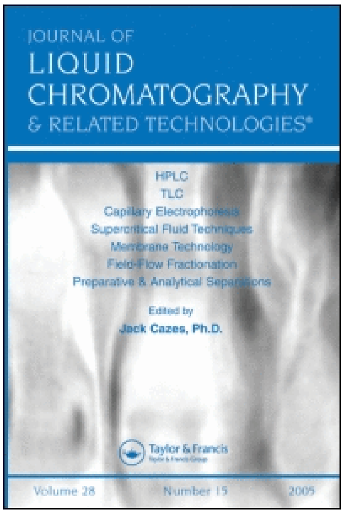

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

RETENTION BEHAVIORS OF POLYBUTADIENE-COATED TITANIA AND COMPARISON TO BONDED PHASE ON LINEAR SOLVATION ENERGY RELATIONSHIPS

Zi -Tao Jiang[a]; Dong -Yu Zhang[b]; Yu -Min Zuo[a]
[a] Department of Chemistry, Nankai University, Tianjin, P.R. China [b] Department of Chemistry, Jinzhou Normal College, Jinzhou, P.R. China

To cite this Article Jiang, Zi -Tao , Zhang, Dong -Yu and Zuo, Yu -Min(2000) 'RETENTION BEHAVIORS OF POLYBUTADIENE-COATED TITANIA AND COMPARISON TO BONDED PHASE ON LINEAR SOLVATION ENERGY RELATIONSHIPS', Journal of Liquid Chromatography & Related Technologies, 23: 8, 1159 — 1169

To link to this Article: DOI: 10.1081/JLC-100100406

URL: http://dx.doi.org/10.1081/JLC-100100406

J. LIQ. CHROM. & REL. TECHNOL., 23(8), 1159–1169 (2000)

RETENTION BEHAVIORS OF POLYBUTADIENE-COATED TITANIA AND COMPARISON TO BONDED PHASE BASED ON LINEAR SOLVATION ENERGY RELATIONSHIPS

Zi-Tao Jiang,[1] Dong-Yu Zhang,[2] Yu-Min Zuo[1,*]

[1]Department of Chemistry
Nankai University
Tianjin 300071, P.R. China

[2]Department of Chemistry
Jinzhou Normal College
Jinzhou 121003, P.R. China

ABSTRACT

The retention behaviors of polybutadiene-coated titania stationary phase (PBD-TiO_2) are investigated by the use of linear solvation energy relationships (LSERs) of 21 solutes. The logarithmic capacity factors measured on PBD-TiO_2 (log k' (PBD-TiO_2)) in a methanol-water (80:20, v/v) mobile versus the solutes' four interaction descriptors, the McGowan characteristic molar volume (V_x), dipolarity/polarizability (π_2*), effective or overall hydrogen bond donor acidity ($\Sigma\alpha_2^H$) and hydrogen bond acceptor basicity ($\Sigma\beta_2^H$) are analyzed by multiple regression analysis and compared to conventional bonded reversed stationary phase. We find that PBD-TiO_2 is very similar to conventional bonded reversed stationary phase. The descriptors, V_x, π_2* and $\Sigma\beta_2^H$ are the most important parameters governing the retention, as they represent more than 96.62% of the log k′ variation. Finally, we come to the conclusion that the retention of PBD-TiO_2 is a partition mechanism.

INTRODUCTION

Up to now silica and its derivatives are still the majority in the high performance liquid chromatography (HPLC) areas. However, there are two obvious drawbacks in the use of these packings. Degradation of the bonded phase occurs outside the range pH 2-8, due to hydrolysis of the siloxane bond at low pH and dissolution of the silica at high pH. In addition, the presence of residual silanols in these packings always leads to irreversible adsorption of basic compounds and strong peak asymmetry. Although some improvements have been achieved, the drawbacks of silica based packings cannot be overcome thoroughly yet. In order to solve this problem, a new kind of packing material, titania, that is resistant to strong acid and basic conditions has recently been developed.

