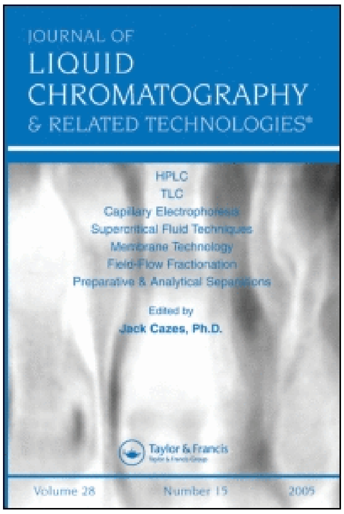

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COMPARATIVE CHARACTERIZATION OF OCTYL BONDED PHASES USING METHYLENE SELECTIVITY DATA

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ABSTRACT

Retention measurements of alkyl benzenes were carried out on the synthesized silica-based octyl bonded phases. The partition-displacement model was employed to analyze chromatographic properties of these phases. Namely, the methylene selectivity data were used to calculate the equilibrium sorption constant, the surface phase composition, and the sorption excess of water for each octyl phase. The differences in the surface phase composition of the phases studied were correlated with the structural and surface properties of the modified silica gels.

INTRODUCTION

Different types of porous silica have been extensively used as starting materials in the synthesis of chemically bonded phases for reverse-phase liquid chromatography (RPLC).[1,2] Chromatographic performance of the synthesized bonded phases not only depends on the properties of these phases (such as their chemical nature, conformation, coverage density, etc.) but also on the surface and structural properties of the silica gel, such as its porosity, surface area, silanol coverage, etc. used for their synthesis.[1-3] It is commonly accepted now[1,4-6] that any rigorous treatment of the retention mechanism under reversed phase conditions should take into account the surface composition of the stationary phase, which is a function of all of the above mentioned factors. In the current work the partition-displacement model[6-8] was used to analyze chromatographic properties of the synthesized octyl bonded phases, which had been previously characterized by high-resolution nitrogen adsorption.[9,10] A special emphasis was given to the characterization of chromatographic performance of silica-based octyl bonded phases. Retention measurements for alkyl benzenes were carried out to evaluate the incremental (methylene) selectivity data, which subsequently were analyzed in terms of the partition-displacement model.[6-8] The methylene selectivity data were used to evaluate the equilibrium sorption constant and surface excess data for acetonitrile-water mixture. The differences in the surface phase composition of these solvents were correlated with the structural and surface properties of the modified silica gels.

EXPERIMENTAL

Reagents and Chemicals

The HPLC grade acetonitrile, 2-propanol, and methanol were obtained from Fisher Scientific (Pittsburgh, PA). The deionized water used to make all chromatographic mobile phases was purified with a Millipore (Milford, MA) model Milli-Q system. The mobile phases were prepared from different compositions of acetonitrile and water. Before use, the mobile phases were degassed under vacuum. Six commercially available silica gels, namely, Vydac (Supelco, PA), Silasorb (Lachema SA, Brno, Czech Rep), LiChrospher (EM Science, NJ), Partisphere (Whatman Inc.), Hypersil (Alltech,IL) and SG-7/G (Polymer Institute, Bratislava, Slovakia) were used to synthesize the bonded phases. The physical characteristics of these materials reported by manufacturers are listed in Table 1, except the BET specific surface area, which was calculated from nitrogen adsorption data.[9,10]

Table 1

The Values of the Mean Particle Diameter (d_p), the Mean Pore Diameter (D), and the BET Specific Surface Area (S_{BET}) for the Silica Gels Studied

Type of silica	d_p, mm	D, nm	S_{BET},* m^2/g
Vydac	5	30	86
Silasorb	10	30	234
LiChrospher	8	30	57
Partisphere	5	30	81
Hypersil	5	30	56
SG-7/G	7	>20	64

* Values are taken from literature.[9,10]

Table 2

Comparison of the Concentration of Bonded Ligands and the Amount of the Structural Water for the Silicas Studied

Silica	Carbon, %	Surface Coverage, $mmol/m^2$	Water Released in TGA in the Range 250-800°C, $mmol/m^2$
Vydac	3.98	4.1	20.60
Silasorb	8.76	3.6	4.80
LiChrospher	2.68	4.1	7.00
Partisphere	3.21	3.5	5.04
Hypersil	2.52	3.9	9.70
SG-7/G	14.84	3.4	2.90

