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Effect of ionic additives on the elution of sodium aryl sulfonates in supercritical fluid chromatography

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Abstract

Addition of a small amount of polar solvent (i.e., modifier) to CO_2 in packed column supercritical fluid chromatography (SFC) has shown major improvements in both polar analyte solubility and interaction of the polar analyte with the stationary phase. Recently, the addition of an ionic component (i.e., additive) to the primary modifier by one of us has been shown to extend even further the application of SFC to polar analytes. In this work, the effect of various ionic additives on the elution of ionic compounds, such as sodium 4-dodecylbenzene sulfonate and sodium 4-octylbenene sulfonate, has been studied. The additives were lithium acetate, ammonium acetate, tetramethylammonium acetate, tetrabutylammonium acetate, and ammonium chloride dissolved in methanol. Three stationary phases with different degrees of deactivation were considered: conventional cyanopropyl, deltabond cyanopropyl, and bare silica. The effect of additive concentration and additive functionality on analyte retention was investigated. Sodium 4-dodecylbenzene sulfonate was successfully eluted using all the additives with good peak shape under isocratic/isobaric/isothermal conditions. Different additives, however, yielded different retention times and in some cases different peak shapes.

Keywords: Packed column; Supercritical fluid chromatography; Ionic compounds and additives; Ion-pair formation

1. Introduction

Many papers [1–3] have been published on the effects of methanol as a secondary mobile phase component, especially with respect to retention characteristics, selectivity, and peak shapes of various test solutes [4–7]. Lee et al. [8] for example resolved free bases of rac-propranolol, rac-pindolol, and rac-metoprolol as well as HCl salts of rac-betaxolol and rac-cicloprolol with Chiralcel OD and CH_3OH/CO_2 (20/80, v/v). Direct, preparative, enantioselective chromatography of rac-propranolol hydrochloride was later reported [9] using a Chiralpak AD stationary phase and CH_3OH/CO_2 mobile phase without the use of basic or acidic additives. After the separation, isolated fractions of the hydrochloride salts were positively identified by mass spectrometry. More recently these investigators have demonstrated [10] on-line polarimetric detection with SFC instrumentation for the enantioseparation of the same HCl salts.

While common binary mobile phases significantly improve the elution of polar analytes in SFC, in general, highly polar or ionic compounds are still not eluted because the organic modifiers that are miscible with liquid carbon dioxide are also only moderately polar cosolvents. Berger et al. [11] conducted solvatochromic dye studies and showed that very polar compounds, such as trifluoroacetic acid (TFA), when added to SFC modifiers, could significantly increase the solvating power of modified mobile phases. Small concentrations (i.e., 10^{-4} M) of such very polar compounds, called additives, improved chromatographic peak shapes

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and allowed the elution of solutes that were normally very strongly retained. Berger speculated that "additives will provide a key to the separation of more polar solutes by SFC". [11].

Various investigations in this regard have been reported in which weak organic acids and bases have been employed as mobile phase additives. Generally, acidic additives such as trifluoroacetic acid are needed to improve the peak shapes of acidic solutes. Basic additives such as isopropylamine are needed to improve the peak shapes of basic solutes. Berger and Deye [12,13] believed that, in most cases, the mechanism of action involved suppression of analyte ionization by the additive. A less conventional additive, tetramethylammonium hydroxide (TMAOH), was later studied by other workers [14,15] that may suggest a role for the additive other than ion suppression. Specifically, the SFC separation of 24 PTH-amino acids was facilitated with a mobile phase of supercritical CO_2, the additive, and methanol. No modifier was required for the elution of neutral PTH-amino acid derivatives, but the addition of TMAOH and methanol to the mobile phase played a major role in the elution of both acidic and basic PTH amino acids. Peak tailing was minimized and the elution order of several peaks was altered by incorporation of this additive into the mobile phase. The base was thought to interact with, or block active sites on, the stationary phase to significantly improve peak tailing.

The use of ion-pairing principles in SFC has been demonstrated to a limited degree [16,17]. The influence on the selectivity of sodium heptane sulfonate and dimethyloctyl amine (DMOA) with cyano and diol bonded phase columns has been investigated. The limited solubility of ion-pairing agents in CO_2-modifier mixtures was noted as being a problem in ion-pair SFC. Elution of propranolol with 25 mM sodium heptane sulfonate in CH_3OH/CO_2 was reported; whereas the analyte failed to elute from the cyano packed column without sodium heptane sulfonate. As a rule of thumb, the paper suggested that the best choice of initial conditions when starting an optimization of the separation of ionizable compounds is to use a diol phase, tributylamine, and acetate ion in methanol as the ion-pairing agent.

Pinkston et al. recently reported the application of mass-spectrometry compatible, volatile ammonium salts as mobile phase additives in SFC. [18] Ammonium acetate, ammonium formate, and ammonium carbonate were used to elute several cationic (quaternary ammonium salts) and anionic (sulfonic acid salts) organic ions under SFC conditions. With the addition of 1.1 mM ammonium acetate in methanol as mobile phase modifier, analytes that were very strongly or irreversibly retained without additive (e.g. same percentage of methanol) were successfully eluted from a deltabond cyano stationary phase. A three-descriptor model was developed in this study where one descriptor, the "relative negative charged surface", explained 61% of the variance in the retention value.

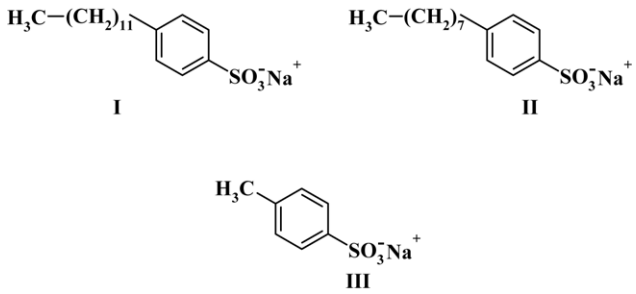

Fig. 1. Structures of three sulfonate analytes. (I) sodium *para*-normal 4-dodecylbenzene sulfonate; (II) sodium 4-octylbenzene sulfonate and (III) sodium *p*-toluene sulfonate.

