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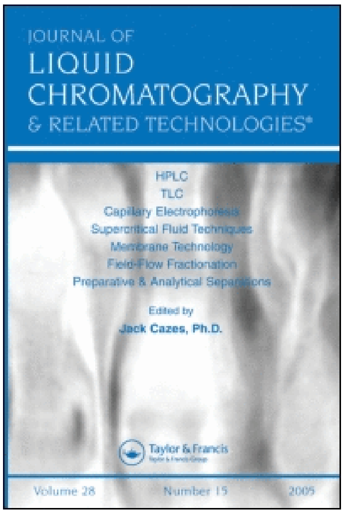

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# LIQUID CHROMATOGRAPHY STUDIES OF ACETONITRILE SORPTION ON SILICA-BASED OCTYL PHASES

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# LIQUID CHROMATOGRAPHY STUDIES OF ACETONITRILE SORPTION ON SILICA-BASED OCTYL PHASES

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## ABSTRACT

A complex mechanism of the reverse-phase chromatography can be envisioned as a combination of partition and adsorption processes. In the partition-displacement (P-D) model, partition accounts for the distribution of solute between the mobile and stationary phases, while displacement mostly involves competitive adsorption of solvents in the stationary phase. Therefore, chromatographic properties of a given stationary phase are largely dependent on the intercalation of solvents in the surface layer. The current work is a continuation of the ongoing studies of the factors affecting the surface composition of the stationary phase. Specifically, the goal of this work was the investigation of chromatographic behavior of two octyl phases of a similar surface coverage, which were synthesized from different silica supports. Analysis of methylene selectivity data showed that sorption of acetonitrile on both octyl phases was similar. This outcome could be related to a significant similarity of their structural and surface properties as demonstrated by analysis of the corresponding nitrogen adsorption and solid-state NMR data.

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## INTRODUCTION

Studies of solute retention in reversed-phase (RP) chromatographic systems are crucial to improve scientific understanding of the retention mechanism. As many literature sources agree the stationary phase plays an important role in this process.[1-4] The interaction of solute with the stationary phase is rather a complex phenomenon. Thus, according to the chromatographic model employed in this study, the retention mechanism in the RP system can be considered as a combination of partition and displacement processes.[4] The partition-displacement model distinguishes two stages in the chromatographic process: (i) formation of a combined solvent-surface stationary phase, and then (ii) partitioning of a solute between the mobile and stationary phases.

The first step takes place during conditioning of a chromatographic column, it leads to the equilibrium composition of solvents in the stationary phase, which is established via the process of competitive adsorption (displacement). In turn, the solvent composition of the stationary phase can significantly affect solute retention even in case of the conventional alkyl bonded phases. The effect could be even stronger for chromatographic phases with the specific ligand functionality.[5] For instance, in the case of the alkylamide phases the composition of solvents and, consequently, the retentive properties of these phases can be changed significantly in the presence of specific interaction sites in the bonded chains.[6,7]

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The current work is the continuation of our investigation on the factors affecting the solvent composition of the stationary phases. In our previous studies the partition-displacement model was used to characterize chromatographic properties of several commercial and home-made silica-based chromatographic columns, and to investigate the dependence of the solvent composition in the stationary phase on the octyl phase surface coverage.[8-11]

In this project acetonitrile sorption was studied on two octyl phases of a similar surface coverage synthesized from different silica supports. Chromatographic behavior of these octyl phases was characterized using retention measurements for a series of homologous alkyl-benzenes. The obtained methylene selectivity data were analyzed in terms of the partition-displacement model in order to evaluate the solvent composition of the stationary phases studied.

The results of chromatographic characterization of these stationary phases were related to the structural and surface properties of the corresponding chromatographic packings characterized by thermal analysis, nitrogen adsorption, and solid state NMR.

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## EXPERIMENTAL

### Materials

Chromatographic silica gels Luna (batch #35119) and Prodigy (batch #960433) were donated by Phenomenex (Torrance, CA). According to manufacturer's information, both silica samples have an average pore diameter of 10nm, and particle size of 5μm.

The silanizing agent, n-octyldimethylchlorosilane, was supplied by Huls (Piscataway, NJ). Acetone, pyridine, methanol, and test solutes (all ACS grade) were bought from Aldrich (Milwaukee, WI). The reaction solvent, toluene of ACS grade, was purchased from Fisher (Pittsburgh, PA). All reagents were used as received.

The HPLC solvents such as methanol, acetonitrile, 2-propanol were purchased from Fisher. The mobile phases were prepared by manually mixing acetonitrile with deionized water. Water was in-house purified using the Milli-Q system produced by Millipore (Milford, MA). All mobile phases were outgassed before use.

