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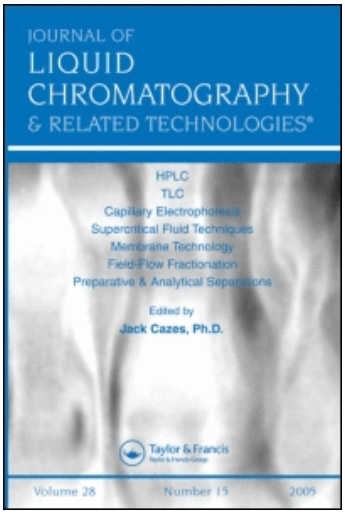

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Selectivity in Micellar Liquid Chromatography: Surfactant Bonded Phase Interactions. II. C-8 and Cyanopropyl

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SELECTIVITY IN MICELLAR LIQUID CHROMATOGRAPHY: SURFACTANT BONDED PHASE INTERACTIONS. II. C-8 AND CYANOPROPYL

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ABSTRACT

Micellar liquid chromatography and solid state ^{13}C NMR spectroscopy have been used to study the interactions of three ionic surfactants with C_8 and cyanopropyl bonded phase columns. The three surfactants, sodium dodecylsulfate (SDS), cetyltrimethyl ammonium bromide (CTAB), and dodecyltrimethylammonium bromide (DTAB), are commonly used in micellar RPLC. Surfactant adsorption is found to produce distinct changes in the selectivity of the stationary phase. Specifically, the differing nature of the surfactant-bonded phase association is largely responsible for the observed differences in selectivity between SDS, CTAB, and DTAB micellar RPLC. For SDS, the association leads to the formation of an anionic hydrophilic surface layer on C_8 (as well as on C_{18}) which would

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explain the superior resolution achieved by SDS for hydrophilic compounds. For CTAB, small surfactant aggregates form within the C_8 stationary phase, which would explain the differences in the observed selectivity of CTAB mediated separations on C_{18} and C_8 alkyl bonded phases. The observed differences in the selectivity of DTAB and CTAB modified C_8 alkyl bonded phase columns towards hydrophilic aromatic compounds are probably due to the differing nature of the CTAB and DTAB C_8 bonded phase association, which suggests that hydrocarbon chain length is an important factor influencing the adsorptive behavior of these amphiphiles on hydrophilic silica surfaces. The unusual behavior of cyanopropyl bonded phase columns in SDS or CTAB micellar RPLC can be attributed to strong interactions between the polar head group of the surfactant and the cyano group of the polar bonded phase. Chemical models depicting the structure of the surfactant coated C_8 and cyanopropyl stationary phase are proposed from the NMR data, and these models are in good agreement with retention data obtained for these micellar RPLC systems.

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INTRODUCTION

In the preceding paper,[1] it was reported that differences in selectivity between SDS, CTAB, and DTAB mediated micellar reversed phase liquid chromatography (RPLC) with C_{18} alkyl bonded phases can be attributed to the differing nature of SDS-, CTAB-, and DTAB-bonded phase association. For SDS, the hydrophobic alkyl tail of the surfactant appears to associate with the C_{18} phase, with the polar head group projecting away from the bonded alkyl phase surface. Incorporation of SDS into the C_{18} alkyl bonded phase in the manner described would lead to the formation of a hydrophilic layer which would explain the superior resolution achieved by SDS for hydrophilic compounds in micellar RPLC. For CTAB or DTAB, the nitrogen head group appears to orient closer to the silica surface due to hydrophobic interactions between the N-methyl groups and the C_{18} alkyl bonded phase. Evidently, CTAB and DTAB surfactant monomers are incorporated partially or wholly into the C_{18} bonded phase, giving rise to a modified bulk phase that is significantly denser. These results suggest that an understanding of surfactant-bonded phase interactions is crucial for developing selective separations in micellar liquid chromatography.

In this paper, the issue of selectivity in micellar liquid chromatography (MLC) as it relates to surfactant-bonded phase interactions is re-examined. MLC and solid state ^{13}C NMR spectroscopy are used to study the interactions of three ionic surfactants with C_8 and cyanopropyl bonded phase columns. The three surfactants, sodium dodecylsulfate (SDS), cetyltrimethyl ammonium bromide (CTAB), and dodecyltrimethylammonium bromide (DTAB), are commonly used in micellar RPLC. Surfactant adsorption is found to produce distinct changes in the selectivity of the stationary phase. Specifically, the differing nature of the surfactant-bonded phase association is largely responsible for the observed differences in selectivity between SDS, CTAB, and DTAB micellar RPLC. For SDS, the association leads to the formation of an anionic hydrophilic surface layer on C_8 (as well as on C_{18}) which would explain the superior resolution achieved by SDS for hydrophilic compounds. For CTAB, small surfactant aggregates form within the C_8 stationary phase, which would explain the differences in the observed selectivity of CTAB mediated separations on C_{18} and C_8 alkyl bonded phases. The observed differences in the selectivity of DTAB and CTAB modified C_8 alkyl bonded phase columns towards hydrophilic aromatic compounds are probably due to the differing nature of the CTAB and DTAB C_8 bonded phase association, which suggests that hydrocarbon chain length is an important factor influencing the adsorptive behavior of these amphiphiles on hydrophilic silica surfaces. The unusual behavior of cyanopropyl bonded phase columns in SDS or CTAB micellar RPLC can be attributed to strong interactions between the polar head group of the surfactant and the cyano group of the polar bonded phase. Chemical models depicting the structure of the surfactant coated C_8 and cyanopropyl stationary phase are proposed from the NMR data, and these models are in good agreement with retention data obtained for these micellar RPLC systems.

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EXPERIMENTAL

Chemical

The six vanillin compounds (see Figure 1) which constituted the hydrophilic test mixture used to characterize the surfactant coated stationary phases were obtained from Aldrich and were used as received. Stock solutions of the various test solutes were prepared in methanol and then diluted to the appropriate working concentration (550 μg/mL) using 50% methanol in water. The surfactants, SDS, CTAB, and DTAB, were obtained from BDH Chemicals (99% purity) and were purified prior to use by first dissolving them in ethanol followed by addition of charcoal to the solution. After the charcoal was separated from the mother liquor by filtration, the surfactant was recrystallized

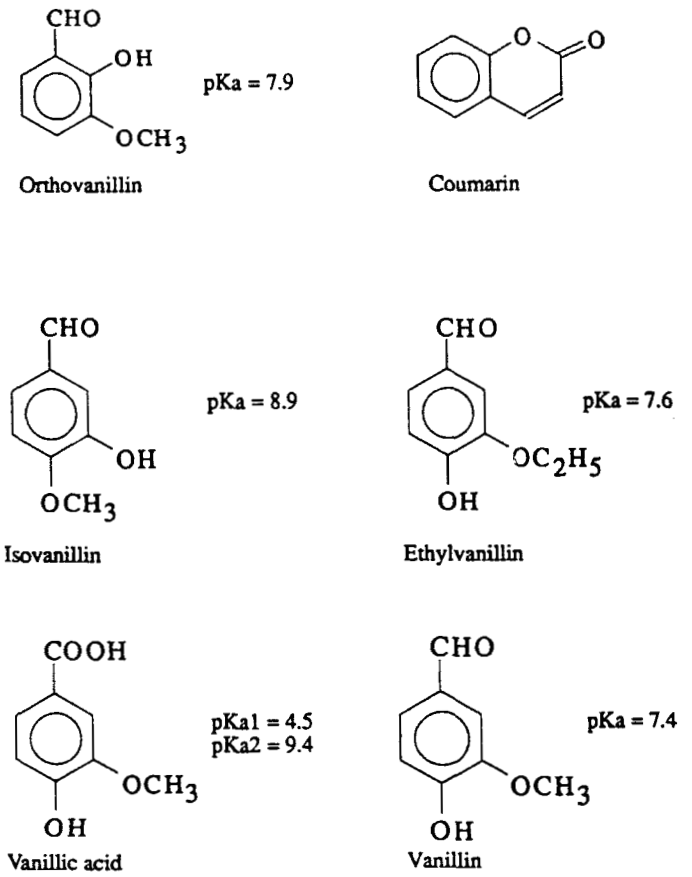

Figure 1. The vanillin compounds. The pKa values are from reference 13.

from the ethanol and dried in an oven at 65°C. Micellar solutions were prepared from the recrystallized surfactants using HPLC grade distilled water. (Methanol-water mobile phases were also prepared using HPLC grade solvents.)