In this work, we have systematically studied the effect of the nature and concentration of mobile phase ionic additives on the elution of sodium 4-dodecylbenzene sulfonate from two cyano bonded silica phases and bare silica itself. Two other sulfonates, sodium 4-octylbenzene sulfonate, and sodium *p*-toluene sulfonate have also been studied in this work.

2. Experimental

2.1. Chemicals

Methanol was HPLC grade, (EMD, Durham, NC, USA). The carbon dioxide was SFE/SFC grade (Air Products and Chemicals, Inc., Allentown, PA, USA) with no helium head pressure. Lithium acetate (99+%, ACS grade), ammonium acetate (99%, ACS grade), tetramethylammonium acetate (90%, tech. grade), and tetrabutylammonium acetate (97%) were obtained from Sigma Aldrich (Milwaukee, WI, USA). Ammonium chloride (ACS grade) was obtained from J.T.Baker (Phillipsburg, NJ, USA).

Sodium *para*-normal dodecylbenzene sulfonate (tech. grade) (Structure I), 4-octylbenzene sulfonic acid sodium salt (97%) (Structure II), and sodiump-toluene sulfonate (95%) (Structure III) were purchased from Sigma Aldrich (Milwaukee, WI), Fig. 1. A solution of each sample was prepared in methanol at a concentration of approximately 0.5 mg/mL.

2.2. SFC-UV instrumentation

The SFC system was a Berger MiniGram SFC with a Varian 320 Variable Wavelength UV–vis Detector (Varian, Inc., Walnut Creek, CA), and Berger Instruments SFC ProNTo™ MiniGram software, running on a Dell Dimension 2350 computer. In the middle of the experiment, due to the failure of the detector, we switched to a Berger Instruments Analytical SFC Instrument (Berger Instruments, Newark, DE) with a Hewlett Packard Model 1050 diode array detector (DAD), which employed a 13 μL high pressure flow cell (10 mm path length) and Berger Instruments 3D SFC ChemStation software, version 3.4.

The chromatographic columns were deltabond cyano (Thermo Hypersil-Keystone, Bellefonte, PA)[1] Supelcosil LC-PCN, and Supelcosil LC-Si (both Supelco; Bellefonte, PA). The column dimensions were 25 cm length and 4.6 mm I.D., with a particle size of 5 μm for all three stationary phases. Supelcosil LC-PCN and Supelcosil LC-Si had a pore size of 120 Å, while deltabond cyano had a pore size of 200 Å.

Unless otherwise specified, the standard chromatographic conditions were: solution injection volume 10 μL, mobile phase flow rate 2 mL/min (measured in the liquid state), column outlet pressure 120 bar, and column oven temperature 40 °C. The isocratic mobile phase composition was 15% modifier in CO_2, unless specified. The modifier consisted of either pure methanol, or methanol with 2.5 mM lithium acetate, ammonium acetate, tetramethylammonium acetate, tetrabutylammonium acetate, or ammonium chloride.

Between each switch of the mobile phase additive, the modifier line leading from the modifier bottle to the pump was first purged with the next additive solution. The system was then equilibrated for about 10 min by pumping the new mobile phase though the column. Finally, a blank injection of 10 μL of pure methanol through the column was made with the new mobile phase modifier composition, in order to make sure that no analyte was retained on the stationary phase from previous injections.

2.3. SFC-MS instrumentation

The SFC-MS system consisted of a Model G1205A (Agilent, Wilmington, DE USA) fluid control module upgraded to a Model FCM-1200, an autosampler, and Version 3.4 Chemstation SFC control software (all three components from Mettler-Toledo Autochem Berger SFC, Newark, DE, USA). A zero-dead-volume chromatographic tee was installed just before the outlet pressure regulator in the fluid control module for the addition of 100 μL/min of 1 mM ammonium acetate in methanol delivered by a Model D Series 260 Isco syringe pump (Isco, Lincoln, NE, USA).

From the outlet pressure regulator of the SFC system, 100% of the flow was directed to the TurboIonSpray source of a PE Sciex API-365 Triple-Quadrupole Mass Spectrometer controlled by LC2Tune v 1.4 acquisition software (Applied Biosystems, Foster City, CA). The TurboIonSpray source was operated with a Turbo gas flow of 8 L/min at 450 °C. Nitrogen gas for the nebulizer was set at 60 psi. The electrospray capillary and orifice were held at a potential of −4500 and −50 V respectively; while the multiplier potential was set at 2200 V. MS data were acquired via a Q1 scan from *m/z* 50 to 500 using a 0.1-μ step value, a 0.300-ms dwell time, and a 5-ms interscan delay. Product ion scans of *m/z* 325 were obtained at a collision energy of 40 V with nitrogen collision gas. Q3 was scanned from *m/z* 25 to 400 with a 0.1-μ step value, a 0.3-ms dwell time, and a 5-ms interscan delay for the product ion scans.

[1] The vendor no longer supplies this stationary phase.

3. Results and discussion

The initial goal of this work was to study the effect of various mobile phase salt additives on packed column supercritical fluid chromatographic elution of sodium 4-dodecylbenzene sulfonate from three different stationary phases: deltabond cyano, conventional cyano, and bare silica. With 100% CO_2 or even 15% (v/v) pure methanol as CO_2 modifier, technical grade sodium 4-dodecylbenzene sulfonate did not elute from any of the three stationary phases. Introduction of 2.5 mM ammonium acetate into the 15% methanol mobile phase modifier with each of the three stationary phases, however, had a dramatic effect on the chromatography. Fig. 2 compares SFC/UV chromatograms of sodium 4-dodecylbenzene sulfonate elution with 15% 2.5 mM NH_4OAc in methanol as the CO_2 modifier on deltabond cyano, conventional cyanopropyl, and bare silica stationary phases. When ammonium acetate was used as additive, the analyte eluted within 6 min with reasonable peak shape under isocratic conditions from each properly conditioned stationary phase. With just methanol modifier, no analyte peaks were detected; thus only a noisy baseline was observed.