### Synthesis of Octyl Bonded Phases

In order to activate the silica surface before modification, approximately 5g of silica in 100 mL of water was stirred, and then sonicated for 2 minutes. After 3 hours allowing the suspended silica to settle down, the water was carefully decanted, and the wet silica was placed in an oven at 393K for 22 hours.

The activated silica gel was placed in the reaction flask containing 150 mL of toluene. The mixture was gently stirred by bubbling dry nitrogen for 20 minutes. After equilibrating the system, 1 mL of pyridine (as an acid scavenger) and a five-time excess of the silanizing agent were added to the reaction mixture. The silanol concentration of 8 $\mu mol/m^2$ was assumed to calculate the amount of modifier. Following the addition of silanizing agent, the reactor temperature was brought up to 122°C to allow the reaction solvent to boil gently. After refluxing the mixture for 22 hours the reaction was stopped. The sample was removed and then washed on a vacuum glass filter with toluene, acetone, acetonitrile, methanol, and deionized water. A post-reaction curing step (isothermal equilibration at 180°C for 2h) was needed to complete the modification reaction. More details on this procedure can be found elsewhere.[10]

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## Elemental Analysis

Control of the pyridine impurities and determination of carbon percentage in the modified silica samples were done using a CHNS-932 Elemental Analyzer produced by LECO Corporation (St. Joseph, MI). The surface coverage of octyl phases was calculated from the carbon content data and the BET specific surface area determined from the adsorption measurements.[6]

## Column Packing

Approximately 2.7 g of the chemically modified silica and 30 mL of 2-propanol were sonicated together to form a slurry. The 4.0 mm i.d. x 100 mm stainless steel columns were packed under the pressure of 6000 psi employing a DSTV-52C air-driven fluid pump (Haskel, Inc., Burbank, CA). Methanol was used as a delivery solvent.

## Chromatographic Measurements

Retention measurements of homologous alkyl-benzenes in acetonitrile-water eluent were carried out using Varian (Walnut Creek, CA) modular liquid chromatograph, which consisted of Varian 9012 solvent delivery system, Varian 9100 autosampler, Varian 9050 variable wavelength UV-VIS detector, Varian Mistrel column oven, and Rheodyne 8025 (Berkeley, CA) injection valve equipped with a 20 μL loop. Data acquisition was done using Varian Star Chromatography Workstation. All experiments were carried out at 25°C and a flow rate of 1 mL/min. The detector was set to a wavelength of 254 nm. Detemination of the void volume was done using solvent disturbance peak.

## Evaluation of the Surface Excess

According to the partition-displacement model[4] the natural logarithm of the methylene selectivity, $s$, can be expressed as:

$$s = \phi_o^\sigma s_o + \phi_w^\sigma s_w \tag{1}$$

where $\phi_o^\sigma$ and $\phi_w^\sigma$ are, correspondingly, the volume fractions of organic solvent and water in the stationary (surface) phase, and $\phi_o^\sigma + \phi_w^\sigma = 1$, since the concentration of a solute is infinitely low. The symbols $s_o$ and $s_w$ denote the logarithmic methylene selectivities in the pure organic solvent and water, respectively. Their values can be determined from the $s$-dependence on the mobile phase composition by extrapolating $\phi_o^1$ to unity and zero. The

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methylene selectivity data can be used to calculate the excess selectivity function, $s_e$:

$$s_e = s - s_o\phi_1{}^{l} - s_w\phi_w{}^{l} = A\,(\phi_o{}^{\sigma} - \phi^{l}{}_o) \tag{2}$$

where $(\phi_o{}^{\sigma} - \phi_o{}^{1})$ is the surface excess of the organic component in the stationary phase, $\phi_o{}^{1}$ is the volume fraction of the organic component in the mobile phase, and $A$ is the proportionality constant.

The volume fraction of the organic component in the stationary phase is a function of the mobile phase composition. For an ideal phase the solvent composition can be evaluated analytically using the Everett's equation for competitive adsorption from solutions:[12]

$$\phi_o{}^{\sigma} = \frac{K_{ow}\phi_o^1}{\left(1 - \phi_o^1 + K_{ow}\phi_o^1\right)} \tag{3}$$

where $K_{ow}$ is the equilibrium constant which describes the competitive sorption of solvents on the stationary phase.

By substituting $\phi_0{}^{\sigma}$ in equation (1) by equation (3) the following expression can be obtained:

$$s = s_w - (s_w - s_\sigma)\,\frac{K_{ow}\phi_o^1}{\left(1 - \phi_o^1 + K_{ow}\phi_o^1\right)} \tag{4}$$

In this expression the only parameter unknown is $K_{ow}$. It can be evaluated by fitting the experimental $s(\phi_o{}^{l})$ data by equation (4), or its linear form:

$$\frac{1}{s_w - s} = \frac{K_{ow} - 1}{K_{ow}\,(s_w - s_o)} + \frac{1}{K_{ow}\,(s_w - s_o)}\,\frac{1}{\phi_o^1} \tag{5}$$

Once the value of the equilibrium adsorption constant is known, equation (3) can be used to calculate the surface excess of the organic component in the stationary phase, i.e. $(\phi_o{}^{\sigma} - \phi_o{}^{1})$.