In recent years, the preparation of porous amorphous titania[1-4] and octadecyltitania[1, 3-9] and their applications to the separation of aniline derivatives, benzylamine derivatives, hindered amines, structural isomers, and fullerenes have been reported. Titania can be used as both an anion and cation exchanger packing material for ion chromatography.[10,11] In addition, the preparation of polyethylene-coated stationary phase was also reported and retention behaviors were characterized.[13] Several methods have been introduced for the characteristics of stationary phases and evaluation and prediction of chromatographic behaviors of test solutes since the 1980's. In liquid chromatography, linear solvation energy relationships (LSERs) have shown greater promise. LSERs established between retention measurements, such as log k' and physicochemical descriptors of test solute give a good understanding of the retention mechanism and an excellent predicting retention of test solute. LSERs are formulated in terms of a system's solvatochromic characterization as follows:

$$\log k' = \log k'_o + M(\delta_s^2 - \delta_m^2)V_x/100 + S(\pi_s^* - \pi_m^*)\,\pi_2^* + A(\alpha_s - \alpha_m)\Sigma\,\alpha_2^H$$

$$+ B(\beta_s - \beta_m)\Sigma\beta_2^H \tag{1}$$

in which log k′ is the logarithmic capacity factor of test solute, log k_o' is a intercept of multiple linear regression, and V_x is McGowan characteristic molar volume that can be calculated from molecular structure.[14,15] α and β are the solute's hydrogen bond donor acidity and hydrogen bond acceptor basicity, respectively, $\sum\alpha_2^H$ and $\sum\beta_2^H$ are the solute's effective or overall hydrogen bond donor acidity and hydrogen bond acceptor basicity, respectively, δ is Hildebrand solubility parameter, π^* is a measure of the solute's ability to engage in dipolarity/polarizability interactions, and M, S, A, and B are basically constants. The subscript m and s present mobile and stationary phases, respectively, and the subscript 2 denotes test solute.

When a system with a fixed pair of mobile and stationary phase is considered, the above equation can be reduced to:

$$\log k' = \log k'_o + mV_x/100 + s\,\pi_2^* + a\sum\alpha_2^H + b\sum\beta_2^H \qquad (2)$$

where m, s, a and b are the fitting coefficients obtained by multiple linear regression, the other signs have the same meanings as the above equation.

It is shown in Equation (2) that the sign and magnitude of the coefficients, m, s, a and b can indicate the direction and relative strength of the different kinds of solute-stationary or solute-mobile interactions that affect the retention behaviors. When a mobile phase is fixed under otherwise identical conditions, the effects of mobile phase on the retention are essentially constant, therefore the change in the fitting coefficients will reflect variations in the stationary phase. In this paper, we have determined the capacity factors of a series of solutes at a given mobile phase on PBD-TiO_2 stationary phases, and have compared it with ODS stationary phase. The retention characteristics of PBD-TiO_2 are investigated by means of LSERs.

EXPERIMENTAL

A series of 21 test solutes, shown in Table 1 were carefully chosen to cover a wide range of solution solvatochromatic properties and these solutes have interaction minimums between LSERs descriptors, V_x, π_2^*, Σ_2^H and $\sum\beta_2^H$. Before used, solutes were dissolved in methanol, respectively to give 0.5-1.0 mg/mL solutions.

Titania support was prepared by the use of a modification of oil emulsion.[1,16] Polybutadiene-coated titania (PBD-TiO_2) was prepared according to the method of polybutadiene-coated zirconia as described earlier.[17] Chromatographic column (150 × 4.6 mm i.d.) was filled with PBD-TiO_2 by the use of a high pressure pump Model 6752B-100, made by Beijing Analytical Instruments Technical Company, Beijing, China. The suspending agent is a mixture of toluene, cyclohexanol, and 1,4-dioxane (1:1:1, v/v). The ODS column used (250 × 4.6 mm i.d., Accusil C-18, 10 μm) was purchased from Chromatographic Scientific Company of Tianjin, China.

The chromatograph Model Varian 5060 equipped with an UV-100 detector was used to determine the capacity factors of test solutes. Detection wavelength is 254 nm. A methanol-water solution (80:20, v/v) was used as a mobile phase; the flow rate is 1.0 mL/min. All determinations had been finished at room temperature, which both PBD-TiO_2 and ODS column were not thermostated. Dead volume was determined by the use of inject 1% sodium nitrate or methanol.