A shoulder or split peak is apparent with all three stationary phases. This is likely due to the presence of alkyl chains that are shorter/longer than twelve carbons in the technical grade sodium 4-dodecylbenzene sulfonate [19]. To gain a better perspective on the nature of the split peak, mass spectrometric detection was incorporated into the SFC experiment with a new bare silica stationary phase, Fig. 3. The UV trace with the new column gave a broader peak with a longer retention time than previously observed, Fig. 3A. A second new bare silica column was then tested to confirm the earlier results. The initial injection indeed yielded a broad peak with retention time in excess of 10 min. Subsequent injections gave a much narrower peak with retention time less than 10 min that was clearly split. The MS contour plot (Fig. 3B) shows clear evidence that the technical grade sulfonate we had been using was in fact a distribution of alkyl groups on the aryl portion ranging from C7 to C15. Thus, this homologous series of sulfonates was only partially separated on the silica phase. Next, an analogous experiment was conducted with the deltabond cyano phase. Fig. 4 shows the UV absorbance chromatogram at 230 nm and the mass chromatogram for *m/z* 325, which corresponds to the $[M-H]^-$ ion for the major component of the mixture, 4-dodecylbenzenesulfonic acid. The UV trace again clearly indicates a mixture of components. The MS data, however, expanded the suspected multiplicity of components because two peaks with the same mass were observed which suggested the presence of isomeric components. Slightly different product ion spectra for different isomers of sodium 4-dodecylbenzenesulfonate would be expected. Fig. 5 shows that, in this case, the differences are apparent but subtle. Specifically, only a small change in the relative abundance of one of the products of *m/z* 325 was evident. The data discussed above help confirm that the

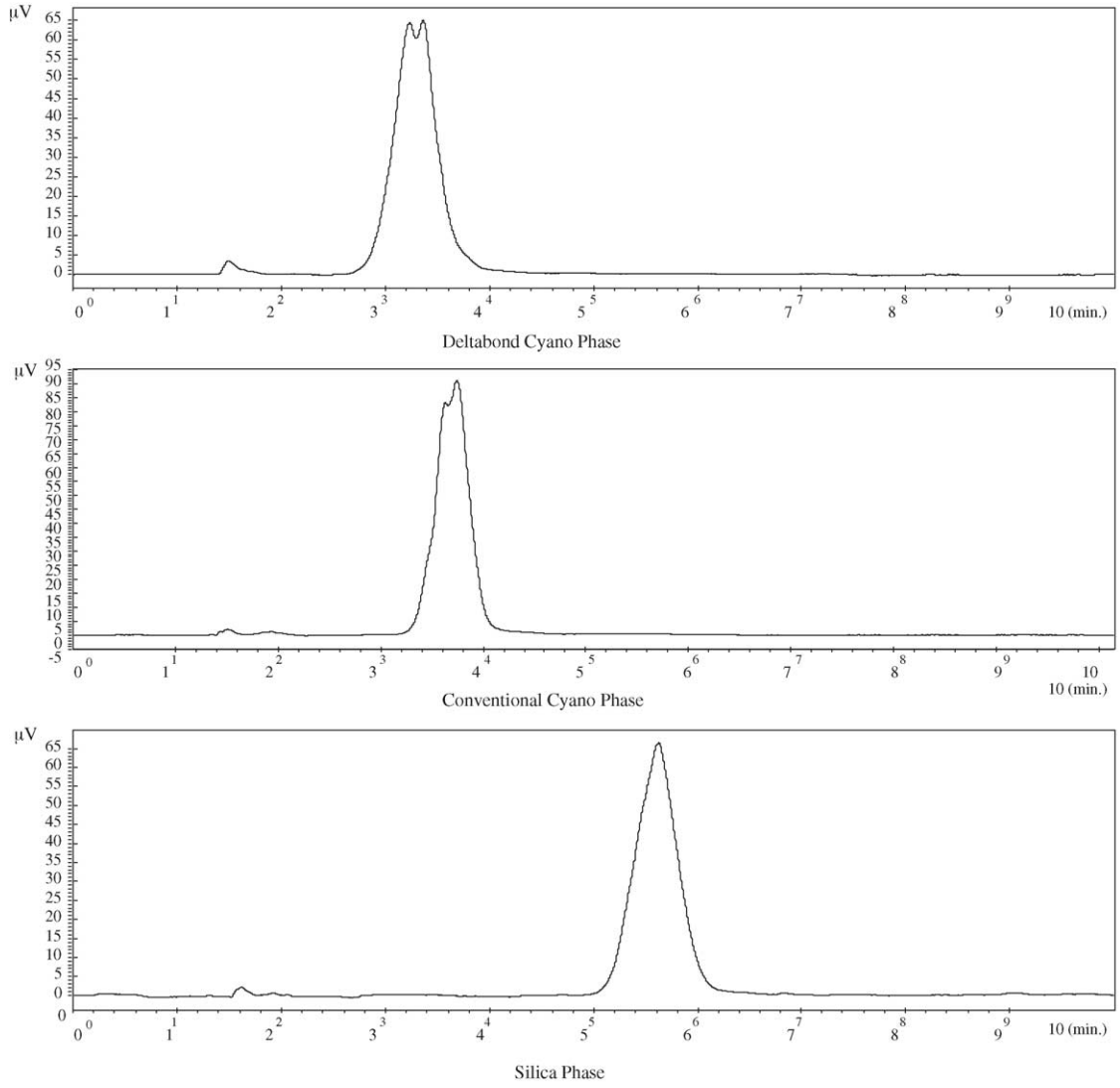

Fig. 2. SFC/UV chromatograms (λ = 230 nm) of sodium 4-dodecylbenzene sulfonate with 15% 2.5 mM NH_4OAc in methanol as mobile phase modifier modified CO_2 employing various stationary phases.

chromatographic peak characteristics we have observed are originating from various components in the sample rather than an undesirable chromatographic event (or mechanism).

Good reproducibility for three injections onto each properly conditioned stationary phase was observed. The highest relative standard deviation (n = 3) for retention time was less than 1%. The analyte eluted fastest from the most deactivated stationary phase, deltabond cyano, and was retained the longest on the most active stationary phase, silica.

