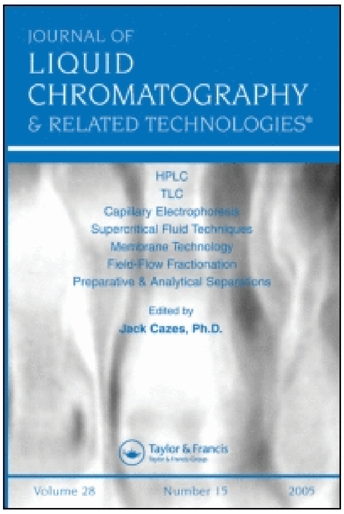

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Evaluation of Octadecene–Polybutadiene-Coated Zirconia Stationary Phase Based on Linear Solvation Energy Relationships

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ABSTRACT

A linear solvation energy relationships model is used to evaluate the retention behavior of a stationary phase based upon octadecene–polybutadiene–coated zirconia (C_{18}–PBD–ZrO_2) in reverse-phase liquid chromatography (RPLC). The logarithmic capacity factors of 29 solutes measured on C_{18}–PBD–ZrO_2 [$\log k'$(C_{18}–PBD–ZrO_2)] in acetonitrile–water (50 : 50, v/v) mobile phase vs. the solute's five interaction descriptors, the McGowan characteristic molar volume (V_2), dipolarity/polarizability (π_2^*), effective or overall hydrogen bond donor acidity ($\Sigma\alpha_2{}^H$), hydrogen bond acceptor basicity ($\Sigma\beta_2{}^H$), and excess molar refraction (R_2) are analyzed by multiple regression analysis and compared

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to other zirconia based stationary phases, and octadecyl-bonded silica (ODS). Through the principal component analysis (PCA), we found the descriptors, V_2, π_2^* and $\Sigma\beta_2{}^{\mathrm{H}}$ are the most important parameters governing the retention, as they represent more than 85.91% of the $\log k'$ variation. Finally, we came to the conclusion that the retention of C_{18}–PBD–ZrO_2 is a partition-like process.

Key Words: Linear solvation energy relationships (LSERs); Octadecene-polybutadiene-coated zirconia (C_{18}–PBD–ZrO_2); Principal component analysis (PCA).

INTRODUCTION

Reversed-phase liquid chromatography (RPLC) is the most commonly used mode of liquid chromatography. However, the retention mechanism in RPLC is still not completely understood. The retention phenomenon in RPLC depends, simultaneously, on various intermolecular interactions between the solute and the stationary phase, the solute and mobile phase, and stationary and mobile phase. Many early studies of RPLC suggested that the mobile phase plays the dominant role in establishing retention and selectivity.[1–5] However, more recent studies have recognized the active role of the stationary phase.[6–8]

LSERs is a simple and accurate method to evaluate the interaction of solute-stationary and solute-mobile phase. Kamlet et al. and Abraham, first developed LSERs in 1979, which allowed one to link physico-chemical solute properties (formation constants, enthalpies of solution, solubilities, and others) to particular solvent interaction parameter, such as π–π interactions, hydrogen bond accepting and donating character, polarity/polarizability, and "cavity term" related to the size of the solute molecule.[9–11] Now, the LSERs method has been extensively and successfully applied in conventional RPLC,[12] gas chromatography,[13] normal-phase liquid chromatography,[14] and more recently, to supercritical fluid chromatography.[15–18] Tan et al.[19] focused on different octadecyl- and octyl-bonded silica-based phases (ODS and C_8–SiO_2, respectively), while Li and Carr[20] compared polybutadiene–coated zirconia–based phases (PBD–ZrO_2) with ODS phases.

