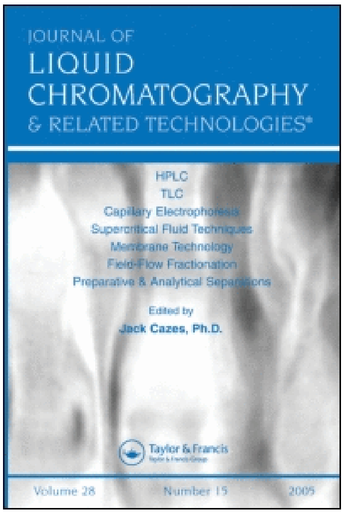

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Study of the Retention Characteristics of Calix[4]arene-bonded Silica Stationary Phase and Comparison with Common Phases for HPLC Using Linear Solvation Energy Relationships

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To cite this Article Huai, Q. Y. and Zuo, Y. M.(2006) 'Study of the Retention Characteristics of Calix[4]arene-bonded Silica Stationary Phase and Comparison with Common Phases for HPLC Using Linear Solvation Energy Relationships', Journal of Liquid Chromatography & Related Technologies, 29: 6, 801 — 814

To link to this Article: DOI: 10.1080/10826070500530252

URL: http://dx.doi.org/10.1080/10826070500530252

Journal of Liquid Chromatography & Related Technologies®, 29: 801–814, 2006

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070500530252

Study of the Retention Characteristics of Calix[4]arene-bonded Silica Stationary Phase and Comparison with Common Phases for HPLC Using Linear Solvation Energy Relationships

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Abstract: The similarities and differences in retention characteristics of *p-tert*-butyl-calix[4]arene-bonded and three other silica-based phases have been elucidated by the use of linear solvation energy relationships (LSERs). These phases were investigated in a common mobile phase. The results of LSERs on *p-tert*-butyl-calix[4]arene-bonded phase shows resemblances and differences to other silica-based reversed-phases. The retention of solutes on all the silica-based phases are dominated by two factors: the solute size and hydrogen bond acceptor basicity. But, for *p-tert*-butyl-calix[4]arene-bonded phase, the main retention governing factor is the solute size, which contribution accounts for 63% of the variance in log *k* values. The *s* coefficient is small, but positive, which is unlike the common reversed phase stationary phases. The *r* coefficient, which is small and positive, showed the new phase has greater $\pi-\pi$ interaction to solutes than all other phases, and relatively high selectivity to polyaromatic hydrocarbons. The retention mechanism of the phase, mainly, is a partitioning mechanism.

Keywords: HPLC, Linear solvation energy relationships (LSERs), *p-tert*-Butyl-calix[4]arene–bonded silica stationary phase, Retention characteristics, Reversed-phases, Solute molecular volume

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INTRODUCTION

Linear solvation energy relationships (LSERs) are an important and successful method for underlying principles and retention mechanism of RPLC. LSERs were first developed by Kamlet, Taft, and their coworkers in the mid-1970s.[1,2] Based on this model, the free energy of retention can be correlated with various fundamental molecular properties in RPLC; they include cavity formation/dispersive interactions, dipolarity/polarizability interactions, and hydrogen-bonding interactions in the LSERs. The new LSER equation for RPLC, as developed by Abraham,[3] relates retention to the solute's properties as follows:

$$\log k = \log k_0 + vV_2 + s\pi_2^* + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + rR_2 \tag{1}$$

Here, log k_0 is the regression intercept. The solute molecular descriptors are V_2, π_2^*, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and R_2, where V_2 is the solute's molecular volume competing according to McGowan;[4,5] π_2^* is its dipolarity/polarizability, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ are the solute's overall hydrogen bond acidity and basicity, respectively, and R_2 is its excess molar refraction. The coefficients v, s, a, b, and r are related to the chemical nature of the mobile and stationary phases. Here, v, s, a, and b are nonzero when there are differences in the mobile and stationary phases' cohesiveness/dispersiveness, dipolarity/polarizability, hydrogen bond acceptor (HBA) basicities, and hydrogen bond donor (HBD) acidities, respectively. The rR_2 term compensates for the inadequacy of lumping the dipolarity/polarizability into a single parameter (π_2^*) and reflects the tendency of the system (mobile/stationary phases) to interact with solutes through π- and n-electron pairs.[6] For a given mobile-/stationary-phase pair, the sign and magnitude of the coefficients indicate the direction and relative strength of different kinds of solute/stationary and solute/mobile-phase interactions affecting retention.