### Adsorption Measurements

Prior to adsorption measurements silica samples were outgassed at 200°C for 2 hour under the vacuum of $10^{-4}$ Torr. Measurements of nitrogen adsorption isotherms were carried out at -195.5°C using an ASAP 2010 volumetric sorption analyzer (Micromeritics, Inc., Norcross, GA). The analysis of adsorption isotherms included evaluation of the specific surface area according to the BET method[13] and the total pore volume using the single point method.[13] The pore size distributions were calculated according to the BJH method using the softare provided by Micromeritics, Inc.[14] In addition, the t-plot method was used to examine the presence of micropores.[14]

A numerical algorithm based on a regularization procedure was employed to evaluate the adsorption energy distributions (AEDs) for the samples studied. The adsorption energy distributions were calculated by inverting the integral equation of adsorption[15] using the INTEG software.[16] In the integral equation of adsorption the local adsorption was modeled by Fowler-Guggenheim equation for random distribution of adsorption sites.[15] In this model the number of nearest neighbors was assumed to be four *(z=4),* and the value of the interaction energy parameter $\omega/k=95$K was used to calculate the adsorption energy distribution.[16] Numerically stable solutions of the distribution function were acquired for the regularization parameter equal to $10^{-2}$.

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## Thermogravimetry

In order to evaluate the surface reactivity of silica supports thermogravimetric (TG) analysis was performed. All measurements were carried out in a flow of nitrogen under quasi-isothermal conditions using a model TGA 2950, high-resolution thermogravimetric analyzer from TA Instruments, Inc. (New Castle, DE). In each measurement approximately 20 mg of the silica sample was placed in an open platinum pan, and heated up to 1000°C at a rate of 5°C/min.

## Solid-State NMR Experiments

The $^{1}$H-$^{29}$Si CP/MAS NMR spectra of the original and modified silica samples were obtained on Bruker DMX 400WB spectrometer (USA Bruker Instruments Inc., San Jose, CA) with $^{29}$Si Larmor precession frequency of 79.5 MHz. The samples were packed in 9mm zirconia rotor and spun at the MAS frequency of 2 kHz using dry air as a driving and bearing gas. The experimental temperature was maintained at 25°C. The proton 90° pulse length was set to 4 μsec. The TMS was used as an external chemical shift reference. Cross-polarization (CP) performance was optimized using 3-(trimethylsilyl)-1-propane sulfonic acid sodium salt (DSS). Line broadening of 50Hz was applied in all spectra.

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For each sample 32 spectra corresponding to different contact times (from 0.2 to 100 μsec) were collected. For each spectra 400 FIDs were accumulated in 2 K data points using the acquisition time of 43 msec and cycle delay time of 5 sec.

For each silica the analysis of signal intensities as a function of contact time was performed using the following equation:[17]

$$I(t) = I_0 \exp(-t/T_{1pH})[1-\exp(-(1-T_{SiH}/T_{1pH})t/T_{SiH}]/(1-T_{SiH}/T_{1pH}) \qquad (6)$$

Fitting experimental cross-polarization (CP) curves with equation (6) yields the values of the cross-polarization time constant $T_{SiH}$, the relaxation time of the proton in rotating frame $T_{1pH}$, and the maximum obtainable magnetization $I_0$. The magnetization parameters of geminal $I_0(Q_2)$, single silanol $I_0(Q_3)$, siloxane $I_0(Q_4)$ and n-octyldimethylsilyl $I_0(M)$ groups were used for quantification.[18] In order to obtain absolute concentrations of silicon groups on the surface $I_0(M)$ was calibrated using surface concentration of n-octyldimethylsilyl group, which was obtained from elemental analysis data.[19] It should be noticed that owing to the surface selectivity of the CP sequence bulk siloxane groups are not detected. However, the inner chromatographically inaccessible silanol groups (typically found in fine micropores) also contribute to the overall intensity of the $Q_2$ and $Q_3$ signals.

## RESULTS AND DISCUSSION

### Thermogravimetric Studies

In order to evaluate the surface reactivity of the unmodified silica samples their thermal stability was investigated. The cumulative (TGA) and differential (DTG) curves of the samples studied are shown in Figures 1 and 2. Both silica samples exhibit similar behavior. The TGA curve of each sample exhibited two well-defined steps.

The first step on the TGA curve located below 250°C, corresponds to thermodesorption of physically adsorbed water from the silica surface. The temperature derivative of the cumulative weight curve in this temperature range provides information about surface heterogeneity of the silica surface (as determined with respect to thermodesorption of water molecules). Thus, the DTG curves of Luna and Prodigy samples exhibited a sharp peak located at ~60°C (see Fig. 2), which indicates that their surface heterogeneity is similar.