Synthesis of Octyl Bonded Phases

About 3 g of each silica gel was dried by heating at 185°C for twelve hours, under vacuum (10^{-2} Pa), in a sealed glass reactor. Subsequently, octyldimethylchlorosilane (in 1:1 proportion to silica) and dry morpholine (in 2:1 proportion to dimethylchlorosilane) were added to it and the reactor was sealed again. The reactor was heated for 12 hours at 115°C ± 5°C. After reaction was complete, the bonded silica was washed with 100 mL portions of toluene, methanol, and hexane, and dried at room temperature under vacuum. The coverage densities, calculated from the elemental analysis data, are given in Table 2.

Thermogravimetry

All thermogravimetric measurements were carried out in a flow of nitrogen under quasi-isothermal conditions using a model TGA 2950, high-resolution thermogravimetric analyzer (TA Instruments, Inc., New Castle, DE).

The silica samples were placed in an open platinum pan, and heated up to 1000°C at a rate of 10°C/min.

Column Packing

Approximately 1 g of the bonded silica and 30 mL iso-propanol were stirred together to form a slurry. The 2.1 mm i.d. x 60 mm stainless steel columns were packed in upward flow of the delivery solvent using a dynamic slurry method.

The columns were packed under the pressure of 6000 psi, employing a model DSTV-52C (Haskel, Burbank, CA) air-driven fluid pump. Methanol was used as a delivery solvent.

Retention Measurements

Chromatographic retention measurements were carried out using an HPLC system which consisted of a model SP-8810 isocratic pump (Spectra-Physics, San Jose, CA), a model Spectra 100 variable UV detector (Spectra-Physics), and a model Chromjet integrator (Spectra-Physics). The UV detector was set at 254 nm.

The injection valve, Rheodyne (Berkeley, CA) model 7125, was equipped with a 20 mL loop. The flow rate of the mobile phase was controlled by a model F1080A electronic flowmeter (Phase Separation, Queensberry, UK).

The flow rate of the mobile phase was maintained at 0.7 mL/min. Retention of five alkyl benzenes, namely, benzene, toluene, ethyl benzene, propyl benzene and butyl benzene, on six chromatographic columns, were measured using different compositions of the acetonitrile-water eluent.

Partition-Displacement Model

The retention mechanism in the reverse-phase liquid chromatography (RPLC) is a complex phenomenon which is controlled by various interactions between components of the stationary and mobile phases. It has been shown, previously, that homologous compounds are attractive for studying retention under RPLC conditions.[11,12] In RPLC, homologs allow the evaluation of such quantity as methylene selectivity, which measures the ability of a chromatographic system to discriminate between molecules that differ by a single methylene group. This quantity is denoted by a_C, which is the ratio of the capacity factors of two successive members of a homologous series. The natural logarithm of the methylene selectivity is obtained from the slope of the plot of $ln\ k'$ vs carbon number n_C,[11,13] where n_C is the number of carbon atoms in the aliphatic chain. At a constant mobile phase composition, $lnk'(n_C)$ is the linear function over a range of homologous compounds.[14,15] From the thermodynamical viewpoint, the logarithm of the methylene selectivity, $s = ln\ a_C$, is proportional to the change in the Gibbs free energy of the transfer of a methylene group from the mobile phase to the stationary phase.[13,14]

In earlier RPLC studies, the mobile phase was considered to be the main contributor towards the retention of solutes, while the stationary phase was regarded as an inert, passive phase.[16-18] However, recent studies of retention demonstrate that molecular interactions in the stationary phase should be taken into account.[1,3,4,6-8] Various properties of the stationary phase, such as type of the bonded phase, coverage density, surface properties of the support, chemical nature of the surface silanol groups, and the amount of residual silanol groups affect the retention of solutes.

Two different types of molecular models [1,19-22] are often used to describe a solute's retention between two phases:

(i) partition model, which describes the distribution of solute between the mobile and stationary phases and

(ii) displacement model, which involves the competitive adsorption of solute and solvent onto the stationary phase.

The displacement process is controlled by the difference between the adsorption energies of the solute and solvent. The partition mechanism is controlled by the difference in the molecular interactions of the solute molecules in the stationary and mobile phases.