Some researches using linear solvation energy relationships (LSERs) have been carried out to elucidate the intermolecular processes and to predict retention data in RPLC. Tan[7,8] focused on different octadecyl- and octyl-bonded silica based phases (C_{18}-SiO_2 and C_8-SiO_2, respectively) while Li and Carr[9] compared polybutadiene-coated zirconia based phases (PBD-ZrO_2) with C_{18}-SiO_2 phases. Abraham et al.[3] characterized artificial membrane stationary phases. Zhao and Carr compared the retention characteristics of aromatic and aliphatic reversed phases.[10] Recently, we compared the retention characteristics of ferrocene bonded silica stationary phase and other silica-based reversed phases.[11]

LSER studies on C_8-SiO_2, C_{18}-ZrO_2, PBD-ZrO_2[7–9] indicate that, on all of these phases, the solute's size (V_2) and its HBA basicity ($\Sigma\beta_2^H$) are the two major contributions to the retention; the solute's dipolarity/polarizability (π_2^*) and its HBD acidity ($\Sigma\alpha_2^H$) are much less important while, on ferrocene-bonded silica phase, the retention is dominated by excess molar refraction and hydrogen bond acceptor basicity.

Most recently, we have synthesized and evaluated an end-capped *p-tert*-butyl-calix[4]arene bonded stationary phase C[4]-SiO_2 for reversed phase HPLC[12] and found its retention character is quiet similar to that of ODS. Here, we attempted to assess the chemical origin of the differences in retention characteristics between our phase and C_{18}-SiO_2, C_8-SiO_2, and Ph-SiO_2 phases. First, we obtained retention data for a single, carefully chosen, set of solutes for the *p-tert*-butyl-calix[4]arene bonded stationary phase. Second, we compared the LSER coefficients for the different stationary phases in a fixed mobile phase. Since the mobile phase is fixed, the variables corresponding to the mobile phase properties are constant and, hence, the differences in the LSER coefficients reflect different properties of the stationary phases as they exist in equilibrium with the mobile phase. Finally, we wanted to determine whether there is any difference in the selectivities of C[4]-SiO_2. Such studies will permit us explore the practical applications of C[4]-SiO_2.

EXPERIMENTAL

Instruments

HPLC was performed using a Shimadzu LC-AA liquid chromatograph equipped with an ultraviolet detector and a computer based SSI Chem Station which was used to carry out the chromatographic measurements.

Reagents and Materials

The organic solvent for the chromatographic measurements was HPLC grade acetonitrile. HPLC water was produced by treatment of house deionized water with a Brarnsted Nanopure deionizing system, which was equipped with an organic-free cartridge and a 0.2-μm filter. All test solutes were commercially available and were dissolved in acetonitrile at a concentration of 1–2 $\mu g \cdot L^{-1}$, depending on their solubilities.

Four bonded phases were used in this study. C[4]-SiO_2 was *p-tert*-butyl-calix[4]arene-bonded phase, based on Kromasil silica (pore size = 100 Å).[12] C_{18}-SiO_2 was Hypersil C_{18} (Phenomenex; pore size = 120 Å). C_8-SiO_2 was Zorbax C_8 (Dupont; pore size = 100 Å). Ph-SiO_2 was an Alltima Phenyl column (Alltech Associate Inc.). The particle size for all phases was 5 μm. All the phases were slurry-packed into stainless columns (150 mm × 4.6 mm i.d.).

Chromatographic Conditions

All chromatographic measurements were made in triplicate at 25°C, at a flow rate of 1 $mL \cdot min^{-1}$ with UV detection at 254 nm. The dead time was detected by injecting acetone. The mobile phase is 50:50 acetonitrile:water. The injection volume was 2 μL.