The most recent LSERs equation for RPLC, as developed by Abraham,[21] relates retention to the solute's properties as follows:

$$\log k' = \log k'_0 + \gamma V_2 + s\pi_2^* + \Sigma\alpha_2{}^{\mathrm{H}} + b\Sigma\beta_2{}^{\mathrm{H}} + rR_2 \tag{1}$$

where k' is the experimental retention factor, the $\log k'_0$ term is the intercept of the regression and is comprised of constant contributions from the solutes and the chromatographic system. The V_2, π_2^*, $\Sigma\alpha_2{}^{\mathrm{H}}$, $\Sigma\beta_2{}^{\mathrm{H}}$ and R_2 are the solute descriptors, where V_2 is the solute's molecular volume computed according to McGowan; π_2^* is the solute's dipolarity/polarizability that evaluates the ability of the solute to take part in dipole–dipole or dipole-induced interactions; $\Sigma\alpha_2{}^{H}$ is the solute's overall hydrogen bond acidity, and measures the ability of the solute to release its overall hydrogen atoms to form hydrogen bonds with the solvent; $\Sigma\beta_2{}^{H}$ is the solute's overall hydrogen bond basicity, and measures the ability of the solute to take part in the formation of hydrogen bonds by attracting hydrogen atoms from the solvent; R_2 is the excess molar refraction determined from the compound's refractive index, and represents the tendency of the solute to interact with a solvent phase through π- and n-electron pairs. The subscript "2" simply signifies that these parameters are solute descriptors.

The coefficients of these descriptors γ, s, a, b and r are obtained from multiple linear regression of $\log k$ vs. the solute descriptors. The sign and magnitude of the coefficients indicate the direction and relative strength of different kinds of solute/stationary phase and solute/mobile phase interactions affecting retention for a given pair of mobile–stationary condition. When the mobile phase is fixed, the coefficients of the descriptors reflect the characteristics of stationary phase.

In this paper, we used the LSERs equation to examine the retention-governing interactions of C_{18}–PBD–ZrO_2 stationary phase. The regression coefficients will be compared to those obtained on other phases, by other authors. Finally, we established the predicting equation that predicts the retention of the test solutes successfully.

EXPERIMENTAL

Materials

Acetonitrile, used as the mobile phase, was HPLC grade solvent. HPLC water was deionized water that was redistilled with silica equipment and treated through a 0.2 µm filter film. A series of 29 test solutes, shown in Table 1, were carefully chosen to cover a wide range of solute solvatochromatic properties. All solutes were commercially available and were dissolved in methanol, respectively, to give 0.5–1.0 mg/mL solutions.

HPLC

The zirconia support was synthesized by use of a modified method of polymerization-induced colloid aggregation (PICA).[22] C_{18}–PBD–ZrO_2 was prepared according to the method of C_{18}–PBD–Al_2O_3, as described earlier.[23] A chromatographic column (150 × 4.6 mm i.d.) was filled with C_{18}–PBD–

Table 1. Solutes, solute descriptors[24] and $\log k'$ determined on C_{18}–PBD–ZrO_2 in 50% acetonitrile/water mobile phase.