Tetramethylammonium acetate (TMAA), tetrabutylammonium acetate (TBAA), ammonium chloride, and lithium acetate were chosen to augment and evaluate the effect of different salts as mobile phase additives. The same isobaric and isocratic conditions were applied as in the ammonium acetate case to provide clearer information concerning the effect of various additives and stationary phases. Fig. 6 shows the effect of different additives on the elution from the deltabond cyano column. While the positive effect of ammonium acetate was expected from previous reports, results for the other additive salts were not expected and suggested a general phenomenon that seems to be neither cation (e.g. ammonium, tetraalkylammonium, and lithium) nor anion (e.g. acetate and chloride) specific. A similar effect on elution of the sulfonate from the conventional cyanopropyl and silica columns with each additive was observed, Figs. 7 and 8. With the exception of TMAA on the silica column, the analyte was successfully and isocratically eluted within 10 min in all situations. Interestingly, TMAA provided the fastest elution on the Deltabond stationary phase among the five additives, but the longest retention on the silica phase. Evidence for split peaks was observed in some instances as was the case with ammonium acetate. The deltabond cyano phase and TBAA showed the best resolution of the target analyte and its congeners under isocratic conditions.

The fact that bare silica yielded analogous results to the two bonded phases suggests some alteration of the stationary

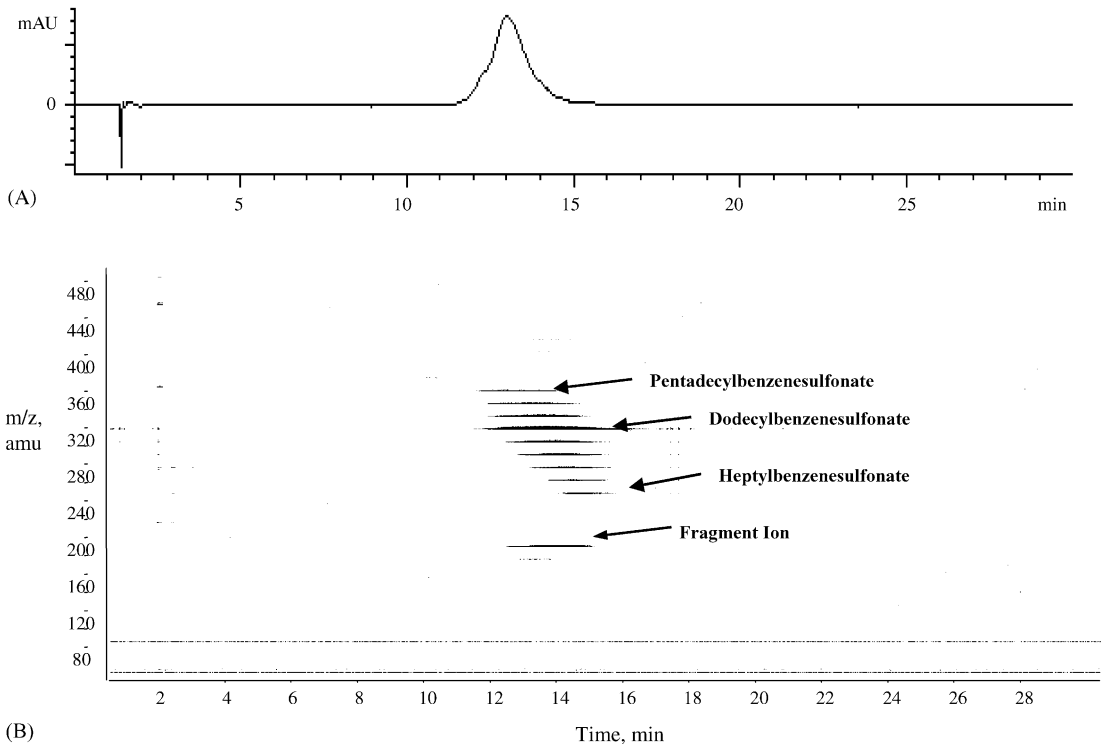

Fig. 3. SFC/UV (230 nm) trace (A) and SFC/MS contour plot (B) for the elution of sodium 4-dodecylbenzene sulfonate on a silica column. Additive concentration in methanol was 2.5 mM. See Section 2 for other chromatographic conditions.

phase by the additive is strategically involved. Table 1 shows the average retention time and peak area of each analyte for each additive on the three stationary phases with percent relative standard deviation (RSD) in parenthesis. Good reproducibility was achieved since the highest RSD for retention time was 2.35%. Although not shown, reproducibility with tetramethylammonium acetate was equally good. From the highly deactivated deltabond cyano phase to the highly active silica phase, the sulfonate was retained longer on the more active phase with the same additive present. This is probably