Table 1

The Solutes' LSERs Descriptors and log k' Corresponding to 80% Methanol as a Mobile Phase Determined on Polybutadiene-Coated Titania and Octadecyl Bonded Silica[a]

No.	Solutes	$V_x/100$	π_2^*	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	Log k' (ODS)	Log k' (PBD-TiO_2)
1	Benzene	0.716	0.52	0.00	0.14	0.0389	-0.0343
2	Toluene	0.857	0.52	0.00	0.14	0.2361	0.2881
3	Ethyl benzene	0.998	0.51	0.00	0.15	0.4853	0.6835
4	i-Propyl benzene	1.139	0.50	0.00	0.15	0.7705	1.0562
5	Chlorobenzene	0.839	0.65	0.00	0.07	0.1948	0.2712
6	Bromobenzene	0.891	0.73	0.00	0.09	0.2616	0.4123
7	Benzyl bromide	1.032	0.98	0.00	0.20	0.2443	0.3687
8	Pyridine	0.675[b]	0.86	0.00	0.52	-0.5618	-0.7756
9	Aniline	0.816[b]	0.96	0.26	0.41	-0.5786	-0.5823
10	N-Methyl aniline	0.957[b]	0.90	0.17	0.43	-0.1784	-0.1563
11	o-Methyl aniline	0.957[b]	0.92	0.23	0.45	-0.4063	-0.4574
12	p-Methyl aniline	0.957[b]	0.95	0.23	0.45	-0.3625	-0.2578
13	N,N-Dimethyl aniline	1.098	0.84	0.00	0.42	0.1523	0.3123
14	Anisole	0.916	0.75	0.00	0.29	0.0015	0.0846
15	Allylbenzene	1.096	0.60	0.00	0.22	0.5434	0.7594
16	Biphenyl	1.324	0.99	0.00	0.22	0.7935	1.0862
17	o-Nitrotoluene	1.032	1.11	0.00	0.27	-0.0177	0.0908
18	m-Nitrotoluene	1.032	1.10	0.00	0.25	0.0306	0.1693
19	p-Nitrotoluene	1.032	1.11	0.00	0.28	-0.0076	0.0989
20	Naphthalene	1.085[b]	0.92	0.00	0.20	0.4945	0.6742
21	Anthracene	1.454[b]	1.34	0.00	0.26	0.8552	1.2089

---

[a] LSERs descriptors were taken from References 15, 19-22. [b] $V_x/100$ of several compounds are calculated based on References 14, 15.

Retention parameters of test solutes were analyzed by regressing against a set of LSERs parameters. Principal component analysis (PCA), multiple linear regression and calculation related were run on a personal computer.

RESULTS AND DISCUSSION

Test solutes' capacity factors were determined on two different columns, PBD-TiO_2 and ODS and logarithmic capacity factors are shown in Table 1.

Linear intercorrelation between those obtained from both PBD-TiO_2 and ODS is shown as follow:

$$\log k' (\text{PBD-TiO}_2) = 0.0718(\pm 0.0157) + 1.2689(\pm 0.0361) \log k' (\text{ODS})$$
$$n = 21,\ R = 0.9924,\ s = 0.0679,\ p \leq 9.6025E\text{-}19 \qquad (3)$$

where n is the number of test solutes, R is correlation coefficient, s is standard error of regression, p is significance level of a whole equation of individual regress terms. The numbers in parenthesis are standard error of regression coefficients. The plot of log k′ (PBD-TiO_2) versus log k′ (ODS) is shown in Figure 1.

It may be seen that a good correlation is obtained between PBD-TiO_2 stationary phase and ODS stationary phase. This result suggests to us that PBD-TiO_2 stationary phase is similar to ODS stationary phase, but retention of solutes on the PBD-TiO_2 column is a bit larger than on the ODS column. It is well known that the retention mechanism of solutes on ODS stationary phase is