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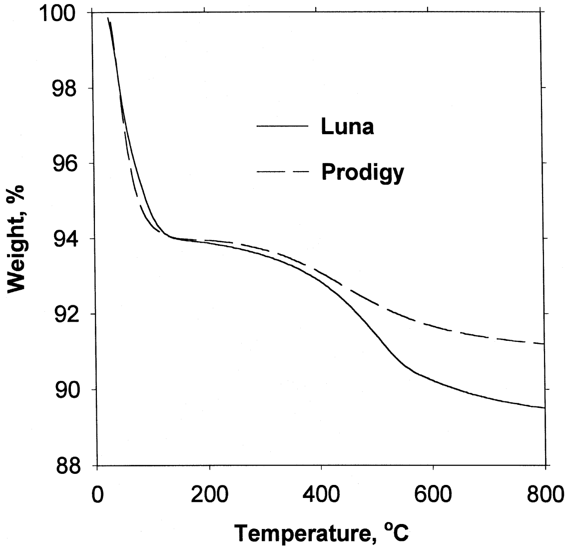

**Figure 1**. Cumulative TGA curves for unmodified silica gels.

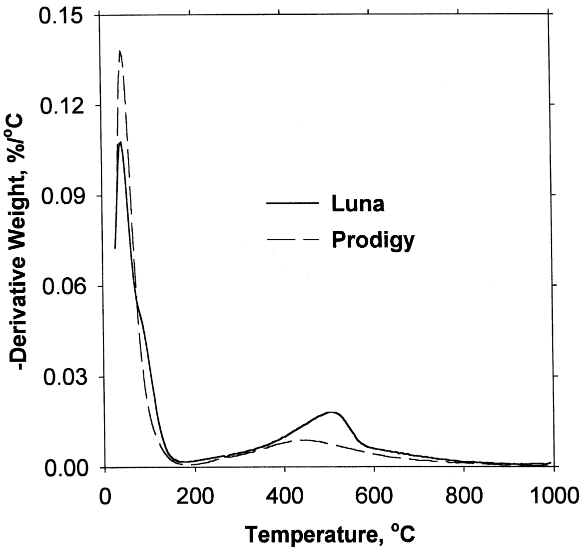

**Figure 2**. Differential (DTG) weight curves for unmodified silica gels.

A sample weight at 250°C corresponds to a silica with removed physically adsorbed water. Further heating of the sample above this temperature results in the dehydroxylation of its surface. Therefore, for each silica the sample weight at 250°C was used to calculate the amount of water thermodesorbed between 250 and 800°C, which could provide information about surface silanol coverage. Thus, Luna and Prodigy released, respectively, 5.40 and 3.91 $\mu$mol($H_2O$)/$m^2$. If all thermodesorbed water came from decomposition of silanols, in order to calculate their coverage the numbers above should be multiplied by two, since condensation of two moles of surface hydroxyls produces one mole of water (i.e. 10.80 and 7.82 $\mu$mol(OH)/$m^2$, correspondingly). Therefore, the silanol coverage of Prodigy could be close to the theoretical limit of 8 $\mu$mol(OH)/$m^2$, while the surface concentration of silanols for Luna well exceeded the theoretical limit.[20] Although the TGA analysis provides helpful information about surface properties of the sample studied, the evaluation of the surface silanols coverage by this method can be biased due to thermodesorption of structurally bonded water, which can be removed at the temperatures above 250°C.

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Additional information on the surface properties of the silica supports was obtained from comparison of their DTG curves above 250°C. The DTG curve of Luna sample exhibited a maximum at ~510°C, while DTG curve of Prodigy silica exhibited a similar peak only at ~450°C. The DTG peak corresponds to a temperature with maximum decomposition rate. Thus, for Prodigy the highest rate was achieved at lower temperature. This observation may be partially explained by the fact that bridged silanols more readily condense into siloxane groups due to a close geometric proximity, while the single silanols decompose at higher temperatures because they have no counterparts for condensation reaction. Other reasons for such distinct behavior may include the presence of structural water in Luna sample.

## Solid-State NMR Studies

Before and after modification the $^1$H-$^{29}$Si CP/MAS NMR variable contact time spectra of the samples were recorded. Analysis of the cross-polarization curves using equation (6) yielded the values of magnetization parameters for the silicon groups present on the surface. Thus, the ratio of magnetization parameters ($I_0(Q_2)$:$I_0(Q_3)$:$I_0(Q_4)$ ) was used to calculate the percent fractions of silicon groups. These results are shown in Figure 3. As can be seen unmodified Prodigy had higher percentage of single silanols ($Q_3$-sites) while the fraction of geminal silanols in both samples was practically the same. After modification the samples studied showed similar values of the surface coverage, and the percent fractions of $Q_2$, $Q_3$, and $Q_4$ groups in both samples were practically the same.