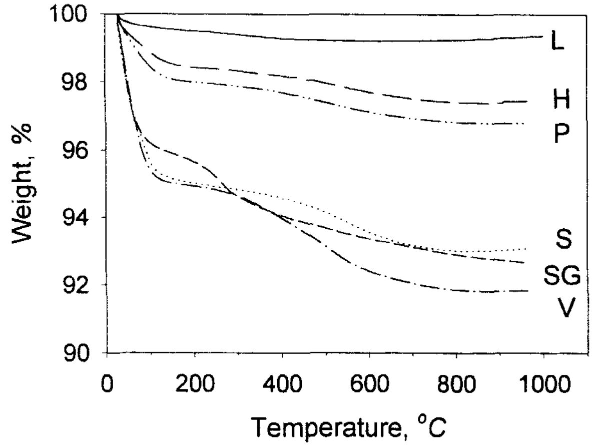

Figure 1. TGA curves for unmodified silica gels.

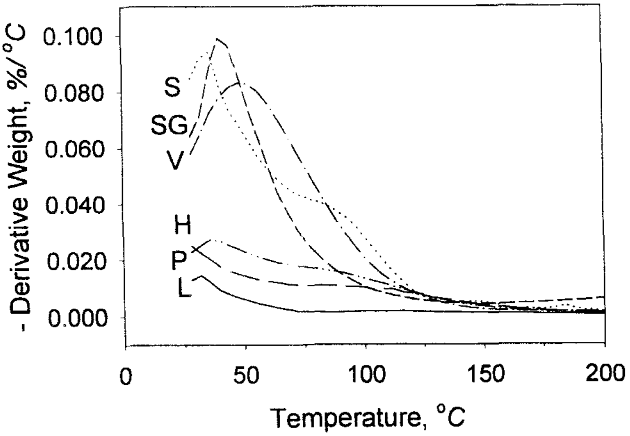

Figure 2. DTG curves for unmodified silica gels.

In RPLC, the retention mechanism cannot be adequately described by a single molecular model, either partition or displacement, since many factors can be responsible for the retention of a solute on the column. For instance, the residual silanol groups on the silica surface affect the retention, to a great extent, by changing the composition of solvents in the stationary phase.[11,14,15] In the present work, a mixed partition-displacement (P-D) model was used to represent the overall

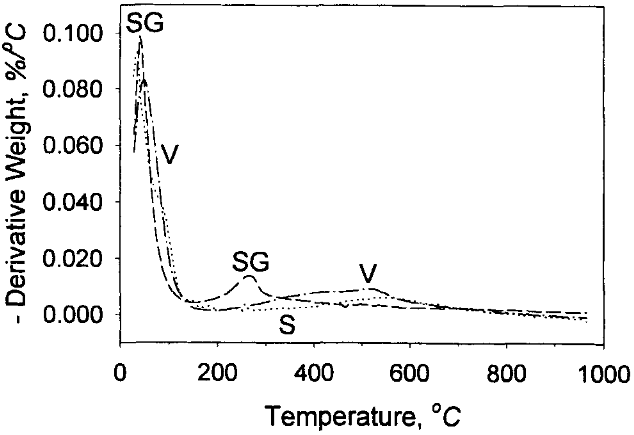

Figure 3. DTG curves for unmodified silica gel samples.

retention of the solute.[6-8] According to the P-D model,[6-8] the natural logarithm of the methylene selectivity, s, can be expressed by the following equation:

$$s = \phi^{\sigma}_{o} s_o + \phi^{\sigma}_{w} s_w \tag{1}$$

where ϕ^{σ}_{0} and ϕ^{σ}_{w} are, respectively, the volume fractions of organic solvent and water in the surface phase; s_o and s_w. are the methylene selectivities in the pure organic solvent and water, correspondingly. Since the concentration of an analyte in the surface phase is much smaller than concentrations of organic solvent and water, the following equation holds: $\phi^{\sigma}_{o} + \phi^{\sigma}_{w} = 1$. The volume fraction, ϕ^{σ}_{w}, is a function of the mobile phase composition, ϕ^{l}_{w}. It can either be evaluated independently by measuring the excess adsorption isotherm of the solvents or by assuming a given sorption model and expressing ϕ^{σ}_{w} as a function of the mobile phase composition. For the ideal phases, the volume fraction ϕ^{σ}_{w} can be expressed as follows[6]:

$$\phi^{\sigma}_{w} = 1 - e^{(-K_{wo}\phi^{l}_{w}/\phi^{l}_{o})} \tag{2}$$

where K_{wo} is the equilibrium constant which describes the competitive sorption of solvents onto the stationary phase, and ϕ_w^{l} and ϕ_o^{l} are, respectively, the volume fractions of water and organic solvents in the mobile phase, which also satisfy the condition: $\phi_o^{l} + \phi_w^{l} = 1$.