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	0.2219
2	Toluene	0.857	0.52	0	0.14	0.601	0.4267
3	Ethylbenzene	0.998	0.51	0	0.15	0.613	0.6675
4	Propylbenzene	1.139	0.50	0	0.15	0.604	0.9255
5	Butylbenzene	1.280	0.51	0	0.15	0.600	1.1767
6	Aniline	0.816	0.96	0.26	0.41	0.955	−0.4042
7	*N*-Methylaniline	0.957	0.90	0.17	0.43	0.948	−0.1222
8	*p*-Toluidine	0.957	0.95	0.23	0.45	0.923	−0.2128
9	*p*-Nitroaniline	0.991	1.91	0.42	0.42	1.220	−0.4507
10	Phenol	0.775	0.89	0.60	0.30	0.805	−0.3522
11	*p*-Nitrophenol	0.949	1.72	0.82	0.26	1.070	−0.4150
12	Benzyl alcohol	0.916	0.87	0.33	0.56	0.803	−0.5190
13	*p*-Xylene	0.998	0.52	0	0.16	0.613	0.6452
14	*p*-Nitrotoluene	1.032	1.11	0	0.28	0.870	0.2930
15	Anisole	0.916	0.75	0	0.29	0.708	0.1794
16	Acetophenone	1.014	1.01	0	0.48	0.818	−0.0823
17	Benzophenone	1.481	1.50	0	0.50	1.447	0.6058
18	*p*-Nitrobenzyl chloride	1.154	0.34	0	0.40	1.080	0.2255
19	*N*,*N*-Dimethylaniline	1.098	0.84	0	0.41	0.957	0.2744
20	Pyridine	0.675	0.86	0	0.52	0.631	−0.7334
21	Methyl pyridine	0.816	0.75	0	0.58	0.598	−0.5494
22	Nitrobenzol	0.891	1.11	0	0.28	0.871	0.0379
23	Ethylbenzoate	1.214	0.85	0	0.46	0.689	0.3631
24	Flurobenzene	0.734	0.57	0	0.10	0.477	0.2492
25	Chlorobenzene	0.839	0.65	0	0.07	0.718	0.4883
26	Bromobenzene	0.891	0.73	0	0.09	0.882	0.5310
27	Iodobenzene	0.975	0.82	0	0.12	1.188	0.6221
28	Naphthalene	1.085	0.92	0	0.20	1.340	0.6493
29	Anthracene	1.454	0.34	0	0.26	2.290	1.4992

ZrO_2 by use of a high pressure pump Model 6752B-100, made by Beijing Analytical Instrument Technical Company, Beijing, China. The packing was carried out under a pressure of 60 MPa, with ethanol as the pressure fluid and a mixture of toluene, cyclohexanol, and 1,4-dioxane (1 : 1 : 1, v/v) as the suspension medium.

The chromatograph, Model Varian 5060 equipped with an UV-100 detector was used to determine the capacity factor of test solutes. Fifty percent acetonitrile–water was used as mobile phase. All chromatographic measurements were made at a flow rate of 1.0 mL/min; the column temperature was 25°C. The UV detector was set at 254 nm, since all solutes were aromatic compounds. The dead time was determined by injecting acetone.

RESULTS AND DISCUSSION

Figure 1 shows the retention tendency of the 16 solutes on the three different phases, C_{18}–PBD–ZrO_2, polybutadiene coated zirconia (PBD–ZrO_2), and polystyrene coated zirconia (PS–ZrO_2). The retention tendency on the C_{18}–PBD–ZrO_2 phase is similar to that on the PBD–ZrO_2 phase, while the retention tendency on the PS–ZrO_2 is somewhat different; this is because C_{18}–