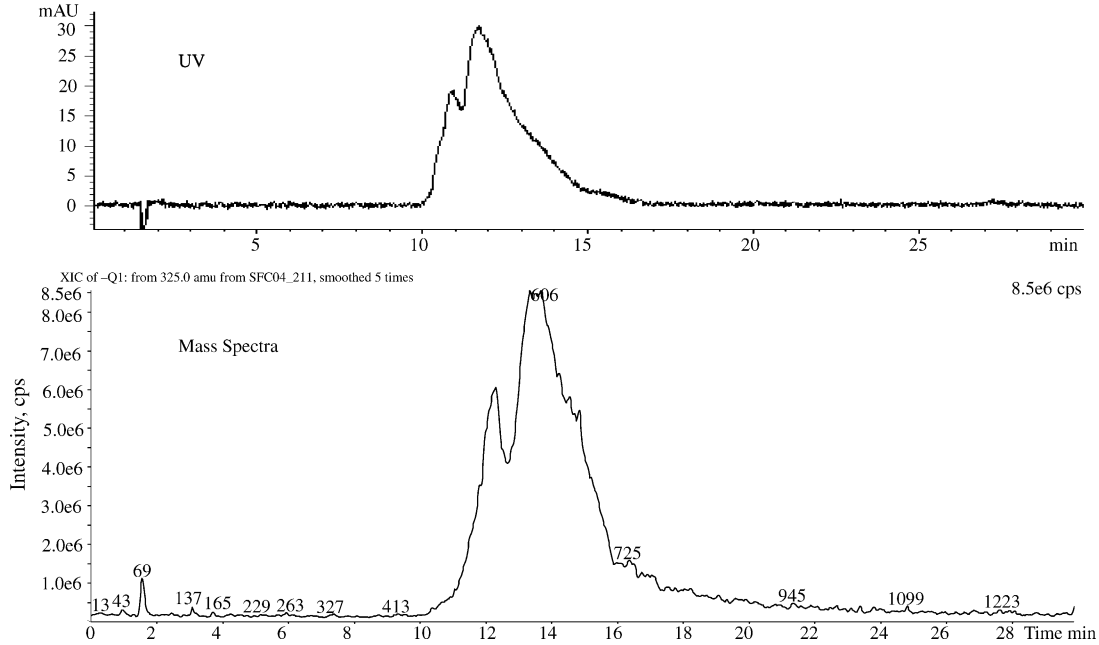

Fig. 4. SFC/UV trace (230 nm) and mass chromatogram of *m/z* 325 $[M - H]^-$ ion for the elution of sodium 4-dodecylbenzene sulfonate on deltabond cyano column. Additive concentration in methanol was 2.5 mM. See Section 2 for other chromatographic conditions.

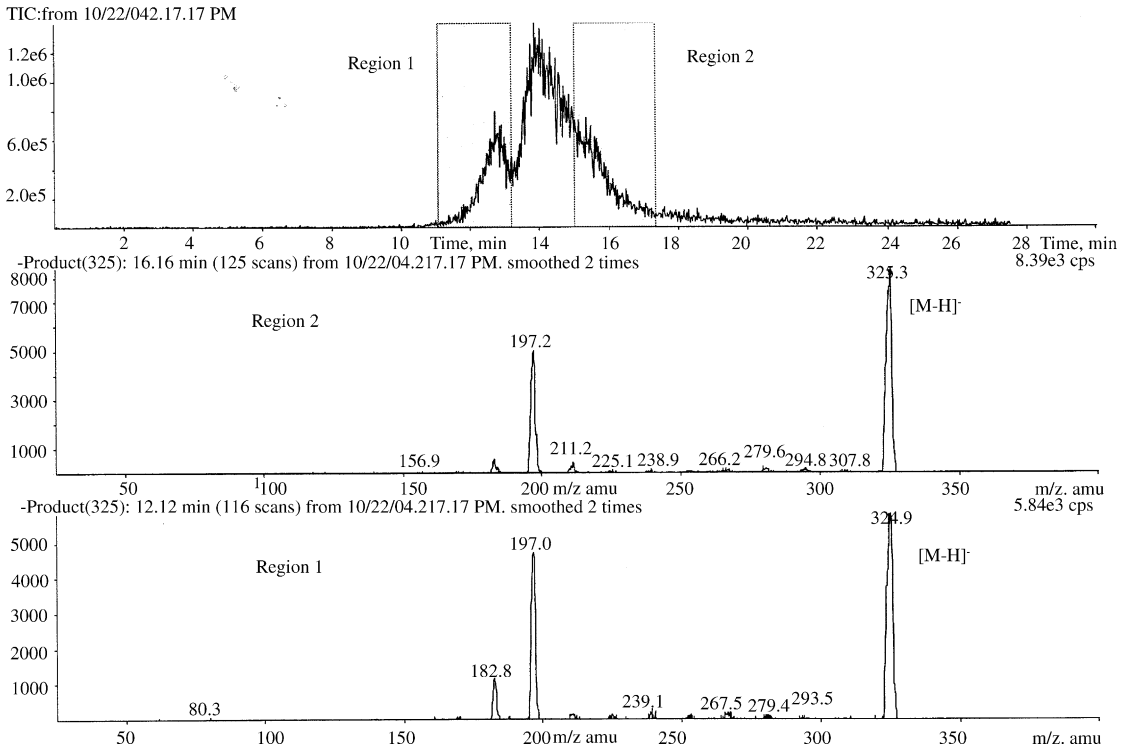

Fig. 5. MS/MS reconstructed-total-ion-current chromatogram and product ion spectra of different peak components. Analyte is sodium 4-dodecylbenzene sulfonate. Additive concentration in methanol was 2.5 mM. See Section 2 for other chromatographic conditions.