RESULTS AND DISCUSSION

LSER Study of Retention Data

The 36 solutes listed in Table 1 were carefully selected from 87 test solutes in ref.,[7] which cover a very wide range of solvatochromic parameter values (V_2, π_2^*, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and R_2). In Table 1, we report the log k values for 36 solutes on the *p-tert*-butyl-calix[4]arene-bonded stationary phase in acetonitrile:water (volume ratio, 50:50), based on triplicate determinations of the retention time. The average standard deviation of all the measurements of the retention factor is less than 2%. The LSER equation of C[4]-SiO_2 is obtained from multivariable linear regression of log k against the solute descriptors, V_2, π_2^*, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and R_2.

$$\begin{aligned}\log k = {} & (-0.50 \pm 0.03) + (1.29 \pm 0.04)V_2 + (0.03 \pm 0.01)\pi_2^* \\ & - (0.60 \pm 0.03)\Sigma\alpha_2^H - (1.63 \pm 0.04)\Sigma\beta_2^H + (0.12 \pm 0.03)R_2 \\ & n = 36, \overline{sd} = 0.03, r = 0.06, P < 0.001. \end{aligned} \tag{2}$$

The variance-covariance matrix of these descriptors is shown in Table 2. As we expected, V_2 and R_2, π_2^* and R_2 are somewhat correlated. Despite the fact that there is a high proportion of very polar and HB-active solutes, which are usually the hardest solutes to fit to the data set, the result is quite acceptable. In general, the fits become better when the data set has a high proportion of nonpolar solutes with low values of π_2^*, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$. The goodness of fit to the equation can be examined from several perspectives. First, the correlation coefficient (r) for the equation is good ($r = 0.996$). Second, the average residual is 0.03. Third, the plot of experimental log k against calculated log k (Figure 1) for C[4]-SiO_2 in 50:50 acetonitrile:water measured in this study shows no serious outliers. The LSER coefficients of the four stationary phases are summarized in Table 3.

Significance of the LSER Coefficients (*v*, *s*, *a*, *b*, *r*) of the Four Different Stationary Phases

In Figure 2, we compare the coefficients of the four phases in the common mobile phase, which is 50:50 acetonitrile:water. The standard deviations of the coefficients are indicated by error bars. This figure shows that C_{18}-SiO_2 and C_8-SiO_2 are very similar, while the Ph-SiO_2 and C[4]-SiO_2 are different.

Table 1. Solutes and solute descriptors

No.	Solutes	V_2	π_2^*	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	R_2	log*k*
1	Benzene	0.716	0.52	0	0.14	0.610	0.2466
2	Toluene	0.857	0.52	0	0.14	0.601	0.3746
3	Ethylbenzene	0.998	0.51	0	0.15	0.613	0.5340
4	n-Propylbenzene	1.139	0.50	0	0.15	0.604	0.7227
5	n-Butylbenzene	1.280	0.51	0	0.15	0.600	0.9030
6	Aniline	0.816	0.96	0.26	0.41	0.955	−0.2717
7	N-Methylaniline	0.957	0.90	0.17	0.43	0.948	−0.0526
8	4-Methylaniline	0.957	0.90	0.23	0.23	0.923	0.1956
9	4-Nitroaniline	0.991	1.91	0.42	0.42	1.220	−0.0932
10	3-Chloroaniline	0.939	1.10	0.30	0.30	1.053	−0.0074
11	Phenol	0.775	0.89	0.60	0.30	0.805	−0.3696
12	4-Nitrophenol	0.949	1.72	0.82	0.26	1.070	−0.1618
13	Benzoic alcohol	0.916	0.87	0.33	0.56	0.803	−0.4512
14	p-Xylene	0.998	0.52	0	0.16	0.613	0.5349
15	4-Nitrotulene	1.032	1.11	0	0.28	0.870	0.3831
16	methoxybenzene	0.916	0.75	0	0.29	0.708	0.2181
17	Acetophenone	1.014	1.01	0	0.48	0.818	0.0092
18	Benzophenone	1.481	1.50	0	0.50	1.447	0.5795
19	1-Chloro-4-nitrobenzene	0.961	0.75	0	0.02	0.825	0.6793
20	N,N-Dimethylaniline	1.098	0.84	0	0.41	0.957	0.3067
21	Pyridine	0.675	0.86	0	0.52	0.631	−0.5160
22	4-Methylpyridine	0.816	0.75	0	0.58	0.598	−0.4075
23	Nitrobenzene	0.891	1.11	0	0.28	0.871	0.1991