All mobile phase solutions were filtered twice with a 0.45 μm Nylon membrane filter (Rainin Instruments, Woburn, MA) to remove particulate matter. Prior to use, the solutions were degassed and their pH adjusted to 3 with hydrochloric acid to prevent ionization of polar solutes in the mobile phase solutions.[2]

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High Performance Liquid Chromatographic (HPLC) Measurements

All HPLC measurements were made using either a Perkin Elmer TriDet HPLC or a Rainin 81-20 M analytical HPLC system. The analytical column was either an Apex I C-8, or an Apex I cyanopropyl (5-μm, 10cm x 4.6 mm i.d.). The columns were purchased from Jones Chromatography (Golden, CO) and were made from the same 5 μm silica support. The analytical column was water-jacketed and temperature controlled. Separate columns were used for each surfactant (as well as the methanol water mobile phase) because of strong and irreversible adsorption of ionic surfactants on the stationary phase of the C_8 and cyanopropyl bonded phase columns. The dead volume of each column which was determined by injecting different solutions such as methanol-water, or water onto the Apex I column was approximately 1.0 mL and was used for all k' calculations. The k' values determined in this study were averages of at least triplicate determinations, and deviations in individual k' values were never greater than 5%. All k' measurements were made at a flow rate of 1.0 mL/min and were measured at 25°C for SDS and DTAB and 30°C for CTAB. (Since the Kraft point of CTAB is 23°C, it was necessary to perform the CTAB studies at a higher temperature.)

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Estimation of Critical Partitioning Parameters in Micellar RPLC

Solute-stationary phase and solute-micelle binding constants were determined for the vanillin compounds using an equation developed by Cline-Love and Arunyanart[3]

$$1/k' = [M]K_2/\theta[L_s]K_1 + 1/\theta[L_s]K_1 \quad (1)$$

where [M] is the concentration of surfactant, K_2 is the solute-micelle binding constant per monomer of surfactant, θ is the chromatographic phase ratio, $[L_s]$ is the concentration of ligate on the stationary phase, and K_1 is the solute-stationary phase binding constant. A plot of 1/k' vs [M] should yield a straight line, and in fact excellent linearity was observed for all six compounds using SDS, CTAB or DTAB.

Solid State NMR Measurements

Adsorption of SDS, DTAB, and CTAB on C_8 and cyanopropyl chemically derivitized silicas was investigated using cross polarization/magic angle spinning ^{13}C NMR with high-power proton decoupling (CP/MAS ^{13}C NMR).

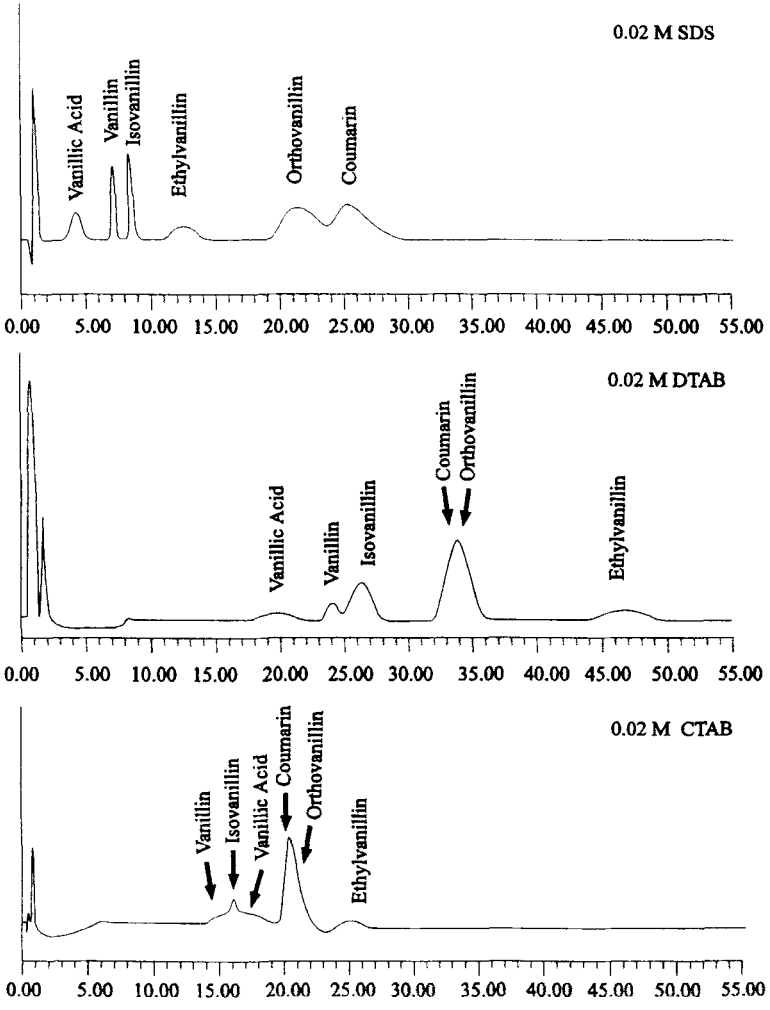

Figure 2. Separation of the vanillin test mixture on Apex I C-8 using a Perkin-Elmer TriDet HPLC with the following mobile phases: (a) 0.02 M SDS; (b) 0.02 M DTAB; and (c) 0.02 M CTAB. Flow rate was 1.0 mL/min, and the pH of each mobile phase was 3.0.

All NMR experiments were performed at 50 MHz on a Bruker/IBM WP-200 SY Spectrometer equipped with an IBM solids control accessory and a Doty-type solid-state probe that was software controlled which permitted

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Table 1

Sodium Dodecylsulfate*

Compound	**$\Theta[L_s]K_1$	K_2
Vanillic Acid	4.4 ± 0.4	21.2 ± 2.9
Vanillin	12.5 ± 1.6	41.1 ± 8.1
Isovanillin	14.2 ± 2.0	37.9 ± 7.8
Ethylvanillin	24.1 ± 0.6	58.9 ± 1.6
Orthovanillin	40.5 ± 1.6	66.6 ± 2.9
Coumarin	49.8 ± 1.2	86.0 ± 2.4

* Compounds are listed in their order of elution from Apex I C-18. Concentraiton of SDS in the mobile phase varied from 0.01 to 0.14M.
**Uncertainties in $\Theta[L_s]K_1$ and K_2 were determined from the statistical parameters of the least squares fitting and from propagation of error.