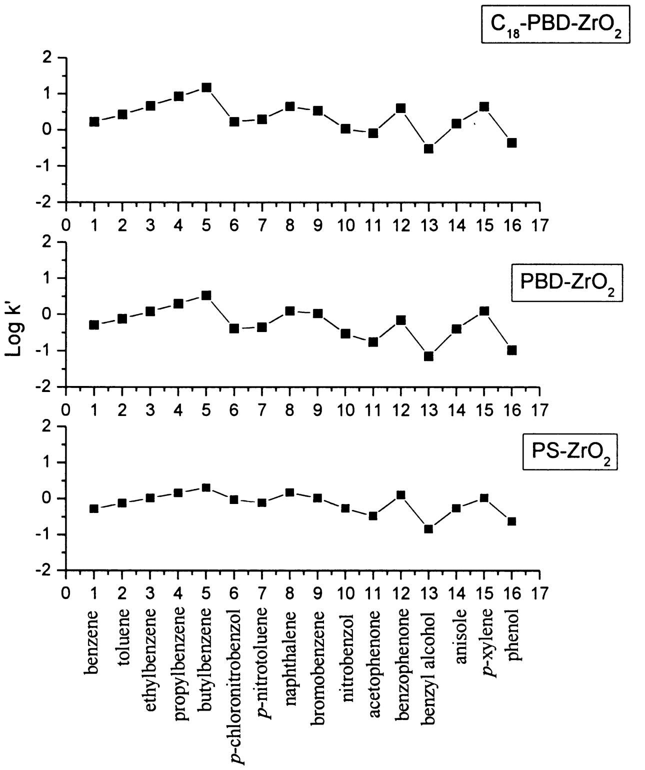

Figure 1. The retention tendency of 16 solutes on different stationary phases in 50% acetonitrile/water mobile phase. The data on PBD–ZrO_2 and PS–ZrO_2 were cited from Ref.[25]

PBD–ZrO_2 and PBD–ZrO_2 are aliphatic coated stationary phases, PS–ZrO_2 is an aromatic coated stationary phase.

Analysis of LSERs Coefficients

The LSERs coefficients are summarized in Table 2. The resulting values were obtained from multiple linear regression of $\log k'$ vs. the solute descriptors, V_2, π_2^*, $\Sigma\alpha_2{}^{H}$, $\Sigma\beta_2{}^{H}$, and R_2. The data of PS–ZrO_2, PBD–ZrO_2, and ODS were obtained from reference.[25] Through the analysis of these coefficients, we can see that the coefficients on the C_{18}–PBD–ZrO_2, PBD–ZrO_2, and C_{18}–SiO_2 are quite similar, while the coefficients on the PS–ZrO_2 are different. PS–ZrO_2 belongs to aromatic phase coated inorganic oxide based phase; the other three belong to aliphatic phase coated inorganic oxide based phases. The two kinds of packing have two different mechanisms, the retention of PBD–ZrO_2 and C_{18}–SiO_2 is a partition-like mechanism, but that of PS–ZrO_2 is a adsorption-like mechanism. Thus, we considered that the retention of C_{18}–PBD–ZrO_2 is a partition-like mechanism.

γ Coefficient

The γ coefficient reflects the difference in the mobile- and stationary-phase cohesiveness/dispersiveness, complementary to the solute's size. The cohesiveness and dispersiveness have opposite influence on the γ coefficient, we should consider them respectively.

When we compared the γ coefficients of the phases, we noticed that the aliphatic and aromatic phases have distinguishable γ coefficients (for example, C_{18}–PBD–ZrO_2 is 1.78 ± 0.02, PS–ZrO_2 is 1.09 ± 0.13). If the

Table 2. The results of multiple linear regression.

	Stationary phase			
	PS–ZrO_2	PBP–ZrO_2	C_{18}–SiO_2	C_{18}–PBD–ZrO_2
$\log k'$	-0.95 ± 0.11	-1.07 ± 0.05	-0.23 ± 0.05	-0.69 ± 0.02
γ	1.09 ± 0.13	1.58 ± 0.06	1.62 ± 0.05	1.78 ± 0.02
s	-0.20 ± 0.09	-0.42 ± 0.04	-0.32 ± 0.03	-0.32 ± 0.01
a	-0.27 ± 0.09	-0.40 ± 0.04	-0.54 ± 0.04	-0.46 ± 0.02
b	-1.48 ± 0.14	-2.01 ± 0.07	-1.77 ± 0.06	-1.89 ± 0.03
r	0.34 ± 0.12	0.17 ± 0.06	0	0.04 ± 0.01
sd	0.08	0.04	0.03	0.02
R-square	0.980	0.998	0.998	0.998