(*continued*)

Table 1. Continued

No.	Solutes	V_2	π_2^*	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	R_2	log*k*
24	Ethyl benzoate	1.214	0.85	0	0.46	0.689	0.3366
25	Fluorobenzene	0.734	0.57	0	0.10	0.477	0.2906
26	Chlorobenzene	0.839	0.65	0	0.07	0.718	0.4500
27	Bromobenzene	0.891	0.73	0	0.09	0.882	0.4729
28	Iodobenzene	0.975	0.82	0	0.12	1.188	0.5572
29	Naphthalene	1.085	0.92	0	0.20	1.340	0.5705
30	Bithphenyl	1.324	0.99	0	0.22	1.360	0.7719
31	Acenaphthene	0.988	0.77	0	0.20	1.001	0.4185
32	Phenanthrene	1.454	0.34	0	0.26	2.290	0.8902
33	Anthrancene	1.454	1.29	0	0.26	2.056	0.9071
34	Fluorene	1.357	1.06	0	0.20	1.588	0.8855
35	Pyrene	1.585	1.71	0	0.29	2.808	0.9972
36	Benzo[a]pyrene	1.954	1.98	0	0.44	3.625	1.2483

Values of V_2, π_2^*, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and R_2 were obtained from ref.[4,5]

Table 2. Variance-covariance of solute descriptors

	V_2	π_2^*	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	R_2
V_2	1				
π_2^*	0.4733	1			
$\Sigma\alpha_2^H$	−0.2536	0.3895	1		
$\Sigma\beta_2^H$	0.1231	0.4186	0.2005	1	
R_2	0.8493	0.6201	−0.0739	0.1570	1

The *v* Coefficient

As we mentioned above, the *v* coefficient reflects the difference in the mobile- and stationary-phase cohesiveness/dispersiveness, complementary to the solute size.[7] When we compared the *v* coefficients of the phases in the fixed mobile phase (Table 3), we noticed that the two aliphatic phases (C_{18}-SiO_2, C_8-SiO_2) and C[4]-SiO_2 have the largest and most comparable *v* values (1.62 ± 0.05, 1.47 ± 0.03, and 1.29 ± 0.03, respectively), but the aromatic phases (Ph-SiO_2) have considerably smaller and distinguishable *v* coefficients (0.70 ± 0.08).

The *v* coefficient is influenced by two factors, which are cavity formation and dispersion interaction. We rationalize these differences as being due to the