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automatic variation of all pulse parameters. The magic angle spinning probe used was a double-tuned, single-coil design with a bullet type rotor which held a sample volume of 0.75 cm^3. Two different pulse sequences[1] were used in these NMR experiments. However, each pulse sequence was performed with a constant 3-s recycle time. The ^{13}C spectra collected were externally referenced to para-di-t-butyl benzene. All chemical shift values were expressed as parts per million downfield from tetramethylsilane. The ^{13}C data were collected in 2 Kbytes of memory, exponentially multiplied prior to Fourier transformation, and zero-filled to 8 kilobytes.

Sample Preparation

To prepare a sample for solid-state NMR, 0.5 g of 5μm C_8 or cyanopropyl reversed phase material was equilibrated with 10 mL of 0.05 M aqueous CTAB, DTAB, or SDS solution. The equilibration period for the stationary phase material and surfactant was at least 24 h. During equilibration, a wrist action shaker was periodically used to agitate the samples. After equilibration, each sample was vacuum filtered onto a 0.45 μm Nylon 66 membrane filter and vacuum dried at 35°C for 2 days prior to being packed into the rotor of the solid-state probe.

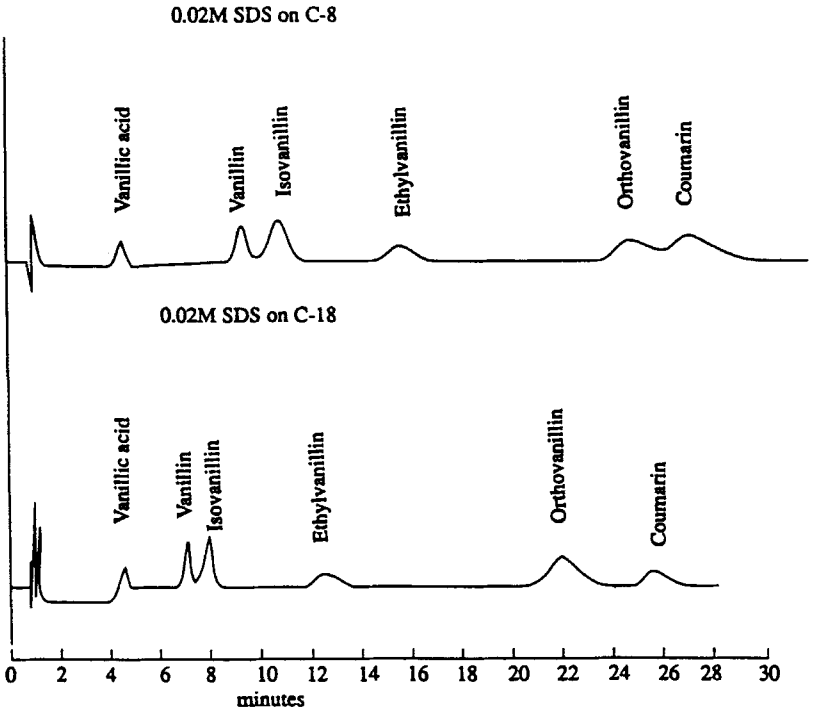

Figure 3. Chromatograms of the test mixture on a C-18 and C-8 Apex I column with a 0.02 M SDS mobile phase. Flow rate was 1.0 mL/min, and the pH of the mobile phase was 3.0.

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RESULTS & DISCUSSION

C_8

Figure 2 shows the separation of the vanillin test mixture with the same three mobile phases used in the Apex I C-18 study (see preceding paper). Several things are apparent from an examination of this data. First, the test mixture is completely separated by the 0.02 M SDS micellar mobile phase. As with C_{18}, elution order clocks K_1 suggesting that solute-stationary phase interactions again play a decisive role in the SDS micellar RPLC separation process (see Table 1). Because of the similarity in the micellar RPLC data (see Figure 3), we must conclude that SDS probably forms a similar association with C_8 and C_{18} alkyl bonded phases.

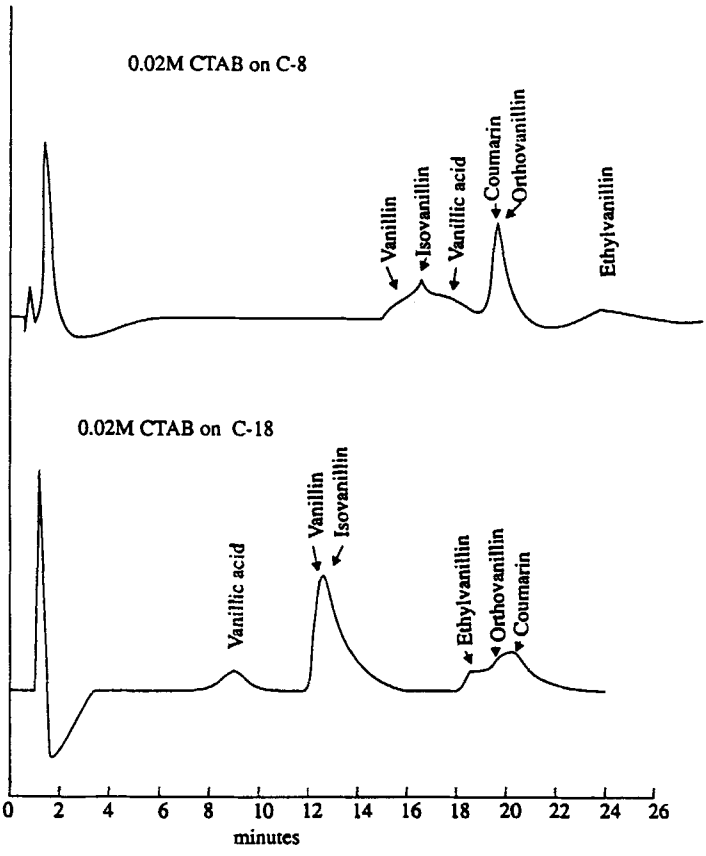

Figure 4. Chromatograms of the test mixture on a C-18 and C-8 Apex I column with 0.02 M CTAB mobile phase. Flow rate was 1.0 mL/min, and the pH of the mobile phase was 3.0.

Second, there is a degradation in the separation of the vanillin test mixture and a change in the elution order when an Apex I C-8 column is used, in lieu of an Apex I C-18 column, with the 0.02 M CTAB mobile phase (see Figure 4). The retention time of the vanillin compounds is also longer on C_8 then on C_{18}. On the basis of these effects, longer retention times, reversals in elution order, and a decrease in resolution, we must conclude that differences in the observed selectivity of CTAB mediated separations on C_{18} and C_8 alkyl bonded phases are due to the differing nature of the CTAB C_{18} and C_8 alkyl bonded phase association. In all likelihood, small surfactant aggregates form

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Table 2

Cetyltrimethylammonium Bromide*

Compound**	$\Theta[L_s]K_1$***	K_2
Vanillin	20.4 ± 0.8	46.4 ± 2.3
Isovanillin	21.2 ± 3.2	41.3 ± 7.5
Vanillic Acid	37.9 ± 7.2	126 ± 24
Coumarin	25.1 ± 0.6	44.1 ± 1.3
Orthovanillin	27.3 ± 2.2	36.5 ± 3.6
Ethylvanillin	38.6 ± 1.5	69.1 ± 2.9

* Compounds are listed in their order of elution from Apex I C-8. Concentration of CTAB in the mobile phase varied from 0.006 to 0.15M.
**The correlation between $\Theta[L_s]K_1$ and elution order for the vanillin compounds is greater on C-8 than on C-18. (If vanillic acid is removed from the table, the correlation between $\Theta[L_s]K_1$ and elution order is very high.)
***Uncertainties in $\Theta[L_s]$ determined from the parameters of the least squares fitting and from propagation of error.