By substitution of ϕ^{σ}_{w} from equation (2) into equation (1), the following equation can be obtained:

$$\ln(s_w - s) = C - K_{wo}\phi_w^l / \phi_o^l \qquad (3)$$

where $C = ln\ (s_w - s_o) = constant$. The values of s_w and s_o can be evaluated by extrapolation of the $s(f_w^l)$-dependence to $\phi_w^l \rightarrow 1$ and $\phi_w^l \rightarrow 0$, respectively.[6,8]

According to equation (3), the dependence of $ln\ (s_w - s)$ on the ratio of the volume fractions is linear with the slope equal to the equilibrium constant K_{wo}. Thus, by plotting $ln\ (s_w - s)$ against ϕ_w^l/ϕ_o^l, the equilibrium constant, K_{wo}, can be evaluated. Consequently, K_{wo} permits the calculation of the surface phase composition, ϕ_w^s, using equation (2).

RESULTS AND DISCUSSION

Thermodesorption of Water from the Silica Surface

The unmodified silicas were heated up to 1000°C in a thermogravimetric analyzer. The cumulative (TGA) and differential (DTG) weight change curves are shown as functions of temperature in Figures 1, 2, and 3. As can be seen from these figures, each TGA curve has two characteristic steps. The first step (step I), which is located below 250°C, reflects thermodesorption of physically adsorbed water. Therefore, the corresponding DTG peak can be used to evaluate the surface heterogeneity of the samples studied. An irregular shape of this peak suggests that a given sample is energetically heterogeneous.

Among all silicas studied, Vydac and Silasorb appeared to be more heterogeneous, compared to the other samples. On the other hand, the SG-7/G sample appeared to be the most homogeneous because its DTG peak is narrow and regular.

The second TGA step is located after step I, between temperatures 250 and 800°C. Table 2 shows the amount of water released in step II. For all silicas studied, this value varied significantly, ranging from 2.9 to 20.6 mmol/m^2 (SG-7/G and Vydac, correspondingly). It was not possible to calculate this quantity for LiChrospher because its weight started to increase above 600°C. During the dehydration, the sample appeared to be thermally unstable. The value listed in Table 2 for LiChrospher was taken from a reference source.[23]

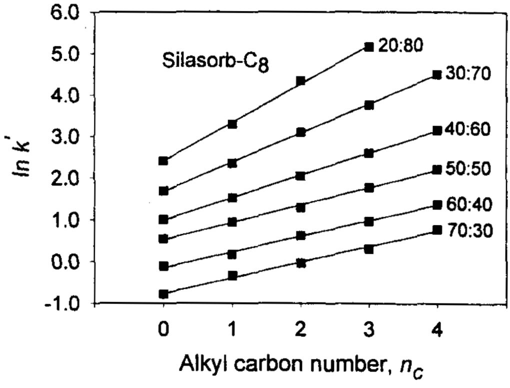

Figure 4. Dependence of *lnk'* on the alkyl carbon number n_c for Silasorb C-8 phase.

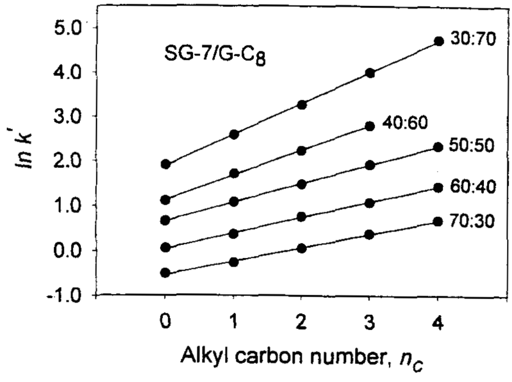

Figure 5. Dependence of *lnk'* on the alkyl carbon number n_c for SG-7/G C-8 phase.