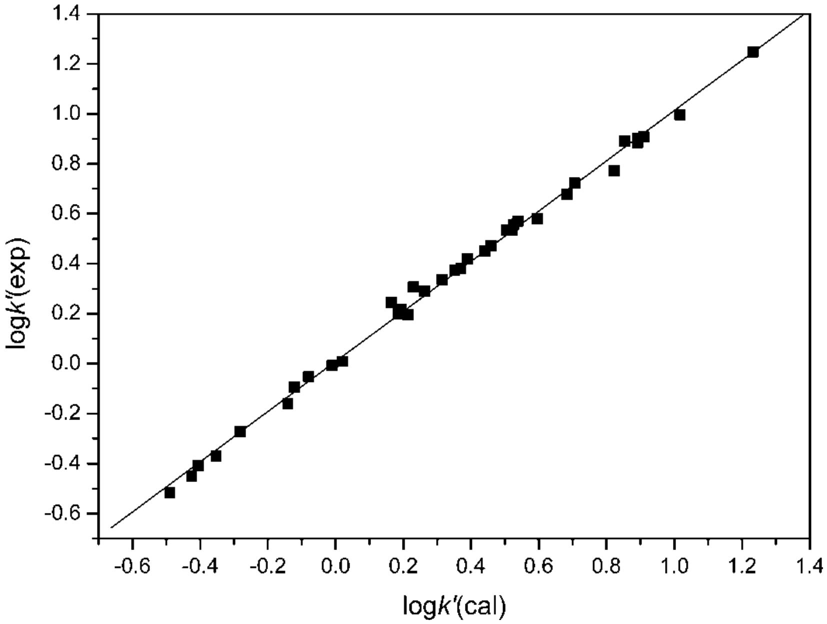


Figure 1. Experimental vs calculated log *k* for C[4]-SiO_2 in 50:50 acetonitrile:water.

Table 3. Coefficients of LSERs equations[a]

Phase	log k_0	v	s	a	b	r	$\overline{sd}$[c]	r[d]
C[4]-SiO_2	−0.50 ± 0.03[e]	1.29 ± 0.04	0.03 ± 0.01	−0.60 ± 0.03	−1.33 ± 0.04	0.12 ± 0.03	0.03	0.996
Ph-SiO_2[b]	−0.22 ± 0.66	0.83 ± 0.07	−0.15 ± 0.05	−0.34 ± 0.05	−0.99 ± 0.07	0.09 ± 0.07	0.04	0.990
C_{18}-SiO_2[b]	−0.23 ± 0.05	1.62 ± 0.05	−0.32 ± 0.03	−0.54 ± 0.04	−1.77 ± 0.06	0[f]	0.03	0.998
C_8-SiO_2[b]	−0.28 ± 0.03	1.47 ± 0.03	−0.25 ± 0.03	−0.41 ± 0.04	−1.71 ± 0.04	0[f]	0.06	0.995

[a] Regression results of log k against the solute descriptors, V_2, π_2^*, $\Sigma\alpha_2^{\mathrm{H}}$, $\Sigma\beta_2^{\mathrm{H}}$, and R_2.

[b] Regression results incited from ref.[10] which mobile phase was 50:50 acetonitrile:water, experimental temperature was 25°C.

[c] Average residual of the fit.

[d] Correlation coefficient.

[e] Standard deviation.

[f] Not statistically significant.

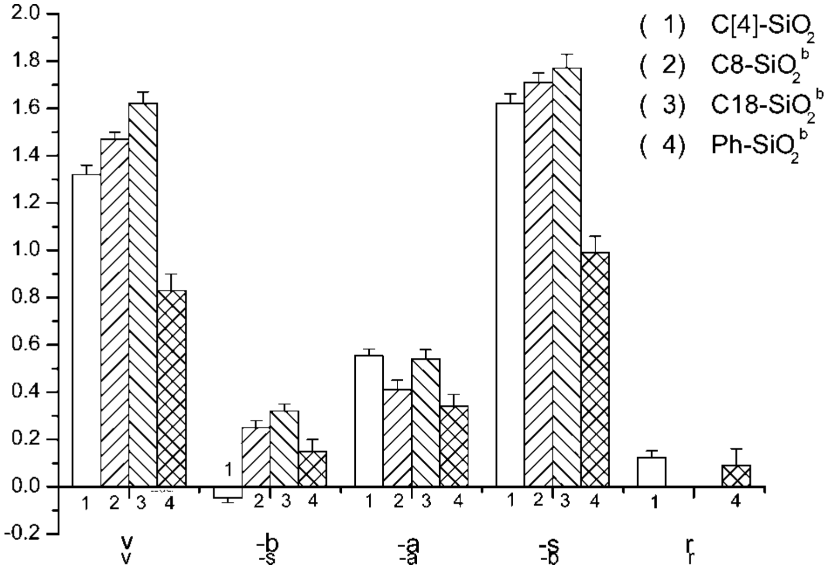


Figure 2. Comparison of the *v*, *s*, *a*, *b*, and *r* coefficients for four different stationary phases in 50:50 acetonitrile:water:(1) C[4]-SiO_2; (2) Ph-SiO_2; (3) C_{18}-SiO_2; (4) C_8-SiO_2.

opposing effects of the net unfavorable cavity formation arising mostly in the mobile phase and is predominant in the stationary phase.[7,13,14] The free energy of the methylene group (G^0_{CH2}) from the gas phase to bulk hexadecane or toluene is very large and negative (-634[13] and $-697\,cal \cdot mol^{-1}$[15], respectively); on the other hand, ΔG^0_{CH2} from the gas to water is only $+159\,cal \cdot mol^{-1}$. This clearly indicates dispersive interaction between the solute and the nonpolar stationary moieties.