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within the C_8 stationary phase and are responsible for the longer retention times and reversals in elution order. These aggregates are probably similar in nature to surfactant clusters that form in the presence of water soluble polymers, e.g., polyethylene-oxide in aqueous media.[4]

It has been shown that CTAB aggregates exhibit strong selectivity toward phenols and other aromatic compounds containing acidic functional groups. This selectivity has been attributed to a secondary chemical equilibrium process involving a transfer of a proton from an ionogenic solute to water molecules in the Stern region of the surfactant aggregate.[5] A decrease of 0.5 to 3.0 in the pKa value of a dissociable amphiphile can occur upon incorporation of the guest molecule into a cationic micelle. Clearly, the aforementioned acid-base effect can explain the strong interaction of vanillic acid with the CTAB modified C_8 stationary phase (see Table 2). The existence of surfactant aggregates within the stationary phase would also explain the reversals in elution order, the loss of resolution, and the longer retention times (or greater affinity of the vanillin compounds for the surfactant modified C_8 stationary phase). Since elution order clocks K_1 (see Table 2) which was not the case

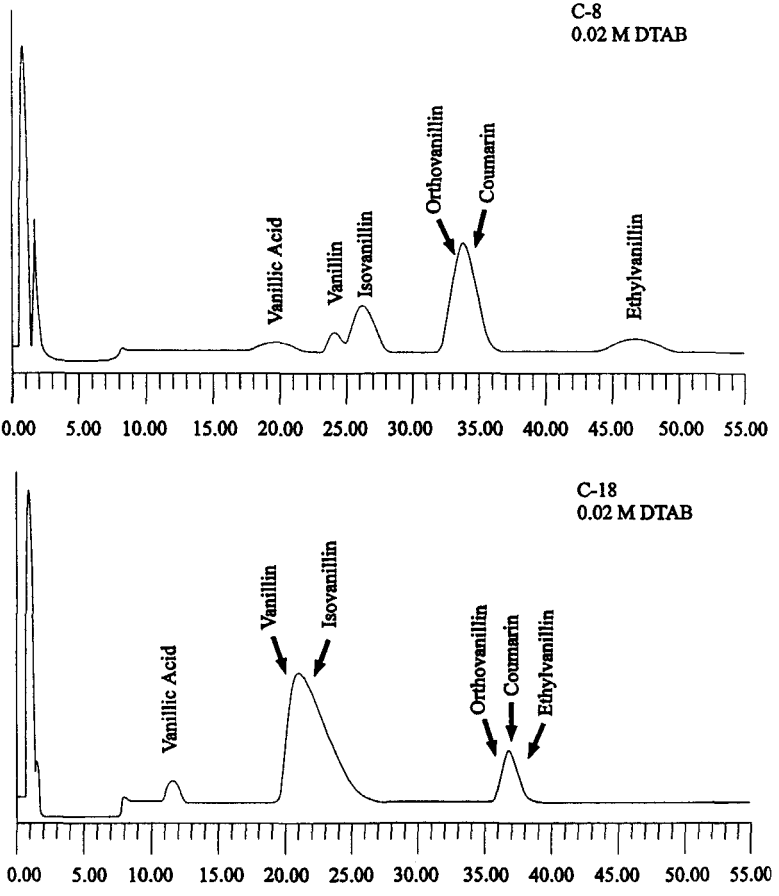

Figure 5. Chromatograms of the test mixture on a C-18 and C-8 Apex I column with a 0.02 M DTAB mobile phase. Flow rate was 1.0 mL/min, and the pH of the mobile phase was 3.0.

when a C_{18} column was used (see Table 4 of preceding paper), we must conclude that solute-stationary phase interactions play a more important role in the separation of the polar test mixture on C_8 than on C_{18} when CTAB micellar mobile phases are utilized.

Third, the separation of the vanillin test mixture is better when an Apex I C-8 column is used, in lieu of an Apex I C-18 column, with the 0.02 M DTAB micellar mobile phase (see Figure 5) which is the opposite to what is observed

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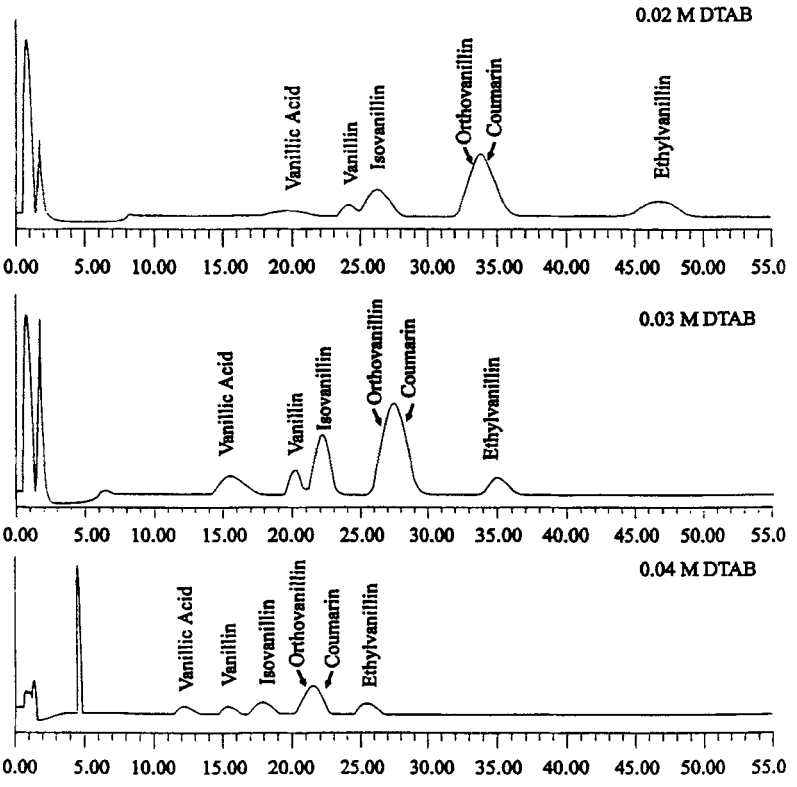

Figure 6. Separation of the vanillin test mixture on Apex I C-8 with DTAB micellar solutions of differing surfactant concentration. Flow rate was 1.0 mL/min, and the pH of each mobile phase was 3.0.

with CTAB (see Figure 4). As with C_{18}, the separation of the test mixture is better at higher DTAB concentrations, but the improvement in the separation of the test mixture with increasing DTAB concentration is far more dramatic with C_8 (see Figures 15 of the preceding paper and Figure 6 of this study). When a C_8 column is used, elution order clocks K_1 (see Table 3) which was not the case when a C_{18} column was used (see preceding paper). Finally, changes occur in elution order when a C_8 column is used; the retention time of most of the vanillin compounds is also longer on C_8. On the basis of these three effects, longer retention times, reversals in elution order, and improved resolution, we must conclude that differences in the observed selectivity of DTAB mediated separations on C_{18} and C_8 columns are due to the differing nature of the DTAB

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Table 3

Dodecyltrimethylammonium Bromide*

Compound	$\Theta[L_s]K_1$**	K_2
Vanillic Acid	14.9 ± 2.1	32.8 ± 4.1
Vanillin	19.1 ± 1.1	31.8 ± 1.5
Isovanillin	21.1 ± 1.6	24.1 ± 1.6
Orthovanillin	23.1 ± 2.2	26.5 ± 4.3
Coumarin	27.4 ± 3.1	30.6 ± 2.3
Ethylvanillin	40.1 ± 2.4	44.6 ± 3.5

* Compounds are listed in their order of elution from Apex I C-18. Concentration of DTAB in the mobile phase varied from 0.01 to 0.14M.
**Uncertainties in $\Theta[L_s]K_1$ and K_2 were determined from the statistical parameters of the least squares fitting and from propagation of error.