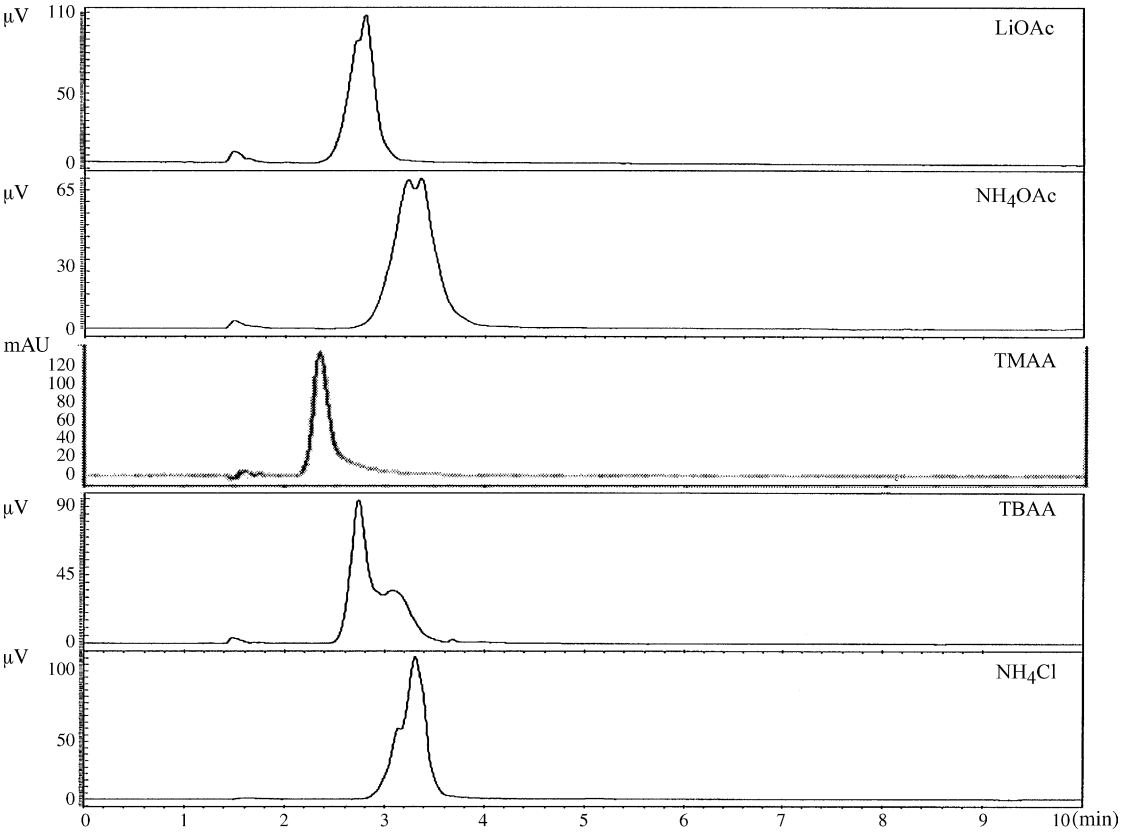

Fig. 6. Effect of different mobile phase additives for the elution of sodium 4-dodecylbenzene sulfonate with deltabond cyano column. Additive concentration in methanol: 2.5 mM. See Section 2 for other chromatographic conditions. (The chromatogram with TMAA was conducted with different instrumentations, which each used unique software. Thus the *y*-axis for TMAA was different from the other chromatograms.).

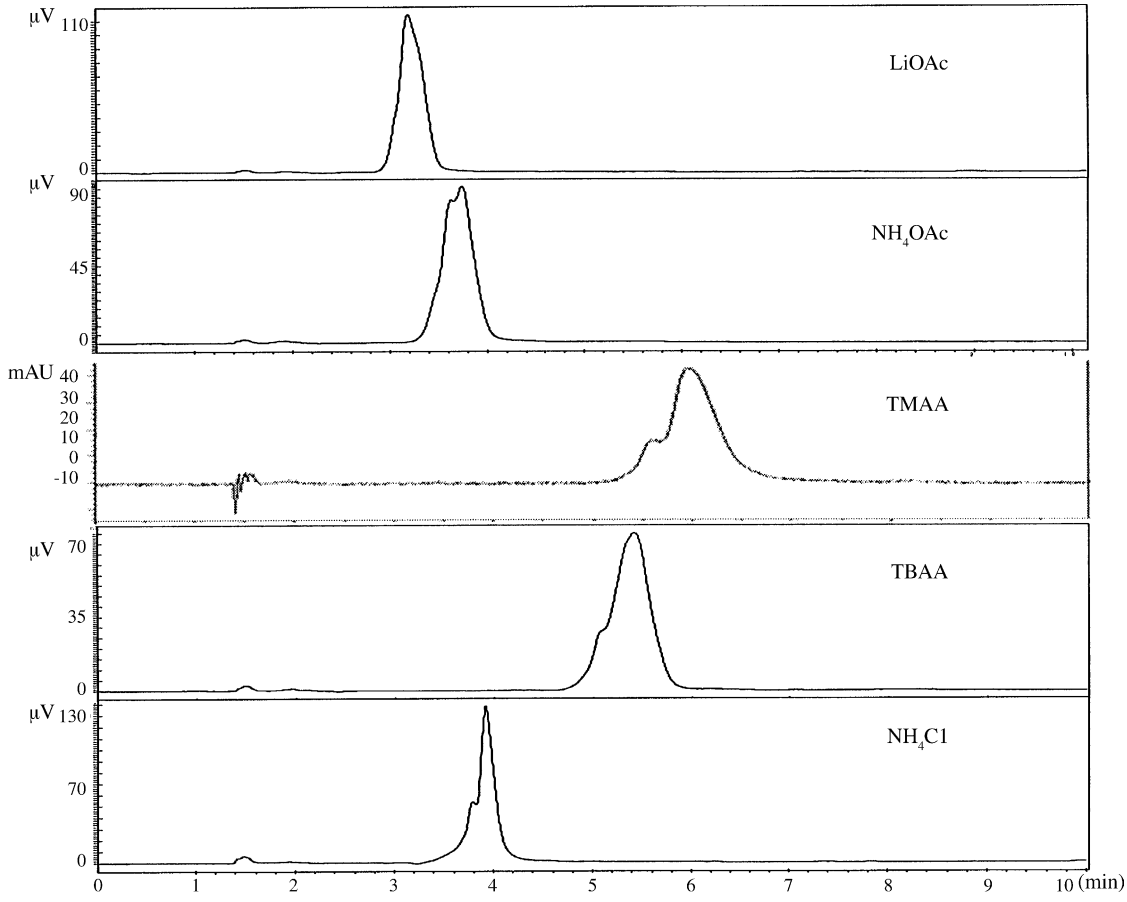

Fig. 7. Effect of different mobile phase additives for the elution of sodium 4-dodecylbenzene sulfonate with conventional cyano column. Additive concentration in methanol: 2.5 mM. See Section 2 for other chromatographic conditions. (The chromatogram with TMAA was conducted with different instrumentations, which each used unique software. Thus the *y*-axis for TMAA was different from the other chromatograms.).

due to interaction between the negatively charged sulfonate ion and the partial positive proton charge of residual, active silanol sites on the solid support of the stationary phase.

We also studied the effect of column outlet pressure on the elution of sodium 4-dodecylbenzene sulfonate with the three stationary phases and five additives. In each case, the analyte eluted slightly earlier at higher pressure than it did at lower pressure. We believe this may be due to the greater solvating power of the mobile phase at higher pressure.