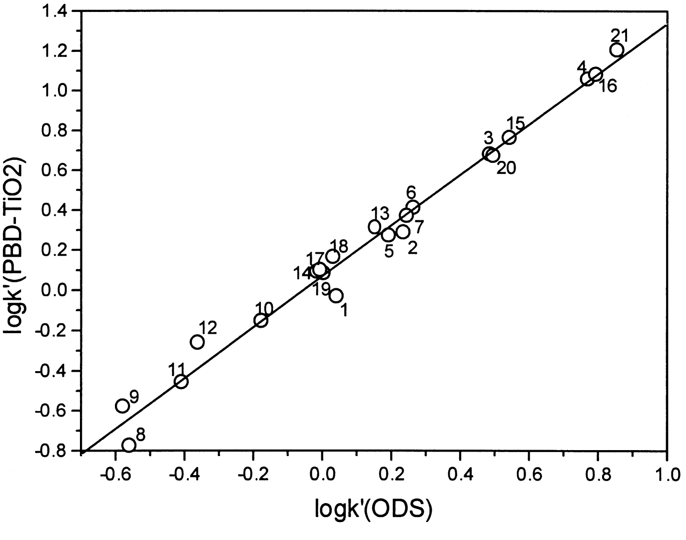

Figure 1. Plot of logarithmic capacity factors determined on polybutadiene-coated titania stationary phase (PBD-TiO_2), log k′ (PBD-TiO_2) versus on conventional bonded reversed stationary phase (ODS), log k′ (ODS) in a methanol-water (80:20, v/v) mobile phase. Test solutes numbered as Table 1.

Table 2

The Results of Principal Component Analysis (PCA)

PC Variables	1	2	3
$V_x/100$	0.4511	-0.7203	0.5270
π_2^*	0.8658	0.2166	-0.4438
$\Sigma\alpha_2^H$	0.0570	0.3394	0.4278
$\Sigma\beta_2^H$	0.2088	0.5649	0.5851
Variances	0.0682	0.0307	0.0099
Explained	60.5805	27.2485	8.7909

principally partition mechanism. Therefore, we may arbitrarily conclude that PBD-TiO_2 stationary phase belongs to partition mechanism. This result was also supported by retention behaviors of different carbon loading of polybutadiene-coated zirconia stationary phase as reported earlier.[18]

The structure descriptors shown in Table 1 were analyzed by means of PCA. The matrix of component loadings after rotation of varimax normalized is given in Table 2. All variables' loadings in the three first principal components (PCs) show that all four descriptors can be represented by three PCs, PC_1 60.58%, PC_2 27.25%, and PC_3 8.79%. Their sum is 96.62%. Therefore, the information is not lost when we conclude that three PCs represent total structure descriptors. The contribution of descriptor, π_2^* is the biggest in PC_1, $V_x/100$ in PC_2 and $\sum\beta_2^H$ in PC_3. Principal component solute scores were calculated for individual compounds. The positions of solutes on the space determined by the three first PCs (PC_1, PC_2, and PC_3) are displayed in Figure 3. Solutes do not form clusters on the three-dimensional scatter map. The result supports our conclusion that the LSERs parameters of the solute are different, resulting in different retention.

Pareto analysis was carried out and the result is shown in Figure 2. It may be seen that V_x, π_2^* and $\sum\beta_2^H$ are important factors that affect the retention. The result is identical with that of PCA.

Regression results of log k′ determined on PBD-TiO_2 and ODS stationary phases, respectively, against the solutes' LSERs parameters, V_x, π_2^* and $\sum\beta_2^H$ listed in Table 1 are shown as follows:

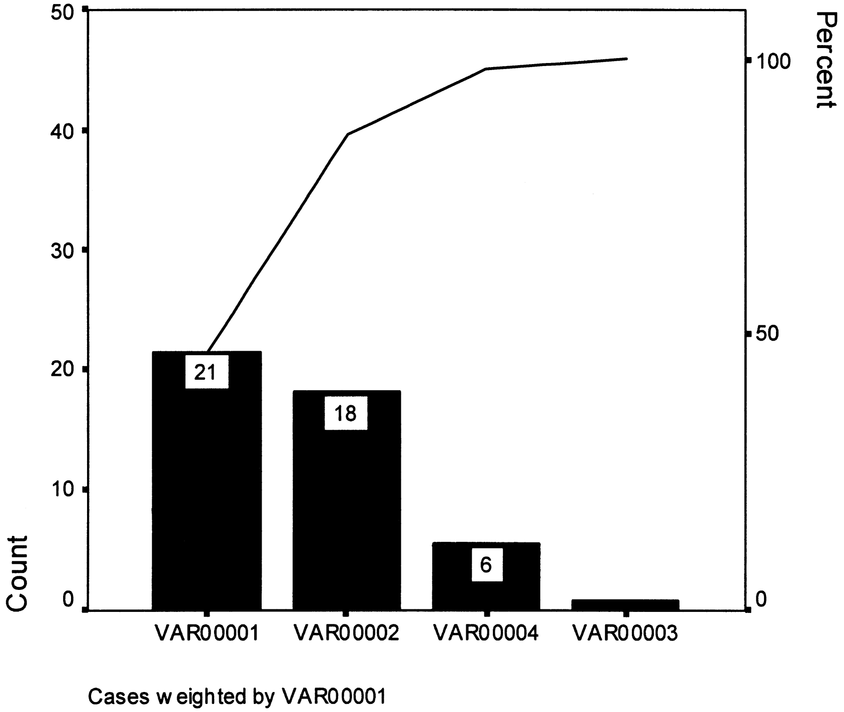

Figure 2. The result of Pareto analysis. VAR00001 ~ VAR00004 donate $V_x/100$, π_2^*, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$, respectively.

$$\log k' (\text{PBD-TiO}_2) = -1.3088(\pm 0.1380) + 2.5952(\pm 0.1513)V_x/100 - 0.6794(\pm 0.1288)\pi_2^* - 1.6747(\pm 0.2044)\Sigma\beta_2^H \quad (4)$$
$$n = 21, R = 0.9856, s = 0.0986, p < 0.0001, F = 192.1030$$

$$\log k' (\text{ODS}) = -0.9016(\pm 0.1437) + 1.9266(\pm 0.1576)V_x/100 - 0.5905(\pm 0.1341)\pi_2^* - 1.4013(\pm 0.2129)\Sigma\beta_2^H \quad (5)$$
$$n = 21, R = 0.9743, s = 0.1027, p < 0.0001, F = 105.8369$$

where F is the value of statistical significance F-test, numbers in parenthesis are standard error of regression coefficients. R, p and s have the same meanings as the above equations. The plots of log k′ (determined), versus log k′ (calculated) are shown in Figures 4 and 5.

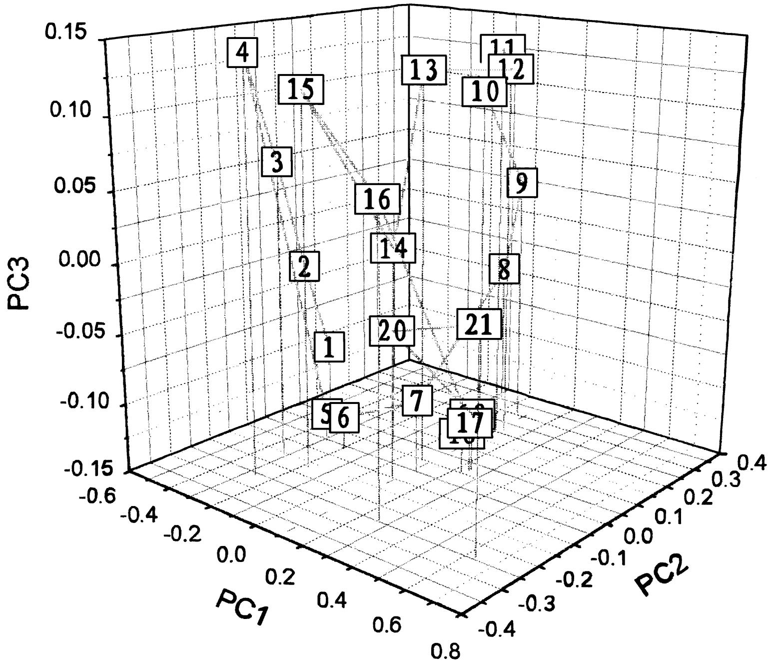

Figure 3. Principal component solute scores for individual solute on the space determined by the three first PCs (PC_1, PC_2 and PC_3). Test solutes numbered as Table 1.