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C_{18} and C_8 alkyl bonded phase association. Furthermore, DTAB and CTAB do not form the same type of association with the C_8 alkyl bonded phase as evidenced by differences in the separation of the vanillin test mixture on C_8 with these two surfactants. Apparently, hydrocarbon chain-length is an important factor, influencing the adsorptive behavior of these amphiphiles on hydrophobic silica surfaces. (CTAB and DTAB micelles interact in much the same manner with aromatics so they cannot be the source of the observed differences in selectivity exhibited by these two surfactants towards the vanillin compounds.)

Because of differences in silanol activity between C_{18} and C_8 alkyl bonded phases, the possibility that silanol groups could be responsible for observed differences in selectivity must also be considered. If the silanol groups were responsible for the differing selectivities, then there would be marked differences in the retention behavior of the vanillin compounds on Jones Apex I C-18 and C-8 columns with a hydro-organic mobile phase. However, the vanillin compounds on C_{18} and C_8 columns exhibit similar retention behavior (see Figure 7) with a 20% methanol in water mobile phase, as well as with 30%, 40%, and 50% methanol in water solvent mixtures. Hence, it is the differing nature of the CTAB and DTAB monomer C_{18} and C_8 bonded phase association that is responsible for differences in the observed selectivity.

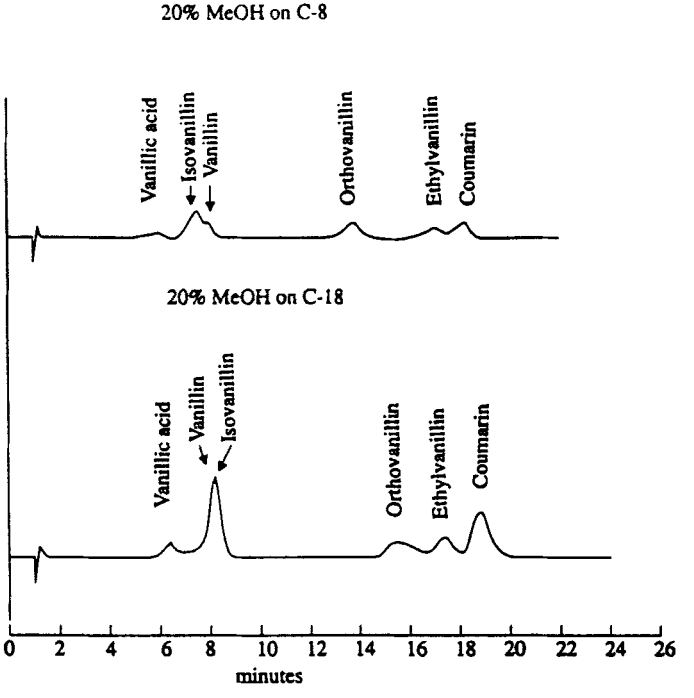

Figure 7. Chromatograms of the vanillin test mixture on a C-18 and C-8 Apex I column with a 20% methanol in water mobile phase. Flow rate was 1.0 mL/min, and the pH of the mobile phase was 3.0.

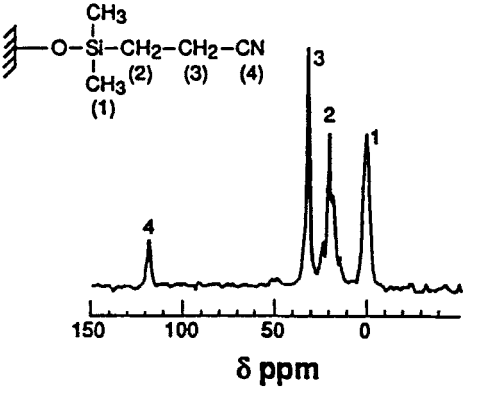

Figure 8. ^{13}C CP/MAS NMR spectrum and chemical shift assignments for the cyanopropyl bonded phase.

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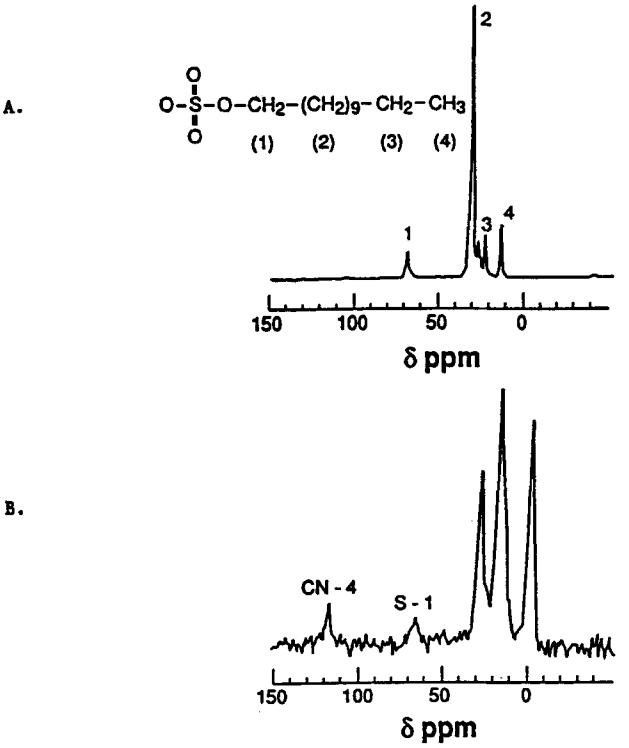

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Figure 9. ^{13}C CP/MAS NMR spectrum and chemical shift assignments for (a) SDS, and (b) SDS adsorbed on cyanopropyl. Bonded phase resonances are indicated by labels starting with CN-, while surfactant resonances are indicated by labels beginning with S (S=SDS).

Cyanopropyl

Figures 8-10 show solid state ^{13}C NMR spectra for the following materials: cyanopropyl, SDS adsorbed on cyanopropyl, and CTAB adsorbed on cyanopropyl. Also included in each figure is a structural model that shows tentative chemical shift assignments. From an examination of the NMR spectra, it is evident that the α-carbon nuclei of CTAB (65 ppm) and SDS (68 ppm) can be used as probes to study changes in molecular motion for surfactant molecules adsorbed onto or in the cyano bonded phase. Resonances associated with the other surfactant nuclei cannot be used as probes since these nuclei are obscured by resonances from the cyano bonded phase or are simply not suitable as quantitative probes of molecular motion due to their rapid rotation.