In Pinkston's previous work [18], 1.1 mM ammonium acetate was dissolved in the modifier in order to elute highly polar compounds. We therefore decided to use ammonium acetate to investigate any additive concentration effect with the Deltabond column. Sodium 4-dodecylbenzene sulfonate did not elute with 0.01 mM or with 0.1 mM NH_4OAc in 25 min. The analyte, however, started to elute with methanol modifier containing 0.25 mM NH_4OAc as a very broad peak at about 11 min. With increased concentration of additive in methanol, the analyte eluted faster and with a sharper peak shape. At 2.5 mM, the analyte eluted at about 3 min compared to 11 min with 0.25 mM. We thought that it would be interesting to do the same concentration study with bare silica. The analyte again did not elute with mobile phase modifier containing 0.1 mM NH_4OAc, but started to elute with

Table 1
Retention time/peak area reproducibility data versus stationary phase and additive

Stationary phase	LiOAc		NH_4OAc		TBAA		NH_4Cl	
	RT[a]	PA[b]	RT	PA	RT	PA	RT	PA
Deltabond cyano	2.81 (0.00)[c]	32.0 (1.11)	3.36 (0.21)	31.4 (1.80)	2.74 (0.26)	32.9 (0.64)	3.32 (0.21)	33.5 (0.84)
Conventional cyano	3.16 (0.22)	32.8 (1.08)	3.73 (0.57)	34.3 (0.62)	5.41 (0.13)	34.9 (0.81)	3.93 (0.18)	31.5 (1.12)
Bare silica	5.09 (1.12)	31.5 (1.12)	5.60 (0.88)	32.1 (0.66)	7.01 (0.91)	32.2 (3.07)	4.21 (2.35)	31.2 (1.14)

2.5 mM in 15% methanol modified CO_2.
[a] RT = retention time (min).
[b] PA = peak area (μV min).
[c] %RSD (n = 3).

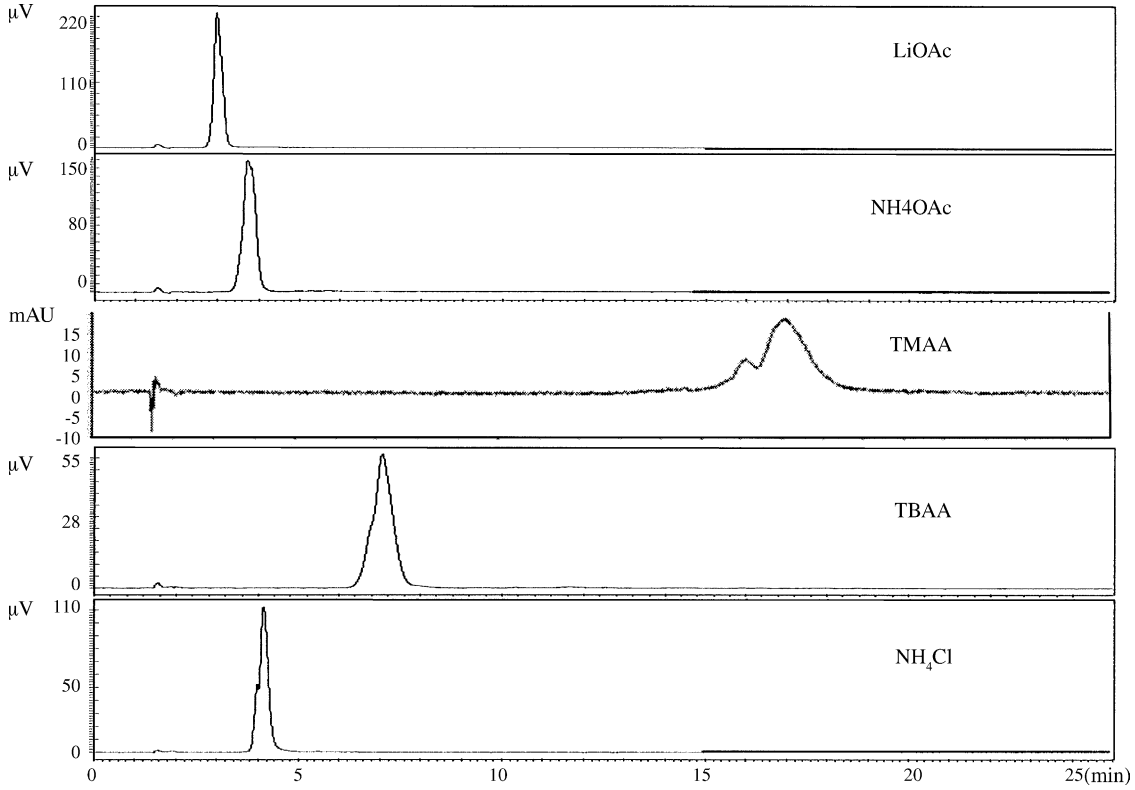

Fig. 8. Effect of different mobile phase additives for the elution of sodium 4-dodecylbenzene sulfonate with silica column. Additive concentration in methanol: 2.5 mM. See Section 2 for other chromatographic conditions. (The chromatogram with TMAA was conducted with different instrumentations, which each used unique software. Thus the *y*-axis for TMAA was different from the other chromatograms.).

0.25 mM NH_4OAc. Interestingly, we found that the sulfonate was retained more strongly on the silica column when the concentration of NH_4OAc in methanol was increased, which was the inverse of the trend we observed with the deltabond cyano phase. These results suggested that different elution mechanisms might dominate with the deltabond cyano and the silica phases.

When ionic salts are introduced into the primary modifier which is then added to the nonpolar CO_2, it is very important that the salts remain dissolved in the resulting ternary mobile phase. Among the five additives we studied, ammonium chloride had the worst solubility in methanol. When we tried, for example, to introduce methanol containing 10.0 mM NH_4Cl into the CO_2 mobile phase, a significant increase in inlet pressure was observed, which suggested the precipitation of the salt in column.