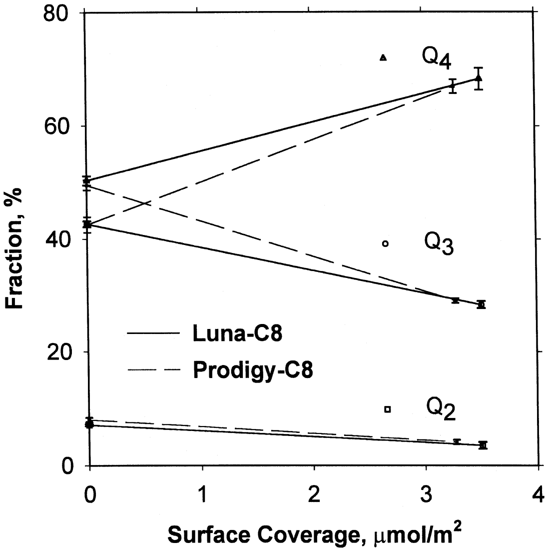

**Figure 3**. Fractions of different silicon groups as a function of the surface coverage determined from $^{1}$H-$^{29}$Si CP/MAS NMR data.

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## Table 1

## $^{29}$SiCP/MAS NMR Characterization of the Silica Samples Studied

| Sample\Silicon Group | | M | $Q_2$ | $Q_3$ | $Q_4$ |
|---|---|---|---|---|---|
| Luna-C8 | $I_0$ (arb. units) | 17.5(2) | 1.8(3) | 14.5(2) | 34.9(9) |
| | Coverage (μmol/m$^2$) | 3.32(4) | 0.34(6) | 2.74(5) | 6.6(5) |
| Prodigy-C8 | $I_0$ (arb. units) | 16.5(2) | 1.9(2) | 14.1(1) | 32.6(5) |
| | Coverage (μmol/m$^2$) | 3.11(5) | 0.36(4) | 2.65(4) | 6.13(11) |

However, it should be noticed that from the NMR experiment alone it is possible to estimate only the percent fractions of different surface species. Therefore, regardless of the percent fractions absolute concentrations of surface species may vary.

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**Table 2**

**Adsorption and Elemental Analysis Characterization of the Silica Samples Studied**

| **Sample** | **Carbon Content (%)** | **Surface Coverage (µmol/m$^2$)** | **$S_{BET}$ (m$^2$/g)** | **$V_t$ (cm$^3$/g)** | **<$Ø_{BJH}$> (nm)** |
|---|---|---|---|---|---|
| Prodigy | 0.00 | 0 | 433 | 0.94 | 8.33 |
| Prodigy-C8 | 13.15 | 3.11 | 251 | 0.55 | 6.66 |
| Luna | 0.00 | 0 | 465 | 1.17 | 9.20 |
| Luna-C8 | 14.66 | 3.32 | 297 | 0.70 | 7.00 |

**Table 3**

**Chromatographic Characterization of the Octyl Phases Studied**

| **Octyl Phase** | $s_W$ | $s_0$ | **$K_{OW}$** | **$r^2$** |
|---|---|---|---|---|
| Luna-C8 | 1.35 | 0.16 | 1.80(12) | 0.99 |
| Prodigy-C8 | 1.37 | 0.16 | 1.78(13) | 0.99 |

In order to obtain absolute concentrations of silicon groups the magnetization parameter $I_0$ has to be calibrated with respect to external standard measured independently from NMR. In this work, the surface concentration of n-octyldimethylsilyl group determined from elemental analysis was used for calibration of the magnetization parameter $I_0$(M). The obtained proportionality constant was used to calculate the surface concentrations of the other silicon groups (Table 1). For example, for Luna-C8 the proportionality constant was equal to 0.189. The magnetization parameters of the other groups were multiplied by this factor to obtain corresponding surface concentrations. As the analysis showed, the amounts of the residual silanols are quite similar in both samples (3.08 µmol(OH)/m$^2$ for Luna-C8 vs. 3.01 µmol(OH)/m$^2$ for Prodigy-C8). Comparable concentrations of octyl ligands (see also Table 2) and residual silanols could indicate close similarity of the surface properties of the modified silica gels.