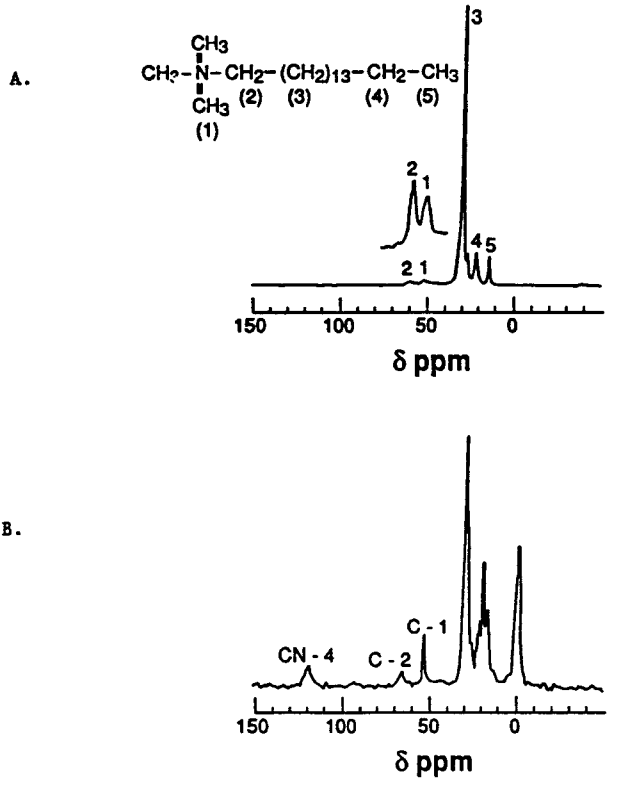

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Figure 10. ^{13}C CP/MAS NMR spectrum and chemical shift assignments for (a) CTAB, and (b) CTAB adsorbed on cyanopropyl. Bonded phase resopnances are indicated by labels starting with CN-, while surfactant resonances are indicated by labels beginning with C (C=CTAB).

Interestingly enough, the cyano group of the polar bonded phase (120 ppm) can be used as a probe to study changes in behavior of the bonded phase ligands which can occur as a result of surfactant adsorption, so direct observation of the bonded phase itself is possible.

Table 4 lists cross polarization time constants for the α-methylene carbon atom of SDS and CTAB before and after adsorption of surfactant on the bonded phase. For either CTAB or SDS, there is a significant increase in T_{CH} after

Table 4

***Relaxation Parameters of α-Carbon Nuclei in Pure and Adsorbed Surfactants**

Surfactant	T_{CH} (ms)	$T_{1\rho C}$ (ms)
CTAB	0.03 ± 0.003	14.5 ± 0.58
CTAB ON Cyanopropyl	0.25 ± 0.05	7.41 ± 1.09
SDS	0.13 ± 0.03	203.4 ± 0.42
SDS ON Cyanopropyl	0.40 ± 0.03	2.19 ± 0.31**

* Uncertainties in T_{CH} and $T_{1\rho C}$ were determined from the statistical parameters of the least squares fitting.
**Computed at short holding times.

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Table 5

Relaxation Parameters of the Cyano Carbon Nuclei Before and After Surfactant Adsorption[1]

Surfactant	T_{CH} (ms)	$T_{1\rho C}$ (ms)
CN	2.92 ± 0.00	Dispersion Pattern
CTAB ON Cyanopropyl	1.17 ± 0.20	42.3 ± 5.93
SDS ON Cyanopropyl	1.4 ± 0.31	8.4 ± 1.0[2]
		143 ± 50[3]

[1]Uncertainties in T_{CH} and $T_{1\rho C}$ were determined from statistical parameters of the least squares fitting.
[2]Short holding times. [3]Long holding times.

adsorption of surfactant onto the polar bonded phase which indicates that the polar head group of the surfactant is more mobile after adsorption than in the pure solid form. Hence, the 68 ppm and 65 ppm resonances probably represent surfactant monomer in direct contact with the polar bonded phase.

Table 5 lists T_{CH} values for the cyano carbon of the polar bonded phase before and after surfactant adsorption. The decrease in T_{CH} as a result of SDS or CTAB adsorption suggests that an increase has occurred in the polarization

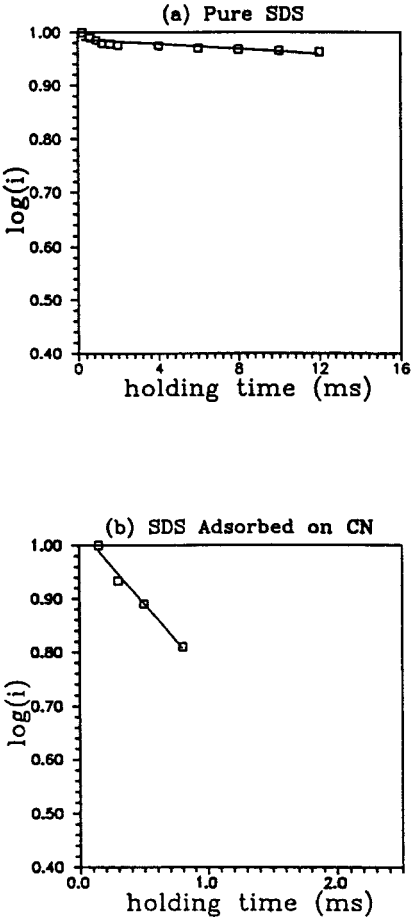

Figure 11. A plot of log intensity versus holding time for the alpha carbon of pure and adsorbed SDS.

transfer rate. Because the cyano functional group carbon atom possesses no direct bonded hydrogen atoms, the enrichment of the hydrogen environment of the cyano phase as a result of CTAB or SDS adsorption is, in all likelihood, responsible for the observed increase in the polarization transfer rate between nonbonded hydrogen atoms and the cyano carbon of the stationary phase. Nevertheless, the decrease in T_{CH} is significant because it is direct evidence for wetting of the cyanopropyl bonded phase by SDS or CTAB.

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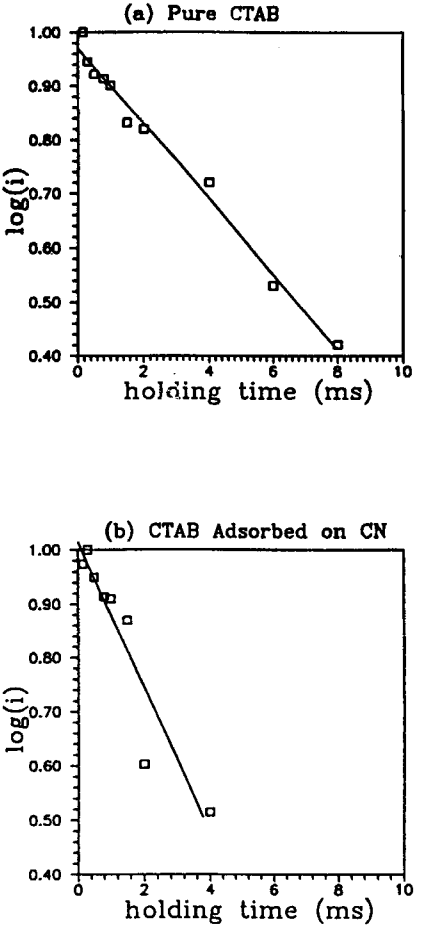

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Figure 12. A plot of log intensity versus holding time for the alpha carbon of pure and adsorbed CTAB.

If SDS or CTAB were only physisorbed on the surface, there would be no direct contact between the cyano functional group of the bonded phase and the hydrocarbon chain of the surfactant because the surfactant would be in a different phase.