It may be seen that the results of multiple linear regression are very satisfying. There are better relationships between LSER parameters and log k′. The same signs of the coefficients of descriptors, V_x, π_2^* and $\sum\beta_2^H$ in Equation (4) and (5) indicate that PBD-TiO_2 and ODS stationary phase are similar in retention.

The above two equations' physical senses are very significant. We know that V_x is a measure of two processes: cavity formation and dispersion interactions. Its coefficients, m are larger positive values in Equation (4) and (5). Therefore, an increase in size of test solute will lead to an increase in retention. The m coefficient's magnitude is larger for PBD-TiO_2 than for ODS stationary phase; this must originate from the stationary phase because the determinations are carried out in the same mobile phase. Based on the above, we conclude that PBD-TiO_2 stationary phase is effectively much more hydrophobic than ODS stationary phase. π_2^* donates the solutes' dipolarity/ polarizability interaction; its coefficient, s is a larger negative value for PBD-TiO_2 stationary phase than for ODS stationary phase. On PBD-TiO_2 stationary phase, an increase in solute dipolarity/

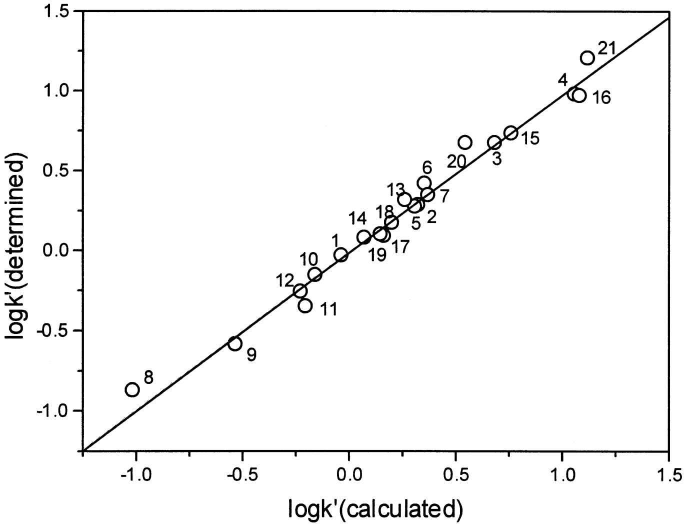

Figure 4. Plot of logarithmic capacity factors determined on polybutadiene-coated titania stationary phase (PBD-TiO_2) in a methanol-water (80:20, v/v) mobile, log k′ (determined) against those calculated, log k′ (calculated) by Equation (4). Test solutes numbered as Table 1.

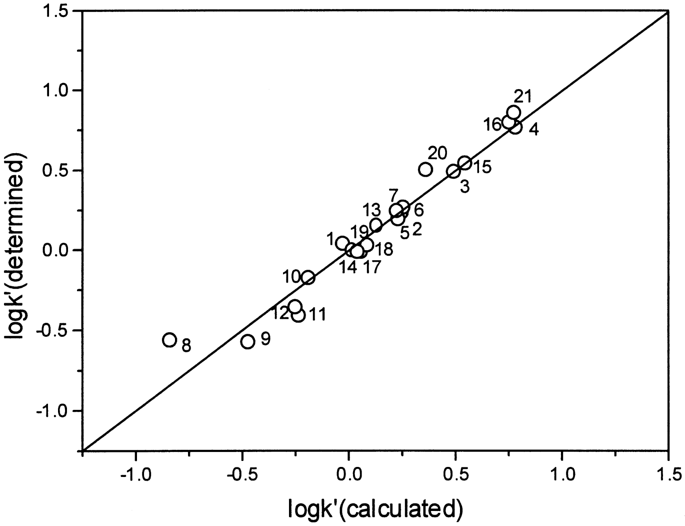

Figure 5. Plot of logarithmic capacity factors determined on conventional bonded reversed stationary phase (ODS) in a methanol-water (80:20, v/v) mobile, log k′ (determined) against those calculated, log k′ (calculated) by Equation (5). Test solutes numbered as Table 1.

polarizability will cause a considerable decrease in retention. The same increase in solute's π_2* causes only a small decrease in retention on conventional boned phase. The large, negative s coefficient indicates a significant electronic component to retention. This coefficient is very sensitive to the mobile phase.

