary anion exchange at the anion exchange ionogenic group. Since anionic surfactants contain both an anionic center and a hydrophobic property due to the hydrocarbon chain, these analytes are likely to participate in a mixed-mode type interaction with polymeric stationary phases that possess both anion-exchange ionogenic groups and a matrix that can participate in a reversed-phase type of interaction with the hydrophobic portion of the analyte. As anion-exchange capacity increases and the number of charged ionogenic groups increases the exchanger surface becomes more polar and the extent of the reversed-phase interaction at the exchanger polymeric matrix should decrease. Mixed mode-type interactions have been observed before with anionic surfactant analytes and an aminefluorocarbon silica bonded stationary phase column [23] as well as with other type of analytes and mixed stationary phase surfaces [34-36] and commercial columns have become available to take advantage of mixed-mode interactions.

The PRP-X100 and the IonPac AS11 are strong-base anion exchangers and participate in typical anion-exchange processes. Both are polystyrene-divinylbenzene copolymer-based, but the macroporous property of the PRP-X100 favors a greater hydrophobic interaction between the anionic surfactant and the exchanger matrix than for the IonPac AS11. However, the exchange capacity of the IonPac AS11 is about one fourth that of the PRP-X100 and the lower capacity suggests that the hydrophobic interaction would also be extensive on this anion exchanger.

As the carbon chain of an anionic surfactant increases, its ability to undergo a hydrophobic interaction with the anion-exchange matrix should also increase. The eluent conditions that will affect this type of interaction are: eluent solvent composition, type of organic modifier, eluent ionic strength, pH if the analyte has weak

acid properties, and mobile phase cation. Eluent ionic strength and the cation dependency are especially important in anionic surfactant separations because these variables when optimized will improve chromatographic peak shape, column efficiency, and resolution and therefore improve both the quality of the separation and the detection limit [14,21].

# 3.2. Effect of eluent organic modifier

Figs. 1A and B show that as organic modifier increases in the eluent anionic surfactant retention on the PRP-X100 and IonPac AS11 decreases. The large change in retention for the C<sub>4</sub> to C<sub>10</sub> RSO<sub>3</sub> analytes used in Fig. 1 is much greater than what would be expected if only anion-exchange processes were involved in anionic surfactant retention and these processes were the only ones being affected. The major effect of the solvent is to influence the interaction between the RSO3 surfactant and the exchanger polymeric matrix. Furthermore, the interaction of the RSO<sub>3</sub> surfactant with the matrix is significantly greater on the PRP-X100, which increases as the alkyl chain length of the RSO<sub>3</sub> surfactant increases, since a much stronger eluent solvent, acetonitrile-water, is required to lower the retention of the RSO<sub>3</sub> surfactants on the PRP-X100. For the IonPac AS11 an acetonitrile-water eluent solvent, which is much weaker in its eluent strength towards reversed-phase interactions, is sufficiently strong to lower the RSO3 surfactant anion exchanger matrix retention.

# 3.3. Effect of mobile phase counter-anion

Increasing eluent counter-anion concentration decreases anionic surfactant retention typical of an anion-exchange process. Fig. 2A and B illustrate how different eluent counter-anions at a fixed counter-anion concentration influence anion surfactant retention on the two anion exchangers. For both anion exchangers the eluent solvent is adjusted to an organic modifier

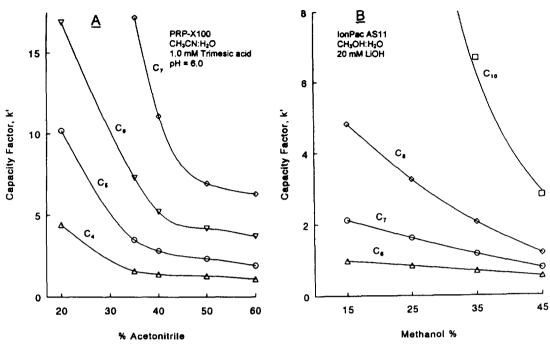


Fig. 1. Effect of mobile phase modifier on the retention of alkane sulfonates of differing alkyl chain lengths on (A) PRP-X100 and (B) IonPac AS11.