The effect of salt additives on the elution of two much purer congeners of sodium 4-dodecylbenzene sulfonate (e.g. sodium 4-octylbenzene sulfonate (OSNa) and sodium *p*-toluene sulfonate (TSNa) was studied with the silica phase. The less complex sulfonates either did not elute (OSNa) or eluted with poor peak shape (TSNa) when pure methanol (15%) was used as the CO_2 modifier, but both compounds eluted with good peak shape when ammonium salts (2.5 mM) were added to the methanol. Each sulfonate sodium salt eluted readily from the silica phase with either ammonium acetate, TMAA, or TBAA as the mobile phase additive. The trend was very similar to the findings obtained with sodium 4-dodecylbenzene sulfonate. TMAA provided the longest retention time among the three ammonium salts; whereas both sulfonates eluted fastest with ammonium acetate. Since these two sodium sulfonates were more pure than sodium 4-dodecylsulfonate, as might be expected the former two components yielded more narrow chromatographic peaks. The results for TSNa are illustrated in Fig. 9, for example.

The elution mechanisms envisioned in this study involve (1) modification of the stationary phase by the ionic additive and (2) ion-pair formation between additive and analyte. On the silica surface modification of the stationary phase may actually convert the silica to an ion-exchange phase. This observation is prompted by the fact that when higher concentrations of ammonium acetate were introduced (e.g. more sites were modified by ammonium cations), the sulfonate was retained longer. On the other hand, ion-pairing formation may be the dominating elution mechanism on the deltabond cyano phase since there should be less silanol sites on the particle surface. In this case, higher concentrations of ammonium acetate should result in more ion-pairing between ammonium cation and sulfonate anions. Our results with the bonded phase indicated that the analyte eluted faster at a higher concentration of additive. This bimodal behaviour is most dramatically seen with the results afforded by tetramethylammonium acetate.

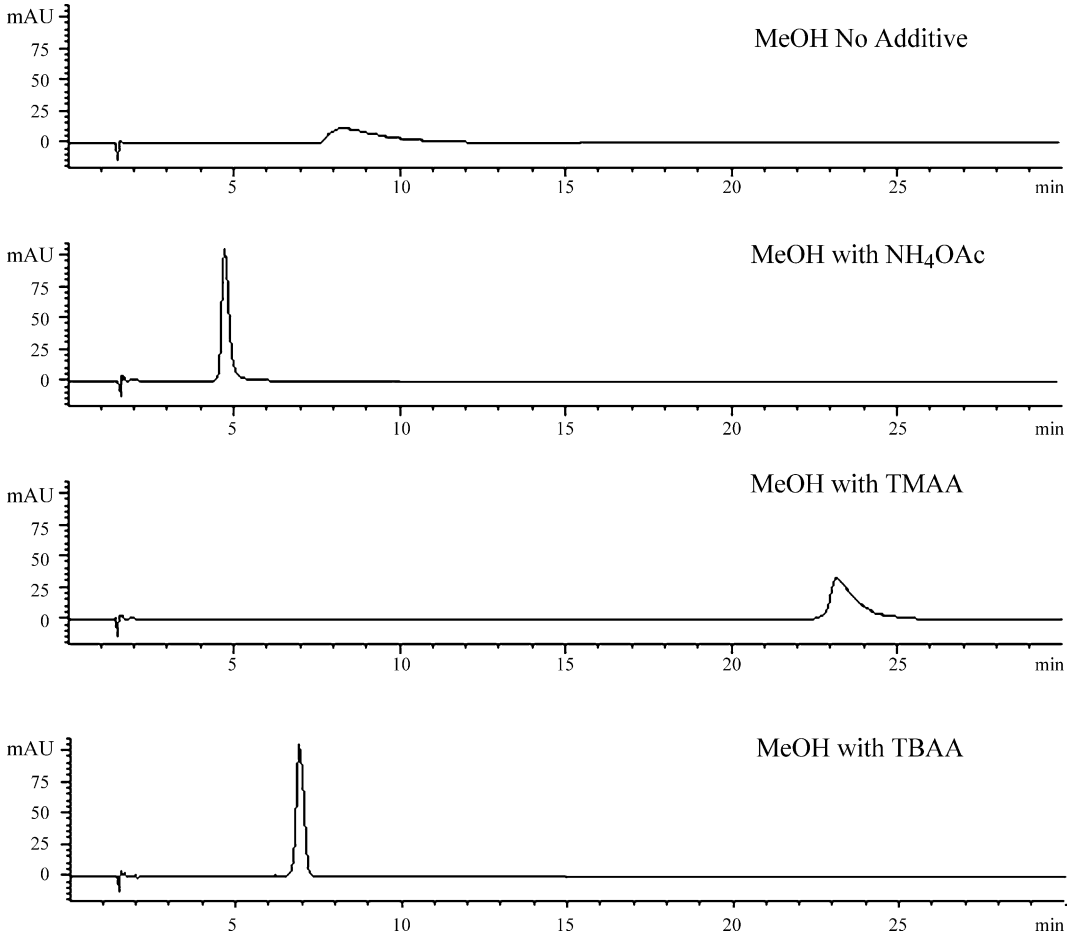

Fig. 9. Effect of ammonium salts as mobile phase additives on the elution of sodium *p*-toluene sulfonate on silica column. Additive concentration in methanol: 2.5 mM. See Section 2 for other chromatographic conditions.

4. Conclusions

In future work, we plan to use NMR and other spectroscopic methods to study the interaction between additives and the stationary phases. We will also compare the various salt additives using computational modelling methods. These methods, in combination with the data presented here, may help shed more light on the retention and elution mechanisms which dominate the CO_2/modifier/salt additive/silica stationary phase system.

The elution mechanisms envisioned in this study involve modification of the stationary phase by the ionic additive and/or ion-pair formation between additive and analyte. The exact elution mechanism for this study remains uncertain at this time. Nevertheless, the data reported in this work are noteworthy: the ionic analytes were eluted with a CO_2-based mobile phase from a highly active packed column stationary phase. Up to now, this achievement under these conditions would have been thought to be highly unlikely. The exact role of the additive appears critical since each of the ionic analytes was irreversibly retained on each of the same stationary phases with only methanol as the modifier.

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