Tan et al. stated that the aqueous/mobile phase is far more cohesive than is the bonded stationary phase.[7] This is, of course, the origin of the hydrophobic effect and the solvophobic model of RPLC.[16] However, at a fixed mobile phase composition (e.g., 50:50 acetonitrile:water), the variations in the *v* coefficients among these four phases are due to the differences in the cohesiveness (also termed the cohesive energy density[17]) and dispersion interactions of the aromatic and aliphatic stationary phases. In general, aromatic liquids are more cohesive than aliphatic liquids. For instance, benzene's solubility parameter (δ^2_H) is $81\,cal \cdot mL^{-1}$ and octadecane's δ^2_H is $66\,cal \cdot mL^{-1}$.[18] In addition, in the case of the inorganic oxide phases, the highly polarzable aromatic of the aromatic phases might allow more of the organic components (acetonitrile) in the mobile phase to sorb than do the aliphatic groups. The net result of the greater cohesiveness of the aromatic phase (Ph-SiO_2) leads to smaller *v* coefficients for the aromatic phases, as compared to the aliphatic phases (C_{18}-SiO_2 and C_8-SiO_2).

C[4]-SiO_2 has both alkyl chains and phenyl groups in its structure, so the *v* coefficient is larger than that of Ph-SiO_2 and smaller than that of aliphatic phases.

Dispersive interactions, also called the London interactions, are related to the refractive index of a material. The lower the refractive index of a substance, the weaker is the dispersive interaction. On the basis of the refractive indices of water (1.333), octadecane (1.44), and benzene (1.501),[18] aqueous mobile phases are much less dispersive than are organic stationary phases; furthermore, among the organic stationary phases, aliphatic stationary phases are less dispersive than aromatic stationary phases. These differences in the exoergic dispersive effects between the mobile and stationary phases should lead to a more positive *v* coefficient for the aromatic phases. However, the *v* coefficients for the aromatic phases are experimentally smaller. Given the high degree of miscibility of toluene and acetonitrile, in comparison to the very low miscibility of hexane and acetonitrile, we believe that the smaller *v* coefficient of the aromatic phase (Ph-SiO_2) results from a very high sorption of acetonitrile from the mobile phase.

The *b* Coefficient

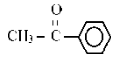
The *b* coefficient represents the difference in HBD acidity of the mobile and stationary phases. The large and negative *b* coefficient indicates that the mobile phase is a much stronger hydrogen bond acid than the stationary phase. Obviously neither alkyl nor phenyl groups have any inherent HBD acidity (α); therefore, the acidity of the stationary phase can only arise from sorbed mobile-phase components and from accessible silanol groups on the support surface. The aqueous mobile phase is highly acidic, since water is a very strong HBD acid ($\alpha_{\text{water}} = 1.17$). Among the four phases, C[4]-SiO_2 has a negative *b* coefficient (-1.6), similar to aliphatic phases ($b_{\text{C18,C8}-\text{SiO2}} = 1.7$), and it is bigger than that of Ph-SiO_2. There are at least two possibilities, for Ph-SiO_2 has higher HBD acidity than do the aliphatic phases. (1) aromatic phases absorb more acidic mobile phase than do the aliphatic; (2) the bonding density of the Ph-SiO_2 is lower and, thus, the surface hydroxyl groups are more accessible.