mobile phase is fixed, the variations in the γ coefficients are due to the differences in the cohesiveness of the aromatic and aliphatic stationary phases. In general, the highly polarizable phenyl groups of the aromatic phase might be easy to absorb more organic components in the mobile phase, than do the aliphatic groups. The net result of the greater cohesiveness of the aromatic phase leads to smaller γ coefficient for the aromatic phase, as compared to the 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 (1.5011), 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 phase. The aromatic phase should lead to a more positive γ coefficient. However, we noticed that the γ coefficient for the aromatic phase is smaller than that for the aliphatic phases. We believe, that the smaller γ coefficient of the aromatic phase results from a very high sorption of acetonitrile from the mobile phase, which makes the dispersive interaction weak, the cavity formation become dominant as compared to the dispersive interaction. In general, the γ coefficient of aromatic phase is smaller than that of aliphatic phases. For the aliphatic phases, C_{18}–PBD–ZrO_2 and PBD–ZrO_2, the long C_{18} chain of C_{18}–PBD–ZrO_2 restricted the sorption of mobile phase on its surface; therefore, C_{18}–PBD–ZrO_2 has a more positive γ coefficient.

s Coefficient

s reflects the difference between mobile- and stationary-phase in dipolar interaction. The small and negative *s* value indicates: (1) increasing dipolarity led to decreased retention, (2) a dipolar solute would have only a slight preference for the mobile phase to the stationary phase. Both components of mobile phase, water ($\pi^*_{\text{water}} = 1.17$) and acetonitrile ($\pi^*_{\text{acetonitrile}} = 0.75$), are strongly dipolar substances. In the nonpolar C_{18}–PBD–ZrO_2 stationary phase, the dipolar interaction is attributed mainly to the sorbed mobile-phase components. Aromatic phases has less negative *s* coefficient than do the aliphatic phases, because aromatic phase is more polarizable than aliphatic phases: the π^* of benzene is 0.52 while the π^* of cyclohexane is zero.

The aromatic phases sorbed more highly polarizable mobile phase, which make the difference between mobile and stationary phases small, therefore, the aromatic phase have a small negative *s* coefficient.

α Coefficient

The α coefficient is determined by the difference of hydrogen bond basicities between mobile and stationary phase. The HBA basicities (β) of mobile and stationary phase are the complementary properties to the solute's hydrogen bond donor (HBD) acidity. Both components of mobile phase, pure water ($\beta = 0.47$) and pure acetonitrile ($\beta = 0.40$) are modestly basic. The bonded alkyl chains and phenyl groups have low basicity ($\beta \approx 0.1$), thus, the HBA basicity of the stationary phase is established by the sorbed mobile phase component and the residual hydroxyl groups on the surface of the silica and zirconia. The more negative of α value, the less of stationary sorbed the mobile phase. The data in Table 2 show that the aromatic phases have smaller absolute values of the α coefficient, as compared to the aliphatic phases. This may originate in the following: (1) the basicity of the aromatic ring ($\beta_{\text{benzene}} = 0.12$) is higher than that of an aliphatic chain ($\beta_{\text{cyclohexane}} = 0$); (2) the mobile phase has greater solubility in the aromatic phases.

An ODS phase has more negative α value as compared to the C_{18}–PBD–ZrO_2, because ODS belong to bonded stationary phase while C_{18}–PBD–ZrO_2 belong to coated stationary phase, the residual hydroxyl groups of coated type phase are less than those of bonded type phase.

b Coefficient

The *b* coefficient represents the difference in HBD acidity of the mobile and stationary phase. The aqueous mobile phase is a highly acidic medium, since water ($\alpha_{\text{water}} = 1.17$) is an extremely strong HBD acid, and acetonitrile ($\alpha_{\text{acetonitrile}} = 0.19$) is a relatively weak HBD acid. Both the bonded alkyl and phenyl groups have no inherent HBD acidity ($\alpha = 0$). The large negative *b* coefficient obtained on all four columns (Table 2) suggests that the bonded phase is a much weaker HBD acid compared to the mobile phase. Thus, the acidity of stationary phase can only arise from sorbed mobile-phase components and from accessible silanol or zircanol groups on the support surface. Among the inorganic oxide-based phases, the aromatic phase has less negative *b* coefficient than do the aliphatic phases. This indicates the aromatic phase has higher HBD acidities than do the aliphatic phase. The probable reason is the aromatic phases sorb more acidic mobile phase than do the aliphatic phases.