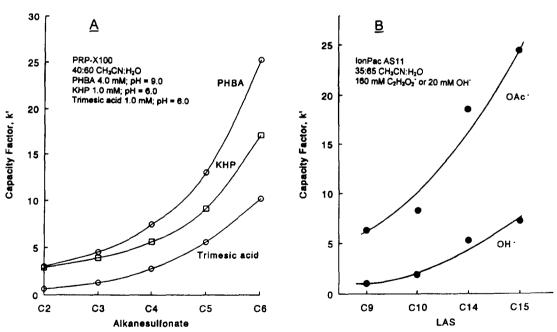


Fig. 2. Effect of mobile phase counter-anion on the retention of (A) alkane sulfonates on PRP-X100 and (B) LAS derivatives on IonPac AS11.

concentration that minimizes anionic surfactantanion-exchange matrix interaction for the series of anion surfactants studied.

For the PRP-X100 anion exchanger (see Fig. 2A), which has the higher anion-exchange capacity, strong eluent counter-anions, such as PHBA, KHP, and trimesic acid that are appreciably multivalent at the pH used, are required to reduce the retention of the RSO<sub>3</sub> analytes where the alkyl carbon chain ranges from C<sub>2</sub> to C<sub>6</sub>. Favorable elution times are obtained only for the shorter-carbon-chain RSO<sub>3</sub> analytes and when the eluent contains the stronger, multivalent counter-anions. If the counter-anion concentration is increased RSO<sub>3</sub> retention decreases typical of an anion-exchange process. When the organic modifier in the eluent in Fig. 2A is decreased, RSO<sub>3</sub> surfactant retention increases and the increase is consistent with a mixed-mode interaction [23]. For longercarbon-chain RSO<sub>3</sub> analytes than used in Fig. 2A retention on the PRP - X100 is even higher and elution, even with the stronger eluent counter-anion sodium trimesate, is not favorable in terms of elution time.

For the IonPac AS11 (see Fig. 2B), or the anion exchanger with the lower anion-exchange capacity and lower matrix interaction, elution of the RSO<sub>3</sub> analytes is possible with weak eluent counter-anions, such as  $OH^-$  and  $C_2H_3O_2^-$ , both of which are also compatible with post-column suppression to enhance conductivity detection. Even the more hydrophobic LAS derivatives, which were the analytes in Fig. 2B, have low retention in the presence of the eluent OH and  $C_2H_3O_2^-$  counter-anions and are eluted in reasonable elution times. When  $C_9$  and  $C_{10}$ RSO<sub>3</sub> analytes were used and eluent OH concentration was increased from 10 to 60 mM,  $\log k'$  versus  $\log OH^-$  concentration curves were linear up to 40 mM OH<sup>-</sup>. Slopes were about 1 indicating that at the eluent solvent conditions in Fig. 2B retention is primarily due to anion exchange [23]. Furthermore, elution time for the anionic surfactants can be reduced even more by increasing the OH or C,H,O, eluent concentration.

### 3.4. Effect of mobile phase cation

In reversed-phase chromatography of anionic surfactants the retention, column efficiency, and resolution are enhanced depending on eluent cation and its concentration. Association between the anionic surfactant and the cation was suggested to be a major contributor to the enhanced chromatographic performance [14,21]. In anion exchange of anionic surfactants association between the eluent cation and the surfactant anion should reduce anion surfactant retention on the anion exchanger. When electrolytes providing different cations and the same counteranion were used as eluent additives retention of the anionic surfactants is influenced by the cation but only to a small extent. This is illustrated in Fig. 3 where retention of benzene-, p-toluene-, and p-ethylbenzenesulfonic acid on the IonPac AS11 is plotted as a function of eluent acetoni-