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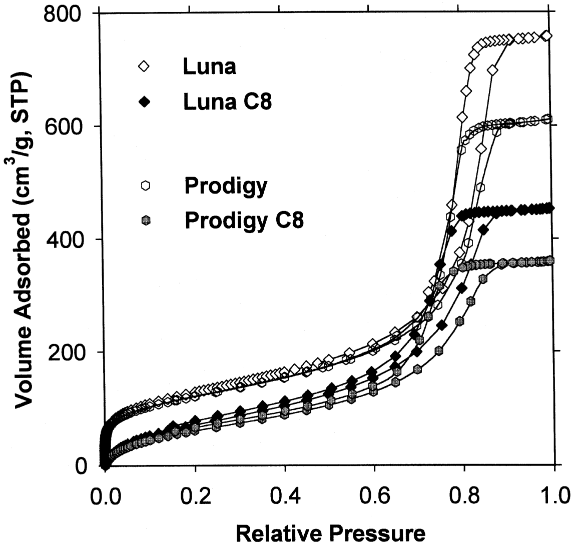

**Figure 4**. Nitrogen adsorption-desorption isotherms for the original and derivatized silica samples measured at -195.5°C.

In addition, from the data presented in Table 1 it is possible to estimate the silanol concentrations in the unmodified silica. The amount of residual silanols should be summed up with the amount of silanols which reacted with the modifier, i.e. 6.40 and 6.12 μmol(OH)/m$^2$ for Luna and Prodigy, correspondingly. This calculation demonstrates that the evaluation of silanol coverage exclusively from TGA data may be grossly overestimated due to overlapping effects of the silanol condensation and the removal of the structural water at temperatures above 250°C.

## Adsorption Characterization

Nitrogen adsorption measurements were carried out to evaluate changes in the surface and structural properties of silica samples upon modification. Adsorption isotherms measured for original and modified silica samples are shown in Figure 4. According to IUPAC,[21] these isotherms can be classified as type IV. For both silica samples modification produced a decrease in the adsorption capacity. Despite these changes, isotherms of the modified samples showed a well-defined H1 type hysteresis loop,[21] which indicated mesoporous structure of the silica gels studied.

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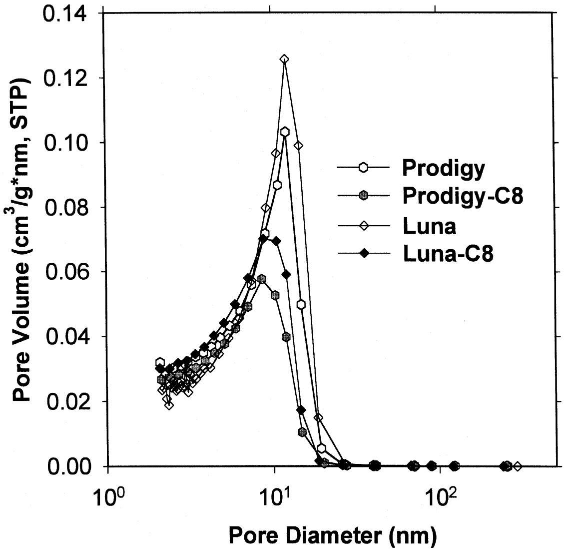

**Figure 5**. The BJH pore size distributions for the silica gels studied.

A quantitative analysis of adsorption isotherms showed a decrease of the total pore volume and the BET specific surface area for the modified samples. The BET data combined with carbon content data obtained from elemental analysis were used to calculate the surface coverage of octyl phases. As can be seen from Table 2 the surface modification of silica gels resulted in comparable surface coverages for the samples studied.

Further analysis of the structural changes included calculations of the BJH pore size distributions (PSD). As can be seen in Figure 5 derivatization of the silica samples resulted in a reduction of the total pore volume and a shift of the PSD maximum towards smaller pores, which demonstrated that surface derivatization took place inside the mesopores. Additionally, adsorption data were tested for the presence of micropores. Application of the t-plot method showed no evidence for the microporosity in the samples studied.

The low pressure region of adsorption isotherms were analyzed to gain information about surface properties of the silica gels studied. The submonolayer range of adsorption isotherms was used to calculate the adsorption energy distributions (AED). As can be seen in Figure 6, the distribution functions for unmodified silica gels were quite similar, except for the part of the distribution function, where Prodigy silica had more high energy sites.

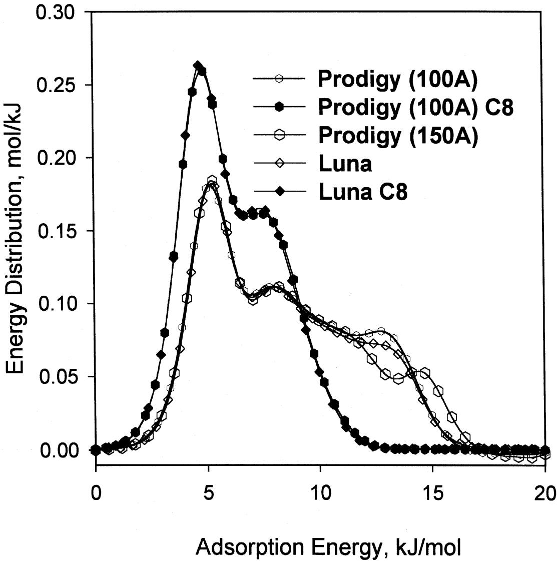

**Figure 6**. Adsorption energy distributions (AEDs) for the silica gels studied.

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Noteworthy, after modification both silica samples exhibited practically coinciding profiles of their distribution functions, which indicated close similarity of their surface properties. For both Prodigy and Luna the AED after modification were bimodal and became narrower compared to unmodified samples.