We also notice that the zirconia-based phases have larger negative *b* coefficients than do the analogous silica-based phases. For example, C_{18}–PBD–ZrO_2 is -1.89, PBD–ZrO_2 is -2.0, while C_{18}–SiO_2 is -1.77. We suspect that this is due to the differences in the acidities of silanol and zircanol groups, the amount of water sorbed on the two surfaces may be different. The ability of silanol group sorbing water is stronger than that of the zircanol group.

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. In contrast to the negative *s* coefficients, the *r* coefficients are either 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. This is particularly true for aromatic phases due to the presence of phenyl groups ($R_{\text{benzene}} = 0.610$ and $R_{n\text{-octane}} = 0.0$). For PBD–$ZrO_2$, the polymer contains some residual olefinic unsaturation ($R_{\text{butadiene}} = 0.320$), which also have the π–π interaction ability. The *r* coefficient of PS–ZrO_2, C_{18}–PBD–ZrO_2, PBD–ZrO_2 are positive, the aromatic phase has more positive *r* values than do aliphatic phases. The experimental data indicates that the *r* coefficient of C_{18}–PBD–ZrO_2 is smaller than that of PBD–ZrO_2, but similar to ODS. The probable reason is: (1) C_{18} bonded on the surface of PBD–ZrO_2 made the olefinic unsaturation less; (2) the long C_{18} chain restricted the contact between the solutes and the surface of stationary phase.

Principal Component Analysis

The structure descriptors listed in Table 1 were analyzed by means of principal component analysis (PCA). The results shown in Table 3 indicate that all five descriptors can be represented by the three PCs, PC_1 38.31%, PC_2 29.92%, and PC_3 17.68%. Their sum is 85.91%. Therefore, the information is not lost when we conclude that three PCs represent total structure descriptors.

Table 3. The results of principal component analysis (PCA).

	PC_1	PC_2	PC_3
V_2	0.5351	0.7521	0.0167
π_2^*	0.7716	−0.4264	−0.0348
$\Sigma\alpha_2{}^H$	0.4067	−0.6713	0.5306
$\Sigma\beta_2{}^H$	0.5946	−0.2499	−0.7096
R_2	0.7176	0.4851	0.3122
Eigenvalue	1.9155	1.4959	0.8842
Total variance (%)	38.3103	29.9180	17.6832

π_2^* and R_2 have high loading on PC_1, which indicates that they have much in common; V_2 and $\Sigma\alpha_2{}^H$ have high loading on PC_2, which also indicate that they have similar characters; $\Sigma\beta_2{}^H$ has high loading on PC_3. One parameter, which has high loading, was selected from each PC as independent variables, and using multiple linear regression analysis, we find that $\log k'$ values have a better correlation with V_2, π_2^*, and $\Sigma\beta_2{}^H$ than with others. This indicates the retention of C_{18}–PBD–ZrO_2 is a more partition-like mechanism. The positions of solutes on the space, determined by V_2, π_2^*, and $\Sigma\beta_2{}^H$, are displayed in Fig. 2. Solutes do not form clusters on the three-dimensional scatter map. The result indicates that different solutes have different LSERs parameters, resulting in different retention.