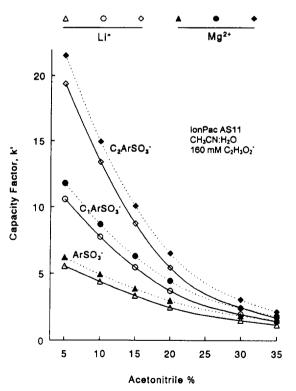


Fig. 3. Effect of eluent cation on the retention of short-alkylchain LAS derivatives on IonPac AS11.

trile/water ratio at a constant Li and  ${\rm Mg}^{2+}$  acetate concentration where the acetate concentration of the two eluents are equivalent. The  ${\rm Mg}^{2+}$  consistently causes a small enhancement in the anionic surfactant retention compared to the Li eluent. This enhancement was also observed when comparing the effects of  ${\rm Mg}^{2+}$  and Li in a 35:65 acetonitrile-water, 160 mM  ${\rm C}_2{\rm H}_3{\rm O}_2^-$  eluent on LAS retention for alkyl chain lengths of C<sub>0</sub> to C<sub>15</sub> and for LAS retention where LiC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> concentrations were increased in a 20:80 acetonitrile-water eluent. A similar  ${\rm Mg}^{2+}$  over Li enhancement in retention for the short-carbon-chain LAS analytes was determined for the PRP-X100 anion exchanger.

The cation, if it undergoes association with the anionic surfactant as suggested previously [14,21], can affect retention on the anion exchanger in two ways. First, the association can affect the interaction between the anionic surfactant and the exchanger matrix to increase retention. The associated cation anionic surfactant is less polar than the dissociated anionic surfactant and therefore is better able to undergo an interaction with the matrix. Or second, the association can cause retention of the anionic surfactant at the anion exchange site to be less since the cation anionic surfactant-associated species reduces the anionic character of the anionic surfactant. The fact that Mg<sup>2+</sup> as the eluent cation has a greater affect over Na<sup>+</sup> or Li<sup>+</sup> as the eluent cation is consistent with the cation having a greater influence on the matrix interaction. The cation effect is not large, however, and manipulation of the eluent cation to alter anionic surfactant retention on the anion exchanger offers only a modest advantage in retention and separation of anionic surfactants on the polymer-based anion exchangers.

### 3.5. Separations

The low-capacity IonPac AS11 anion exchanger is more versatile than the PRP-X100 anion exchanger for the separation of anionic surfactants because on the former anion ex-

changer the matrix interactions are less, elution of the anionic surfactants is possible with weaker eluent counter-anions, column efficiency is better, and resolution is more favorable. For these reasons only separations using the IonPac AS11 anion exchanger are described here; data for anionic surfactant separations on the PRP-X100 are available elsewhere [37]. The low exchange capacity for the IonPac AS11 limits the sample size in order to avoid a sample overload of the column. A acetonitrile-water, LiOH solution, which provides a OH eluent counter-anion and an acetonitrile concentration that reduces matrix interaction with the anionic surfactants, was used. The OH counter-anion is readily handled by post-column suppression which permits an enhanced conductivity detection of the separated anionic surfactants. LAS or other anionic surfactants that contain a chromophore were detected by UV.

Fig. 4 illustrates the baseline separation of a

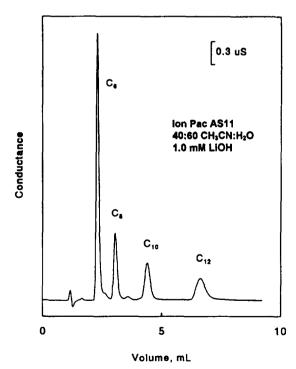


Fig. 4. Separation of  $C_6$  to  $C_{12}$  alkane sulfonates on IonPac AS11.

mixture of even-carbon  $C_6$  to  $C_{12}$  RSO $_3^-$  analytes using an isocratic elution where the eluent is 40:60 acetonitrile—water, 1.0 mM LiOH. Under these eluent solvent conditions interaction of the RSO $_3^-$  analytes with the matrix is low and resolution is primarily due to anion exchange. The RSO $_3^-$  analytes were detected by conductivity following suppression by an anion micromembrane suppresser.