Although the exact amount of the surface silanols can not be measured from the TGA data, the amount of water released in step II can be qualitatively related to the amount of those groups.[24-26] Typically, the larger is the amount of surface silanol groups, the larger is the amount of structurally bound/chemisorbed water. Therefore, a comparison of the amounts of water released in step II can give us some insight into the surface reactivity/properties of the silicas studied. It is also worthwhile to note that, for all bare silica samples, except SG-7/G, the second step of the TGA curve is not steep, and the corresponding DTG peak has a broad shape (see Figure

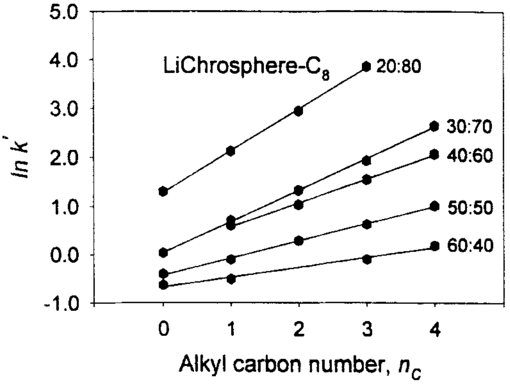

Figure 6. Dependence of *lnk'* on the alkyl carbon number n_c for LiChrospher C-8 phase.

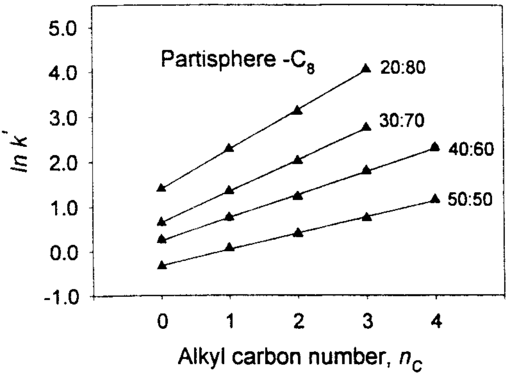

Figure 7. Dependence of *lnk'* on the alkyl carbon number n_c for Partisphere C-8 phase.

3). These observations indicate the fact that the second TGA step reflects rather a complex process of the weight loss due to both thermodesorption of chemisorbed and/or structural water, as well as decomposition of the surface silanol groups.[24-26] As discussed above, in contrast to all other samples, the second DTG peak for SG-7/G sample appeared at much lower temperature (270°C vs. 550-650°C for the others), and it had a relatively well defined symmetric shape. Also, it should be noticed that SG-7/G sample shows the smallest amount of water released in step II. Therefore, taking into account the fact that dehydroxylation of silica surface[24,26] starts at the temperatures above 450°C, it is possible to conclude the following:

(i) the second peak on the DTG curve of the SG-7/G sample can be related to a predominant thermodesorption of structurally bound/chemisorbed water;
(ii) SG-7/G sample contains quite a low concentration of silanol groups.

Chromatographic Results

The retention of five alkyl benzenes was studied on six silica-based octyl columns. The mobile phases used had different compositions of acetonitrile in water. The plots of the natural logarithm of the capacity factors against the number of carbon atoms in the alkyl chain of homologous solutes were linear (see Figures 4-9). This behavior of the $ln\ k'$ vs. n_C plots is in a good agreement with earlier experimental studies.[11,27] The slopes of the linear plots shown in Figures 4-9 are equal to $s = dlnk'/dn_c = ln\ a_C$, where s is the logarithm of the methylene selectivity. The quantity s provides information about hydrophobic interactions. Its value decreases with decreasing amount of water in the mobile phase.

The s values for a given system were plotted as a function of the volume fraction of water, ϕ_w^l, in the mobile phase (see Figure 10). These plots show some differences for the stationary phases studied. For Vydac, LiChrospher, Partisphere, and Hypersil, almost linear relationships were found, while the plots for Silasorb and SG-7/G show nonlinear behavior. This nonlinearity could be caused by various factors such as concentration of surface ligands, length of alkyl chains in the bonded phase, amount of residual silanols, and the chemical nature of silica. For the silica-based stationary phases used in the current study, the major difference is in the amount of residual silanols and the coverage of bonded ligand. These two factors affect, significantly, the selectivity of the column. Since Silasorb and SG-7/G silica based phases have high surface coverages and relatively low amounts of surface silanols, their plots of s vs. ϕ_w^l are nonlinear.