Figures 11 and 12 show the results from several variable holding time experiments for CTAB and SDS. The linear decay curves indicate that the α-methylene carbon atom of both solid and adsorbed SDS and CTAB exhibit

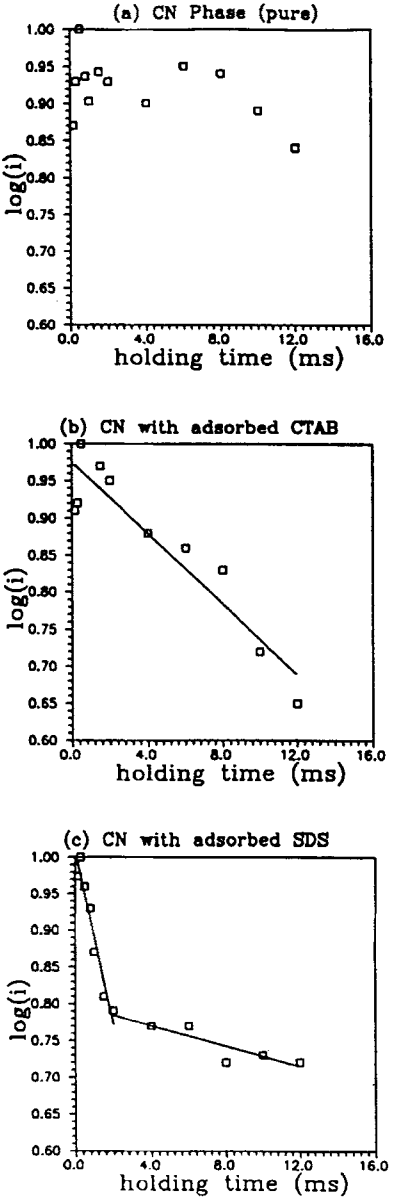

Figure 13. A plot of log intensity versus holding time for the cyano carbon of (a) pure bonded phase, (b) cyano carbon of the bonded phase with adsorbed SDS, and (c) cyano carbon of the bonded phase with adsorbed CTAB.

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homogenous relaxation behavior. (For adsorbed SDS, only data at short holding times are shown due to low S/N at holding times greater than 1 ms.) $T_{1\rho C}$ for the alpha methylene carbon atom of solid CTAB and SDS is greater than $T_{1\rho C}$ for adsorbed CTAB and SDS (see Table 4), which is surprising since the bonded phase constitutes a more liquid-like environment than crystalline surfactant. In other words, one would expect $T_{1\rho C}$ for the adsorbed surfactant to be larger than $T_{1\rho C}$ for the solid surfactant, which in fact is what was observed in our study on surfactant adsorption on C_{18} and C_8 alkyl bonded phases.[6] Since this is not the situation with cyanopropyl, the orientation of the alpha carbon nuclei of adsorbed SDS and CTAB must be different on cyanopropyl than on C_{18} or C_8. We believe this difference is due to the strong association between the head group of the surfactant and the cyano group of the polar bonded phase. In other words, the α-carbon nuclei of the adsorbed surfactant is not experiencing random motion: it is not accessing all of the orientations available to it with respect to the magnetic field because of the strong association between the cyano group of the bonded phase and the polar head group of the surfactant, which would explain the ten-fold and two-fold decrease in the value of $T_{1\rho C}$ for the alpha carbon nuclei of adsorbed SDS and CTAB.

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Figure 13 shows semilog decay curves for the cyano group carbon atom before and after incorporation of SDS and CTAB into the polar bonded phase. The dispersion pattern obtained for the decay curve of the cyano group of the pure stationary phase material can be rationalized on the basis of chemical considerations. Cyano groups are known to interact with residual silanols.[7,8] The fact that some residual silanols will and some will not interact with cyano groups and to the varying degrees they do would be expected to yield a dispersion pattern.

The linear and bilinear decay curves obtained for the cyano group carbon of CTAB- and SDS-modified cyanopropyl suggest that a decrease in the number of relaxation states available to the cyano functional group carbon atom as a result of SDS and CTAB adsorption onto the polar bonded phase has occurred. We attribute the decrease in the number of relaxation states of the cyano group carbon to the strong association between the polar head group of the surfactant and the cyano group of the polar bonded phase. The sulfate head group of SDS and the N-alkyl head group of CTAB probably interact with the cyano functionality of the polar bonded phase through some form of electrostatic interaction.

Our conclusions regarding modification of the cyanopropyl bonded phase by SDS or CTAB adsorption can explain the unusual behavior exhibited by cyanopropyl bonded phase columns in micellar RPLC. For example, the

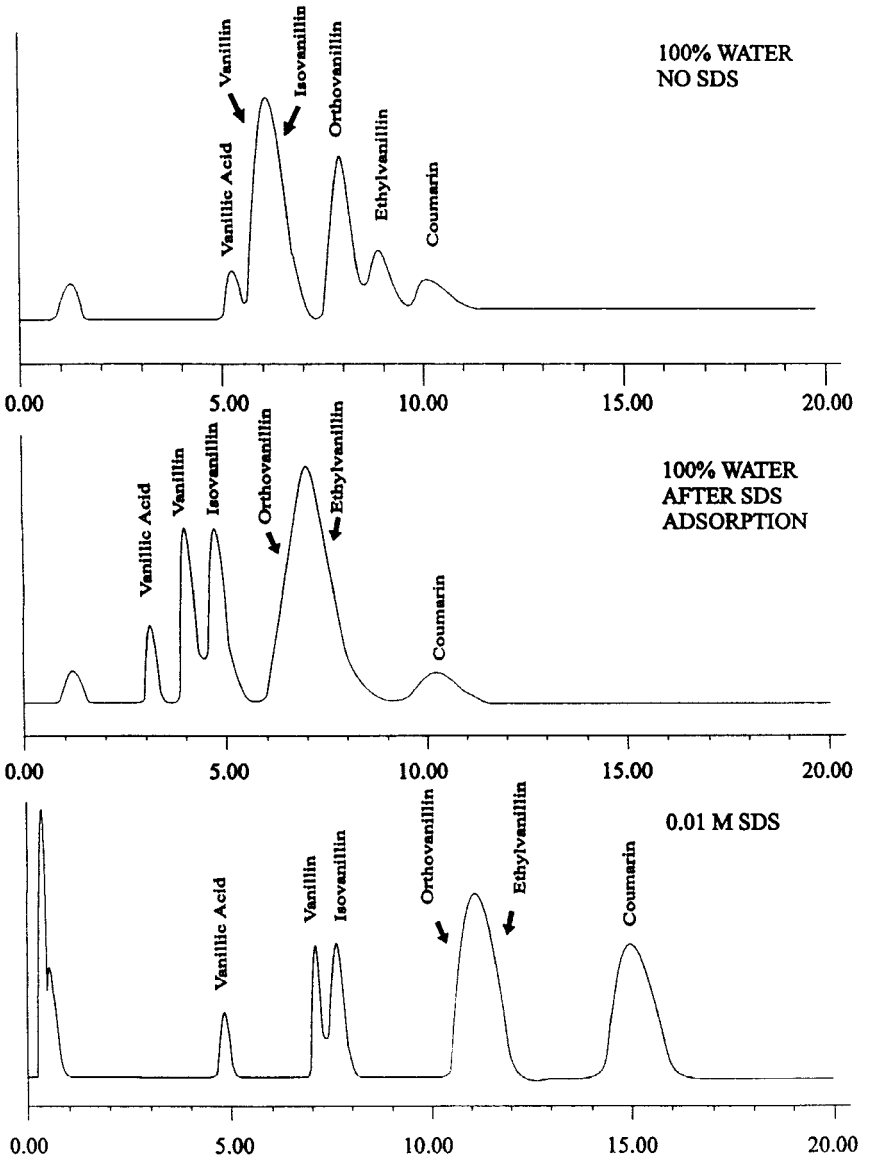

Figure 14. Chromatograms of the vanillin test mixture on a cyanopropyl column before, during, and after separations involving SDS micellar mobile phases. The pH of each mobile phase was 3.0 and the flow rate was 1.0 mL/min.