ROSO<sub>3</sub> analytes of even carbon number in the C<sub>6</sub> to C<sub>12</sub> range are also baseline-resolved on the IonPac AS11 with the same eluent as used in Fig. 4. The ROSO<sub>3</sub> analyte of the same carbon number as the RSO<sub>3</sub> analyte has a higher retention on both the IonPac AS11 and PRP-X100 anion exchangers. This same selectivity is also observed when reversed-phase columns are employed [14]. Because of the difference mixtures of ROSO<sub>3</sub> and RSO<sub>3</sub> analytes are separable by isocratic elution on the IonPac AS11 column. This is illustrated in Fig. 5 where a mixture of even-carbon C<sub>6</sub> to C<sub>12</sub> RSO<sub>3</sub> and ROSO<sub>3</sub> analytes are baseline-resolved. In Fig. 5

the shoulder on the C<sub>6</sub>SO<sub>3</sub> peak and the unidentified peak preceding the C<sub>8</sub>SO<sub>3</sub> where shown to be introduced by the ROSO<sub>3</sub> analyte samples and the two unidentified peaks appear to be due to lower-carbon-number ROSO<sub>3</sub> analytes. When  $\log k'$  values for the retention of the RSO<sub>3</sub> and ROSO<sub>3</sub> analytes are plotted versus carbon number a linear relationship is obtained for each series of homologs. From the ROSO<sub>3</sub> graph the k' values for the two unknown peaks in Fig. 5 correspond to the  $C_4$  and  $C_5OSO_3^$ analytes. No attempt was made to unequivocally identify the two unknown peaks. If the acetonitrile concentration in the eluents used in Figs. 4 and 5 is reduced, interaction between the RSO<sub>3</sub> and ROSO<sub>3</sub> surfactants and the matrix increases, particularly as carbon chain length increases, and the eluent LiOH concentration must be increased to obtain elution times similar to those in Figs. 4 and 5.

Short-chain LAS analytes are baseline-resolved on the IonPac AS11 anion-exchange column. This is illustrated in Fig. 6 where benzene-,

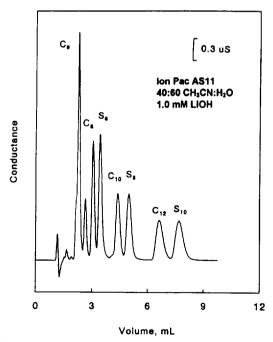


Fig. 5. Separation of  $C_6$  to  $C_{12}$  alkane sulfonates (C) and alkyl sulfates (S) on IonPac AS11.

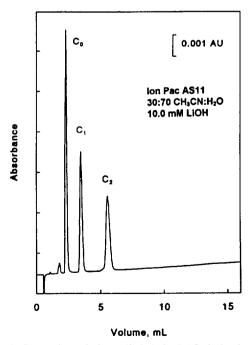


Fig. 6. Separation of short-alkyl-chain LAS derivatives on IonPac AS11.

p-toluene-, and p-ethylbenzenesulfonate are separated and detected by UV at 220 nm. In Fig. 6 the acetonitrile eluent concentration is high enough so that retention is primarily due to anion exchange.

Chromatograms for the separation of a commercial sample of long-chain LAS homologs and isomers in the  $C_{10}$  to  $C_{14}$  range are shown in Fig. 7A and B. In Fig. 7A the eluent was 30:70 acetonitrile-water, 50 mM MgCl2. At this acetonitrile concentration matrix interaction between the IonPac AS11 and the C<sub>14</sub> to C<sub>16</sub> LAS homologs and isomers is significant. Thus, MgCl, was selected as the eluent electrolyte since it provides a counter-anion that increases elution strength and a cation that affects matrix retention. The LAS mixture was known to contain  $C_{10}$  to  $C_{14}$  homologs and for each homolog there are several positional isomers. As shown in Fig. 7A the LAS homologs are completely resolved and the positional isomers are only partially resolved. The resolution between adjacent