The *a* Coefficient

For all RPLC systems studied here and elsewhere, the *a* coefficient is small and negative. The HBA basicities (β) of the mobile and stationary are the complementary properties to the solute's HBD acidity ($\Sigma\alpha_2^H$). The 50/50 acetonitrile/water mobile phase is only moderately basic; pure water ($\beta = 0.47$) and pure acetonitrile ($\beta = 0.40$) are both only modestly basic. Alkyl chains and phenyl groups have almost no basicities ($\beta \approx 0$). Thus, the HBA basicity of the stationary phase arises mainly from absorbed mobile phase and partially from residual silanol groups on the surface of the silica. Based on a solvatochromic study of the HBA basicity of mixture using an —OH hydrogen bond donor, Dallas[19] determined the (β value for an acetonitrile-water (50/50, v/v) mixture to be 0.68, and that for bulk hexadecane saturated with the same mixture to be 0.66. Due to the larger amount of organic modifier and water present in a bonded phase, relative to bulk hexadecane, the β value for a bonded phase is expected to be even closer to that of an organic aqueous mixture. Dallas's studies clearly indicate that the mobile phase is only slightly more basic than is the bonded phase. Based solely on its HB donor acidity, a solute would have only a slight preference for the mobile phase over the stationary phase and, thus, a small and negative *a* coefficient for $\Sigma\alpha_2^H$ is predicted and observed. As the $\Sigma\alpha_2^H$ of a solute increase, the affinity of the solute towards the mobile phases relative to its affinity for the stationary phase increases slightly, thereby, leading to lower retention. In addition, we observe that the C[4]-SiO_4 phase has a relatively larger value of the *a* coefficient ($a = 0.6$) as compared to the other three phases. This may originate in the silica end-capping process[12] which reduces the amount of accessible surface hydroxyl groups on the silica gel.

The *s* Coefficient

In previous studies, all phases used in RPLC have a small negative *s* coefficient, which indicates that the difference in dipolarity/polarizability between the mobile and stationary phases is quite small. The negative sign tells us that dipolar solutes only slightly prefer the mobile over the stationary phase. Both components of the mobile phase, water ($\pi^*_{\text{water}} = 1.17$) and acetonitrile ($\pi^*_{\text{acetonitrile}} = 0.75$), are highly dipolar substances; in the stationary phase, the dipolar interactions are attributed mainly to the sorbed mobile-phase components. The Ph-SiO_2 has less negative *s* coefficients than do the aliphatic phase because the aromatic phase is more polarizable than the aliphatic phases; the π^* of benzene is 0.52, while the π^* of the cyclohexane is zero.

In our study, the *s* coefficient of C[4]-SiO_2 is small, but positive. We think there are two possibilities for this: (1) there is a strong dipolar group ($-\overset{O}{\overset{\|}{C}}-$) in the structure of the C[4]-SiO_2 (π  = 1.13). (2) phenyl groups of calix[4]arene can be easily polarized which then sorb small amounts of mobile phase.

The *r* Coefficient

The *r* coefficient is a correction factor to the dipolar/polarizability term (the *s* coefficient) and reflects the tendency of the system to interact with the solute through π-and n- electron pairs.[6] In contrast to the negative *s* coefficients, the r coefficients are ether nearly zero or positive. A positive r coefficient implies that a stationary phase has more π-π interactions with the solute than does the mobile phase ($R_{\mathrm{water}} = 0.0$ and $R_{\mathrm{acetonitrile}} = 0.237$).

Table 3 shows that the r coefficient of C[4]-SiO_2 is the largest one among the four phases. This indicates that the π-π interaction between the solutes and the stationary phase is significant. This result agrees with our previous study.[12]

Comparison of Fc-SiO_2, Ph-SiO_2, and Aliphatic Phases in Contribution from Different Interactions