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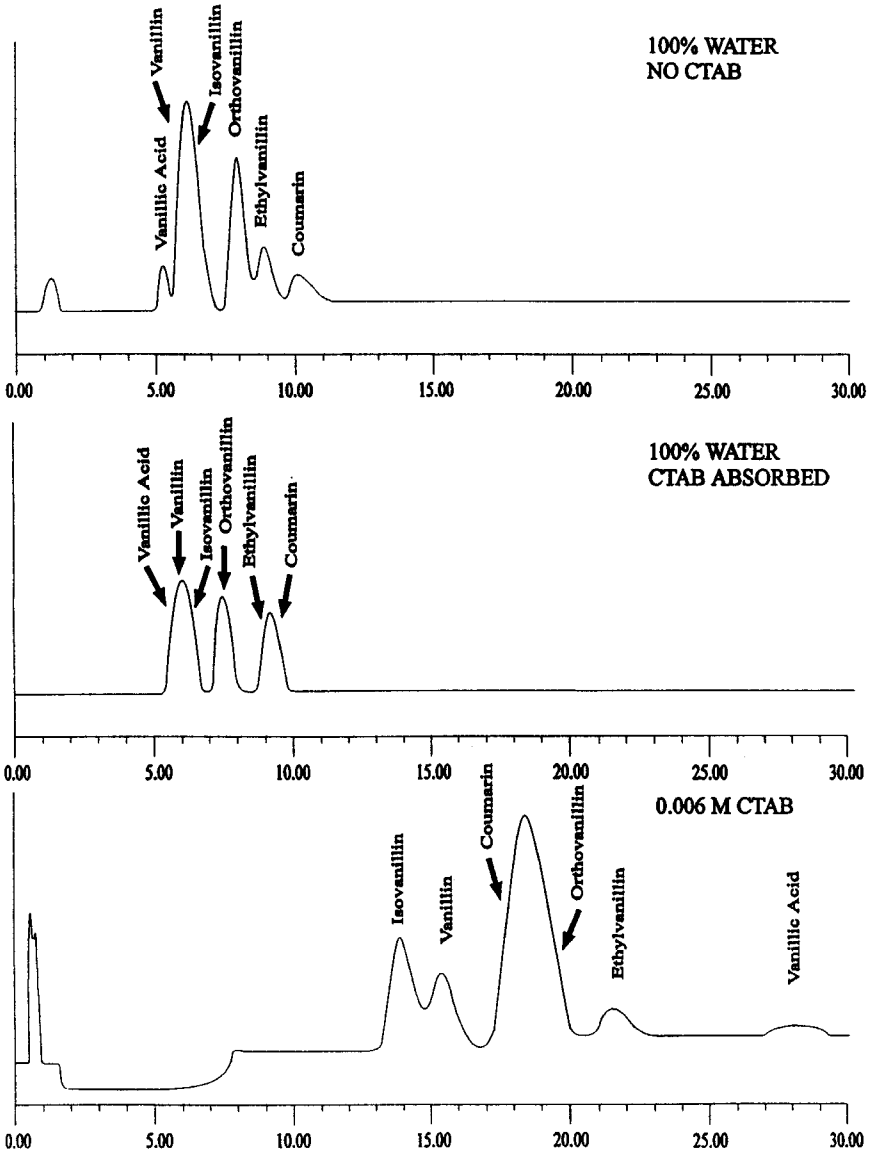

Figure 15. Chromatograms of the vanillin test mixture on a cyanopropyl column before, during, and after separations involving micellar mobile phases. The pH of each mobile phase was 3.0, and the flow rate was 1.0 mL/min.

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retention time of some ionogenic compounds on cyanopropyl bonded phase columns actually increases with increasing micelle concentration which is opposite of what is considered to be normal retention behavior in MLC. This effect which is known as antibinding behavior occurs with compounds that have the same charge as the surfactant and is a direct result of a compound being driven into the stationary phase as the micelle content of the mobile phase is increased because the compound is excluded, not only from the micelle, but from the double layer that surrounds the micelle. Because the charged head group of the adsorbed surfactant monomer is "tied up" by the cyano functionality of the bonded phase, there is little free electrostatic charge to prevent migration of this ionized solute into the bonded phase. By comparison, antibinding behavior does not occur on C_{18} or C_8 columns because of the higher surface charge of the CTAB and SDS modified alkyl bonded phase, which is the result of the sulfate and N-alkyl head groups not being as strongly associated with the C_{18} and C_8 alkyl bonded phase.

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The model for surfactant adsorption developed from the NMR data, however, cannot explain the S-type adsorption isotherms obtained for SDS or CTAB on cyanopropyl columns[9] which can be interpreted as due to cooperative adsorption. Nor can the model explain the longer retention time of the vanillin compounds when either CTAB or SDS micellar solutions are used as mobile phases in lieu of a purely aqueous mobile phase (see Figures 14 and 15). The latter result is surprising in view of the greater solvent strength of CTAB and SDS micellar mobile phases which suggests that solute stationary phase interactions are also greater when these micellar solutions are used as mobile phases instead of a purely aqueous mobile phase. Perhaps, small surfactant aggregates form within the cyanopropyl bonded stationary phase when SDS or CTAB micellar solutions are used as mobile phases. These aggregates could be responsible for the increase in the retention time of the vanillin compounds and could also explain the S-type adsorption isotherms for CTAB and SDS on cyanopropyl.

CONCLUSION

The results of an in-depth study on the effects of surfactant chain length and charge-type on selectivity in MLC has been presented. A hydrophilic test mixture has been separated on a variety of bonded phase columns using either an aqueous anionic SDS or cationic CTAB or DTAB micellar solution as the mobile phase. To explain the differences in selectivity as a function of surfactant charge type and chain length, it was necessary to determine the relevant partition/binding constants, the extent of surfactant adsorption on the stationary phase, and the molecular orientation of the adsorbed surfactant

monomer in the bonded phase. Our conclusions supported by solid state NMR data indicate that different surfactant molecular orientations on the stationary phase can lead to significant selectivity differences in MLC.

Previously published work by Cline-Love and Berthod[10-11] has stated or implied that one of the disadvantages with the use of micellar mobile phases was that the surfactant coating of the stationary phase rendered them all similar in terms of their polarity and thus masked the columns inherent selectivity. That is, regardless of the stationary phase or surfactant charge type, very similar selectivity would be observed. This assumed, of course, that all surfactants regardless of their charge type or chain length sorbed with similar orientations on different stationary phase materials. Hence, the significance of the present study is that it dispels those previous conclusions/speculations and demonstrates that surfactant-charge type and chain length can influence selectivity. In other words, finding the appropriate combination of surfactant and stationary phase is crucial in micelle mediated RPLC, which is the reason why users should be encouraged to experiment with more than one charge-type micellar system.

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