As can be concluded, modification of the samples' surface significantly reduced their heterogeneity. Reduction of the high adsorption energy sites could be clearly related to a decrease of the silanol population after the reaction with organosilane.[11,22]

## Chromatographic Studies

Retention of homologous alkyl-benzenes was measured using chromatographic columns packed with Prodigy-C8 and Luna-C8 octyl phases. In chromatographic experiments concentration of acetonitrile in the mobile phase varied from 10 to 90% (v). For each mobile phase composition a logarithm of the capacity factor lnk' was plotted as a function of the number of carbon atoms in the alkyl chain of solute, $n_c$. Thus, the retention data obtained for Prodigy-C8 phase are shown in Figure 7.

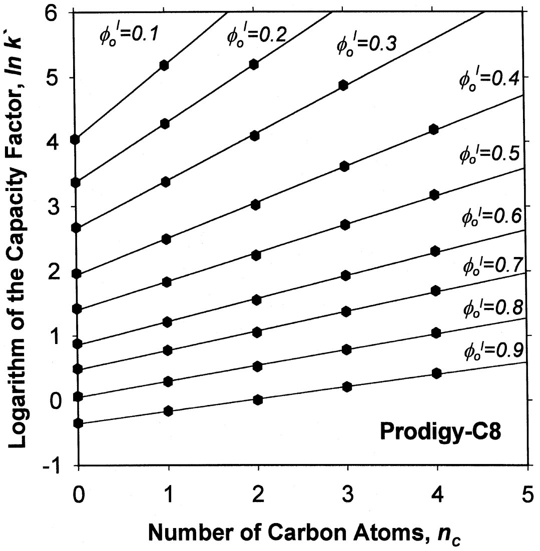

**Figure 7**. Natural logarithm of the capacity factor for Prodigy octyl phase as a function of the number of carbon atoms in the alkyl chain of solutes.

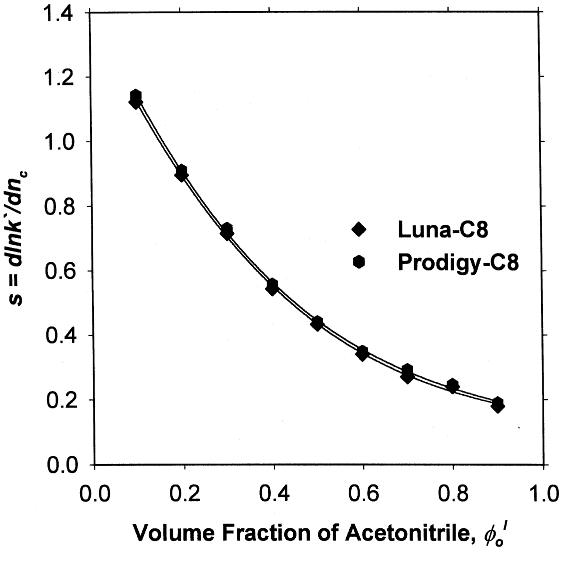

**Figure 8**. Logarithm of the methylene selectivity as a function the mobile phase composition.

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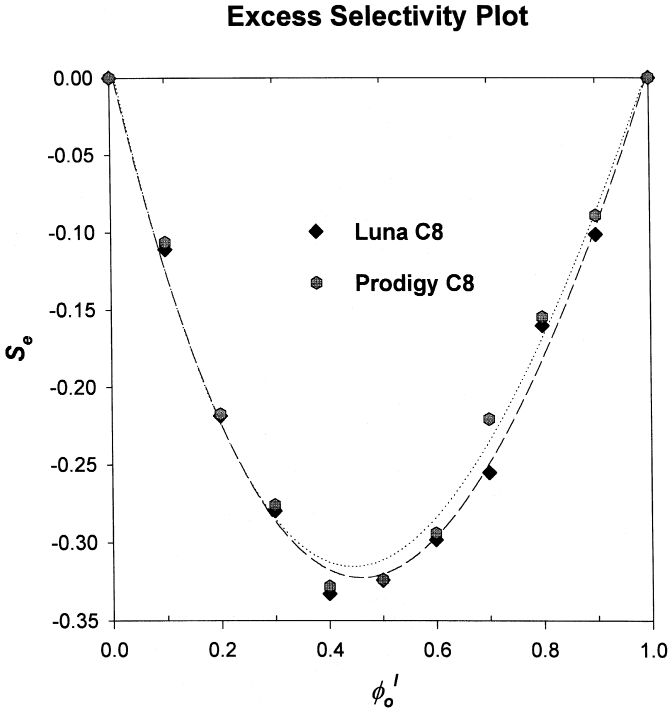