The reason for plotting the logarithm of the methylene selectivity against the volume fraction of water, ϕ_w^l, in the mobile phase was to evaluate its value in pure water, s_w. This value was found by extrapolation $\phi_w^l \rightarrow 1$. For the extrapolation, a linear fit was used for Vydac, LiChrospher, Hypersil and Partisphere and a second order polynomial fit was used for Silasorb and SG-7/G. The s_w values are listed in Table 3.

The s_w value for each stationary phase was used to calculate K_{wo} by plotting $ln\ (s_w\text{-}s)$ against ϕ_w^l/ϕ_o^l. These plots are shown in Figure 11. According to equation (3) the K_{wo} value for a given system is a negative slope of the $ln\ (s_w\text{-}s)$ vs. ϕ_w^l/ϕ_o^l plot (Table 3). All these values are smaller than unity. The values of K_{wo} characterize sorption of solvents onto the stationary phase. For an ideal adsorption model, when

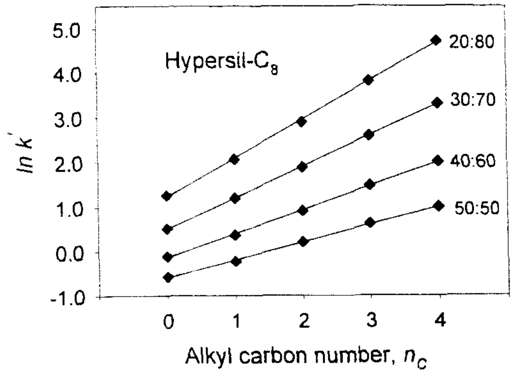

Figure 8. Dependence of *lnk'* on the alkyl carbon number n_c for Hypersil C-8 phase.

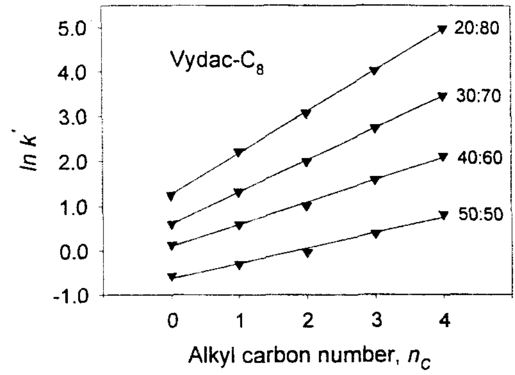

Figure 9. Dependence of *lnk'* on the alkyl carbon number n_c for Vydac C-8 phase.

$K_{wo} = 1$, the concentration of solvents in both phases is equal. When $K_{wo} > 1$, water is adsorbed preferentially in the surface phase and when $K_{wo} < 1$, which is the case in the current study, the organic solvent is preferentially adsorbed in the bonded phase. Equation (2) satisfies this condition at low values of ϕ_w^l/ϕ_o^l. The sorption excesses of water $(\phi_w^s - \phi_w^l)$ in the surface phase were calculated and plotted against the volume fraction of water in the mobile phase for all systems studied (see Figure 12). It was found that for all phases the sorption excess of water is negative. When $(\phi_w^s-\phi_w^l) < 0$, then $(\phi_o^s-\phi_o^l) > 0$, and the organic solvent (acetonitrile) is sorbed preferentially into the surface phase. However, the magnitude of the excess is

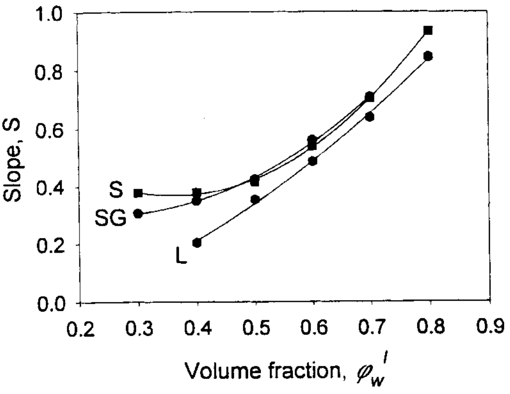

Figure 10. Logarithm of the methylene selectivity, *s*, as a function of the mobile phase concentration.