Table 4 compares the percent variance of log k accounted for by each interaction term in the LSERs. We immediately see some resemblances and differences between these four phases. First, all the four phases show very comparable and large contributions from vV_2 and $b\Sigma\beta_2^{\mathrm{H}}$ terms. On the other hand, the *p-tert*-butyl-calix[4]arene-bonded stationary phase (C[4]-SiO_2) has a large contribution from vV_2 terms, which accounts for 63% of the variance in log k values. It shows a slightly increased contribution from the rR_2 term. Our observation of a relatively high r coefficient for C[4]-SiO_2 is in accord with our previous study. Second, all other phases (C_8-SiO_2, C_{18}-SiO_2 and Ph-SiO_2) have similar contributions from the $s\pi_2^*$, $a\Sigma\alpha_2^{\mathrm{H}}$ and rR_2 terms, while C[4]-SiO_2 has nearly no contribution from $s\pi_2^*$. Third, the rR_2 term for C_8-SiO_2 and C_{18}-SiO_2 are negligible; however, for Ph-SiO_2 and C[4]-SiO_2, it is relatively significant. This implies that the two phases have little polarizability and they might have selectivity towards highly polarizable solutes, such as polyaromatic hydrocarbons (PAHs). The percent variances in Table 4 do not add up to exactly 100, and this is probably because LSER theory does not include all possible interactions in the retention process.

Table 4. Contribution of each interaction term to retention[a]

	Percent variance due to solute term[b]				
Phase	vV_2	$s\pi_2^*$	$a\Sigma\alpha_2^{\mathrm{H}}$	$b\Sigma\beta_2^{\mathrm{H}}$	rR_2
C8-SiO_2[c]	40	4	6	48	0
C18-SiO_2[c]	40	5	6	45	0
Ph-SiO_2[c]	33	4	8	52	1
C[4]-SiO_2	63	0	6	30	2

[a] Based on retention data in 50:50 acetonitrile: water.

[b] Percent variance due to term x in the LSER is computed as $100C_x^2r_x^2/\sigma_{\log k}^2$, where x denotes the solute descriptor, C_x, the corresponding LSER coefficient, r_x^2 and $\sigma_{\log k'}^2$, the variance for x and log k, respectively.

[c] Obtained from ref.[7]

There are two proposed extreme retention mechanisms in RPLC:[20–27] the partitioning mechanism, in which a solute molecule is fully embedded within the stationary phase, and the adsorption process, in which the solute is only in surface contact with the stationary phase and is not fully embedded. On the basis of the work of Tan, the retention is partitioning-like for both the monomeric and polymeric bonded phases whose chains are eight carbons or more in length.[28] In our previous study we found that the retention mechanism of the C[4]-SiO_2 phase involves not only hydrophobic interaction and π-π interaction, but also host-guest interaction. If solutes and the C[4]-SiO_2 phase can form host-guest complexes in the mobile phase, the solutes should be embedded into the body of calix[4]arene. Then, the solute's molecular volume (V_2) should be the main factor which governs its retention on the C[4]-SiO_2 phase. In addition, if the retention mechanism of the C[4]-SiO_2 phase involves π-π interaction, the contribution of the rR_2 term would not be zero. The LSER study of the C[4]-SiO_2 phase shows that the contribution from vV_2 terms, which accounts for 63% of the variance in log k values and rR_2 term, is 2%. These results are in good accord with our previous study. The main retention governing factor for C[4]-SiO_2 is the solute's molecular volume, and thus, the retention mechanism is more partitioning-like.

CONCLUSIONS

Linear solvation energy relationships are an important and successful method for exploring differences in the retention characteristics and selectivity of different phases. *p-tert*-Butyl-calix[4]arene-bonded phase has more significantly different properties than do phenyl-bonded phase and aliphatic phases. The two major retention governing factors for C[4]-SiO_2 are the solute size and hydrogen bond acceptor basicity like other reversed phases, while the solute size is the major retention governing factor. For other stationary phases, the *s* coefficients are all small and negative for other stationary phases. For C[4]-SiO_2, the *s* coefficient is also small, but positive. But, it has no contribution to the solute's retention. C[4]-SiO_2 has the most positive *r* coefficient among other silica-based phases. This indicates that the $\pi-\pi$ interaction between the solutes and the stationary phase is relatively significant. These results are in agreement with our previous study. Because the solute size is a major retention governing factor for C[4]-SiO_2, the retention mechanism on it is more partitioning-like. In general, our LSER results and interpretations suggest that, on the C[4]-SiO_2 phase, a solute undergoes a more partitioning-like retention process.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China. Project number 20275018.

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Received June 3, 2005
Accepted November 14, 2005
Manuscript 6671