The coefficients of $\sum\beta_2^H$ are large and negative for two stationary phases. They are controlled by the complementary system property and influenced by mobile phase composition. When mobile phase is fixed, fitting coefficients, b embody the difference between PBD-TiO_2 and ODS stationary phase. The b coefficient is a larger negative value for PBD-TiO_2 stationary phase than that for ODS stationary phase. This suggests that the binding strength of solute on the surface of titania is fairly weaker than that on silica. Therefore, in reversed-phase titania-based stationary phases, the undesirable side effect of the original adsorption centered on the retention is negligible.

In conclusion, the retention behaviors of PBD-TiO_2 stationary phase are very similar to ODS stationary phase and belong to partition mechanism. Retention of solutes on PBD-TiO_2 stationary phase is a bit larger than that on ODS stationary phase. The cavity formation and dispersion interactions, dipolarity/polarizability interaction, and effective hydrogen bond acceptor basicity are major factors that principally govern the retention of test solutes on PBD-TiO_2 stationary phase. The LSERs descriptor, effective hydrogen bond donor acidity have low effects on the retention behaviors.

ACKNOWLEDGMENT

The authors hope to thank the National Natural Science Foundation Commission of China for financial support, project 29575201.

REFERENCES

1. U. Trüdinger, G. Müller, K. K. Unger, J. Chromatogr. A, **535,** 111-125 (1990).
2. K. Tani, Y. Suzuki, Chromatographia, **38**, 291-294 (1994).
3. A. Yoshida, K. Takahashi, Chemitopia, **15**, 18-29 (1994).
4. K. Tani, Y. Suzuki, J. Chromatogr. A, **722**, 129-134 (1996).
5. J. J. Pesek, M. T. Matyska, J. Ramakrishnan, Chromatographia, **44**, 538-544 (1997).
6. M. Grün, A. A. Kurganov, S. Schacht, F. Schnth, K. K. Unger, J. Chromatogr. A, **740,** 1-9 (1996).

7. A. Kurganov, U. Trüdinger, T. Isaeva, K. K. Unger, Chromatographia, **42**, 217-222 (1996).

8. K. Murayama, H. Nakamura, T. Nakajima, K. Takahashi, A. Yoshida, Anal. Sci., **10,** 49 (1994).

9. K. Murayama, H. Nakamura, T. Nakajima, K. Takahashi, A. Yoshida, Anal. Sci., **10**, 815 (1994).

10. K. Tani, Y. Suzuki, Chromatographia, **46**, 623-627 (1997).

11. K. Tani, H. Kubojima, Chromatographia, **47**, 655-618 (1998).

12. E. Forgas, T. Cserhai, J. Chromatogra. B, **656**, 233-238 (1994).

13. M. Zaharescu, T. Cserhai, E. Forgas, J. Liq. Chromatogra. Relat. Technol., **20**, 2997-3007 (1997).

14. M. H. Abraham, Chem.Soc. Rev., **22**, 73-83 (1993).

15. M. H. Abraham, J. C. McGowan, Chromatographia, **23**, 243-246 (1987).

16. P. W.Carr, E. F. Funkenbusch, M. P. Ringney, P. L. Coleman, D. A. Hanggi, W. A. Schafer, US Patent, 5015373, 1991.

17. M. P. Rigney, T. P. Weber, P. W. Carr, J. Chromatogr., **484**, 273-291 (1989).

18. J. Li, P. W. Carr, Anal.Chem., **68**, 2857-2868 (1996).

19. J. H. Park, J. J. Chae, T. H. Nah, M. D. Jang, J. Chromatogr., **664**, 149-158 (1994).

20. J. Li, P. W. Carr, Anal. Chim. Acta, **334**, 239-250 (1996).

21. M. H. Abraham, G. S. Whiting, R. M. Doherty, W. J. Shuely, J. Chromatogr., **587,** 213-228 (1991).

22. M. H. Abraham, H. S. Chadha, G. S. Whiting, R. C. Mitchell, J. Pharm. Sci., **83**, 1085-1100 (1994).

Received July 8, 1999
Accepted September 14, 1999
Author's Revisions November 22, 1999
Manuscript 5126