**Figure 9**. Excess selectivity as a function the mobile phase composition.

For both octyl phases the logarithmic dependence of the capacity factor for the alkyl-benzenes studied was a linear function of the number of carbon atoms in the alkyl chain of solute, which is in a good agreement with other studies.[9-11,23,24] It should be noticed, however, that even it is true for a given set of solutes noticeable deviations from linearity may occur if the length of bonded phase chains is comparable to that of solutes.[24]

For each mobile phase composition the slope of the lnk' vs. $n_c$ plot was calculated to evaluate the logarithm of the methylene selectivity, i.e. $s = d\ln k'/dn_c = (\ln k'_{n+1} - \ln k'_n)/1 = \ln(k'_{n+1}/k'_n) = \ln\alpha_{CH2}$, which provides information about hydrophobic properties of the stationary phases studied. The logarithmic methylene selectivity functions for both octyl phases studied are shown in Figure 8 and were used to extrapolate the methylene selectivities in pure organic solvent and water (see Table 3). These values were used to calculate the excess selectivity functions, $s_e$ (equation 2), which are shown in Figure 9.

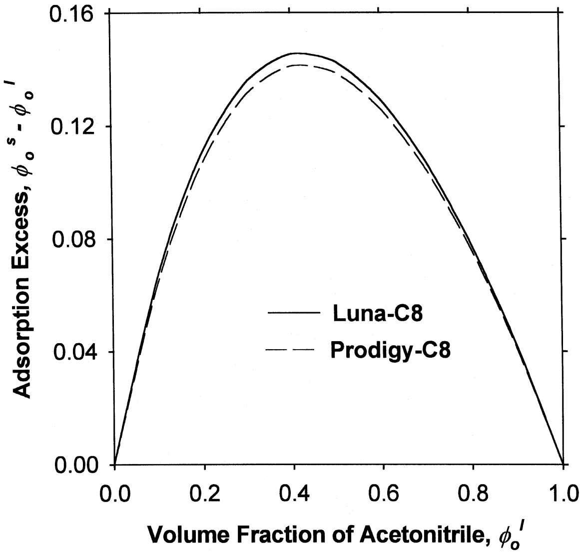

**Figure 10**. Surface excess of acetonitrile as function of the mobile phase composition.

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The excess selectivity plots for Luna-C8 and Prodigy-C8 are essentially the same, which according to the partition-displacement model indicates that the sorption excesses of acetonitrile in these phases are similar. Analysis of the methylene selectivity dependence on the mobile phase composition using equation 5 showed that acetonitrile sorption constants for both phases were greater than one (Table 3), which indicated preferential adsorption of acetonitrile for both stationary phases. Moreover, the stationary phases had essentially identical values of acetonitrile sorption constants. Therefore, as can be easily shown using Everett equation (3), the octyl phases studied should have the same sorption excess of acetonitrile (Figure 10). Such outcome could be expected due to a close similarity of the surface properties of the chromatographic packings as demonstrated by the analysis presented above.

## CONCLUSIONS

Two octyl phases of comparable surface coverages were synthesized from different silica supports. The structural and surface properties of these packings were characterized by thermogravimetry, nitrogen adsorption, and solid state NMR.

Thermogravimetric studies of the unmodified silicas showed significant differences in their properties. In the temperature range between 250 and 800°C Luna released 5.40 $\mu$mol/m$^2$, while under the same conditions the amount of water thermodesorbed by Prodigy was only 3.91 $\mu$mol/m$^2$. Additionally, as shown by analysis of the DTG curves for the same temperature range the maximum decomposition rate occurs at lower temperature in the case of Prodigy silica.

For modified silicas the analysis of adsorption data demonstrated an anticipated decrease in the BET specific surface area, the total pore volume, and the average BJH pore radius. Analysis of the adsorption energy distributions revealed small differences in the high energy region of the distribution functions for the bare silica samples. However, analysis of the AEDs after modification showed that their surface properties are practically identical. This result is consistent with the elemental analysis and solid-state NMR data, which showed that despite differences in the silica supports the synthesized chromatographic packings possess comparable surface properties.

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Retention measurements of alkyl-benzenes on the octyl phases studied showed close similarity of their chromatographic/hydrophobic properties. Thus, the analysis of methylene selectivity data in terms of the partition-displacement model showed that both octyl phases had essentially the same values of the acetonitrile sorption constant and, consequently, the same solvent composition in the stationary phases. This result could be anticipated owing to close similarity of the surface and structural properties of the chromatographic packings studied.

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