Table 3

The s_w and K_{wo} Values for the Silica Columns Studied

Name of the packing	s_w	K_{wo}
Vydac - C_8	1.26	0.31
Silasorb - C_8	1.57	0.18
LiChrospher - C_8	1.14	0.34
Partisphere - C_8	1.22	0.31
Hypersil - C_8	1.17	0.31
SG-7/G - C_8	1.42	0.24

different for each stationary phase depending on its surface properties. The comparison of the surface excesses shows that there is a correlation between the surface excesses of water and the amount of chemically adsorbed water, i.e. its fraction related to the condensation of the surface silanols as well as the coverage density for a given bonded phase.

For SG-7/G and Silasorb the quantity $(\phi_w^s-\phi_w^l)$ is the most negative. It means that acetonitrile is adsorbed stronger in these stationary phases in comparison with the remaining phases. These findings can be related to the amount of the thermodesorbed water in step II and the surface coverage data (Table 2).

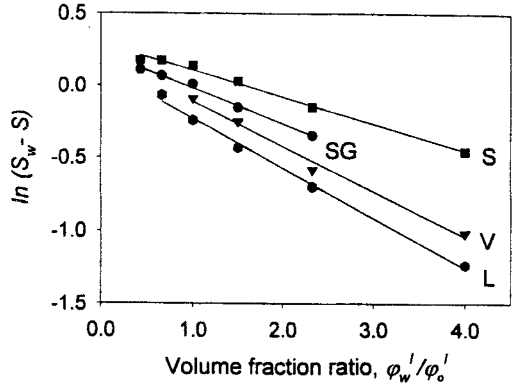

Figure 11. Plot illustrating the determination of K_{wo} according to equation (3).

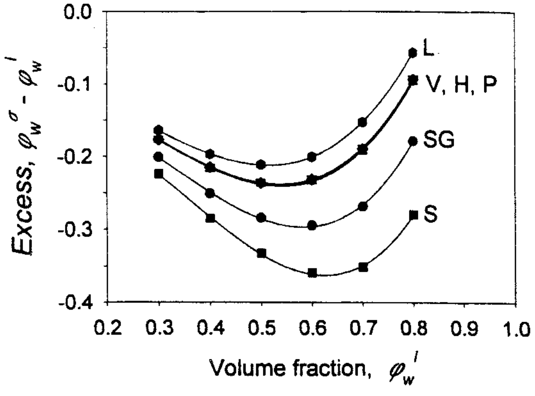

Figure 12. Surface excess of water as a function of the mobile phase concentration, φ_w^l.

The data shown in Table 2 suggest that the maximum negative excess of water should be for SG-7/G, not Silasorb. Silasorb has a greater number of residual silanols than SG-7/G, but also shows greater surface coverage.

Vydac shows a very ambiguous behavior. From the TGA studies, it was found that Vydac has an enormously large amount of water released in step II. Since chemisorbed/structural water is related to number of silanol groups on the surface, Vydac should exhibit a very large excess of water adsorbed. However, this is not the case. The sorption excess of water on Vydac is moderately negative in comparison to other silicas. Therefore, the large amount of water released in TGA step II is probably due, mainly, to chemisorbed/structural water. Only a small part of the water amount released in the step II can be attributed to condensation of surface silanols. Such behavior can be explained by the presence of the metal impurities on the surface of Vydac. However, this interpretation requires a further experimental confirmation.

CONCLUSIONS

In the current work six different silica gels were used to prepare monomeric octyl bonded phases. The surface properties of these materials were evaluated using high-resolution thermogravimetry and reversed-phase chromatography. The TGA data were used to get qualitative information about surface reactivity and surface heterogeneity of the samples studied.

In addition to the thermogravimetric study, retention measurements were carried out for alkyl benzenes on the silica-based octyl phases. The incremental (methylene) selectivities were calculated from these retention data. For each octyl phase, the methylene selectivity values were used to calculate the thermodynamic equilibrium constant, K_{wo}, which describes sorption of solvents into the stationary phase. Substantial differences were observed in the surface compositions of the systems studied. These differences were correlated with the surface and structural properties of the silicas used to synthesize octyl bonded phases. A comparison of the sorption excesses of water showed that, for all systems studied, the sorption excess of water was negative. Thus, organic solvent (acetonitrile) was adsorbed preferentially in each system. The magnitude of the negative excess varied significantly among the systems studied and shows some correlation with the amount of residual silanols and the coverage density of bonded octyl ligand.

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