homologs is about 1.1. Since the positional isomers have the same anionic character, the resolving power of the anion exchanger for these isomers is less favorable than what can be obtained by reversed-phase chromatography [21] and the partial resolution of the isomers is due to the matrix interaction and influence of the Mg<sup>2+</sup> in the eluent. When an eluent containing 1.5 mM LiOH and 40:60 acetonitrile-water was used (see Fig. 7B), each LAS homolog was eluted as a single chromatographic peak. For such an eluent condition the resolving force that influences the interaction between the LAS analyte and the matrix which is necessary to resolve the positional isomers is diminished, thus, the separation is primarily a separation of homologs due to anion exchange. This separation condition would be preferred if an isomeric separation is not required.

The  $C_{10}$  and  $C_{14}$  LAS peaks in Fig. 7A and B were identified by comparison to pure 2-positional  $C_{10}$  and  $C_{14}$  LAS standards while the  $C_{11}$ ,  $C_{12}$ ,

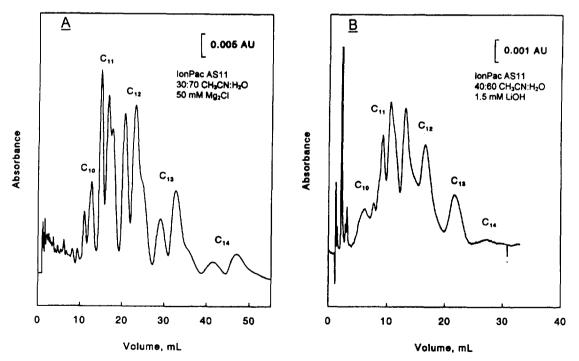


Fig. 7. Separation of a commercial mixture of  $C_{10}$  to  $C_{14}$  (A) LAS homologs and positional isomers and (B) LAS homologs on IonPac AS11.

and C<sub>13</sub> LAS peaks were determined according to the elution order and previous work with the LAS sample by reversed-phase chromatography [21]. All other anionic surfactant analyte peaks in Figs. 4, 5, and 6 were confirmed by comparison to chromatographic data for individually injected standards and/or by peak spiking.

A calibration curve was prepared with the IonPac AS11 column and a standard solution of pure  $C_8OSO_3^-$  as the test analyte. The eluent in Fig. 4 was used and detection was by conductivity following post-column suppression. The calibration curve, which was defined by the equation (peak area) =  $(6.84 \cdot 10^4)$  (nmol of  $C_8OSO_3^-$ ) – 783 where r = 0.9995, was linear throughout the concentration range (0.050-1.0 nmol) studied. Background conductance following suppression was low  $(1-2 \mu S)$  and because of this a detection limit of 14 pmol was obtained for a 3:1 signal-tonoise ratio.

#### 4. Conclusion

Anionic surfactants are retained on PRP-X100 and IonPac AS11 anion exchangers by a mixedmode interaction. The analytes undergo anion exchange as well as an interaction with the exchanger polymeric matrix. The retention due to anion exchange and the matrix interaction is greater on the PRP-X100 which has a higher anion-exchange capacity and a porous polymeric structure. Increasing the eluent organic modifier decreases anionic surfactant retention because of the solvent effect on matrix anionic surfactant interaction. Increasing the eluent counter-anion concentration decreases the retention because of its effect on the anion-exchange process but because the IonPac AS11 has a low anion-exchange capacity weak-eluent counter-anions can be employed to reduce anionic surfactant retention on this exchanger. Eluent cation will affect the matrix interaction but the change in retention due to the cation is small. Isocratic baseline-resolved separations of C<sub>6</sub> to C<sub>12</sub> RSO<sub>3</sub> and ROSO<sub>3</sub> analytes are possible with a 40:60 acetonitrile-water, 1.0 mM LiOH eluent. Since the background conductivity is significantly reduced by post-column suppression detection is very sensitive. LAS homologs are separable while only partial resolution of LAS positional isomers is obtained.

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