The Predicting Equation

We used $\log k'$ of the test solutes on the C_{18}–PBD–ZrO_2 as the attributive variable, three descriptors, π_2^*, V_2, and $\Sigma\beta_2{}^H$, as the independent variables, establishing the predicting equation of C_{18}–PBD–ZrO_2 in 50% acetonitrile/water mobile phase, by means of multiple linear regression method as follow:

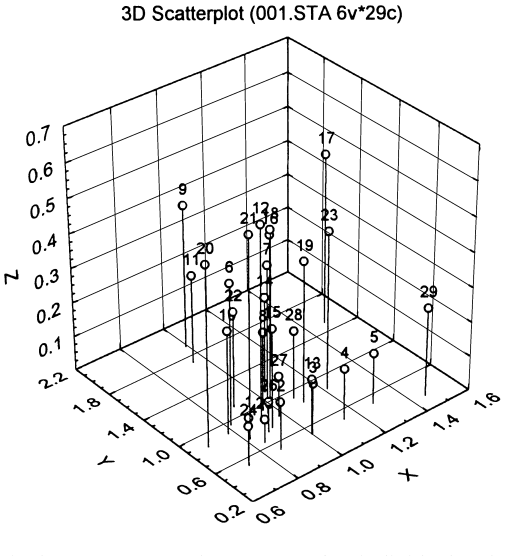

Figure 2. Principal component solute scores for individual solute on the space determined by π_2^*, V_2 and $\Sigma\beta_2{}^H$. The test solutes number is the same as those in Table 1. X represents π_2^*, Y represents V_2, and Z represents $\Sigma\beta_2{}^H$.

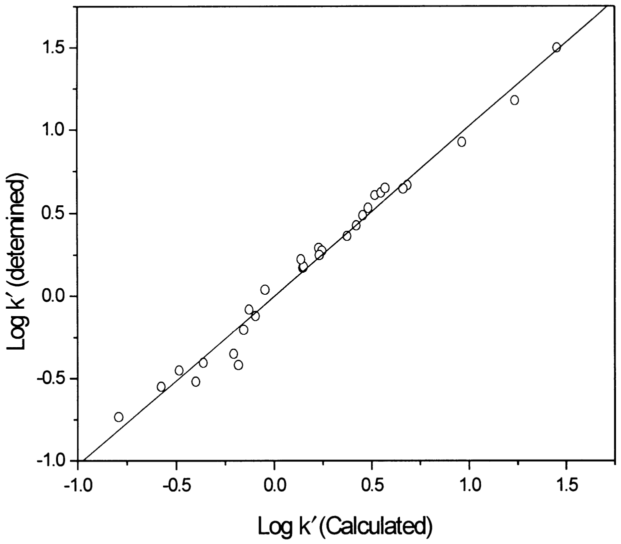

Figure 3. Experimental vs. predicted $\log k'$ for C_{18}–PBD–ZrO_2.

$$\log k'(C_{18}\text{–PBD–}ZrO_2) = -0.7813(\pm 0.0833) + 2.0120(\pm 0.0778)V_2 - 0.4883(\pm 0.0464)\pi_2^* - 1.8566(\pm 0.1096)\Sigma\beta_2{}^{H} \quad (2)$$

$$N = 29, R = 0.9813, p < 0.0001$$

The $\log k'$ value of 29 test solutes can be calculated by this equation [Eq. (2)]. Good correlation can be achieved when we plot the experimental $\log k'$ vs. the calculated $\log k'$ (Fig. 3). The correlation coefficient exceeds 0.99, the relative standard deviation less than 0.1, indicating that the retention behavior of the solutes on C_{18}–PBD–ZrO_2 is well predicted by Eq. (2).

CONCLUSION

LSERs is a useful method in studying the retention mechanism and selectivity of different stationary phases. By analyzing its regression coefficients, we can see which factor has a big or small influence on the retention. C_{18}–PBD–ZrO_2 is an inorganic oxide based phase coated with a layer of reticular polymer on its surface; it has the retention character of aliphatic phases. By comparing the regression coefficients of ODS, PBD–ZrO_2, and C_{18}–PBD–ZrO_2, we can see that C_{18}–PBD–ZrO_2 exhibits the character of long chain stationary phases, which is similar to ODS. The cavity formation and dispersion interactions, dipolarity/polarizability interaction, and effective hydrogen bond donor acidity are major factors that principally govern the retention of test solutes on C_{18}–PBD–ZrO_2 stationary phases.

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