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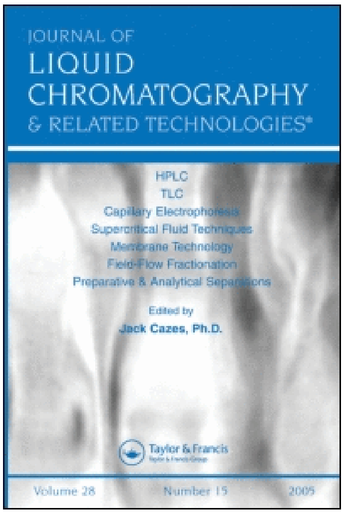

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Jin Ge[ab]; Liang Zhao[a]; Yan-Ping Shi[a]
[a] Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, P. R. China [b] Graduate School of Chinese Academy of Sciences, Beijing, P. R. China

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Chromatographic Evaluation of Octadecyl-Bonded TiO_2/SiO_2 Stationary Phase with Engelhardt and Tanaka Test Mixtures

Jin Ge,[1,2] Liang Zhao,[1] and Yan-Ping Shi[1]

[1]Key Laboratory for Natural Medicine of Gansu Province, Lanzhou
Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou,
P. R. China
[2]Graduate School of Chinese Academy of Sciences, Beijing, P. R. China

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Abstract: Chromatographic performance of octadecyl-bonded TiO_2/SiO_2 stationary phase was evaluated with Engelhardt and Tanaka test mixtures. In the two test protocol, some parameters influencing the retention, such as methylene selectivity (α_{CH2}), steric selectivity ($\alpha_{O/T}$), hydrogen bonding capacity ($\alpha_{C/P}$), and ion exchange capacity ($\alpha_{B/P}$) were obtained. By separating several same compounds with different mobile phases, different results were obtained and they were compared with that in the reference, in which octadecyl-bonded titania packing was prepared and a similar test was carried out. All of the results suggest that the octadecyl-bonded TiO_2/SiO_2 stationary phase not only has good methylene selectivity and steric selectivity, but also shows a large potential in the separation of basic compounds.

Keywords: TiO_2/SiO_2, RP-HPLC, Octadecyl-bonded stationary phase, Basic compounds

INTRODUCTION

Titanium dioxide (titania) has been introduced for HPLC packing since the later 1980s, and has been paid much attention due to its excellent chemical stability in comparison with silica. Up to now, the titania based packings

Correspondence: Yan-Ping Shi, Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China. E-mail: shiyp@lzb.ac.cn

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have already been reported in normal-phase, reversed-phase, ion exchange and affinity chromatography.[1–12] However, the accessibility and variability of surface and pore properties, such as specific surface area, pore volume, total porosity, and particle size of titania are much lower than that of silica.[13–16]

TiO_2/SiO_2 was prepared by coating a titania nanoparticle on microsize silica using a self-assemble technique. It has as good chemical stability as titania particles and some better surface and pore properties, such as high surface area, good pore structure, large pore volume, and variable particle size distribution than that of the conventional titania.[17,18]

In a previous work, we have reported the preparation of octadecyl-bonded TiO_2/SiO_2 stationary phase and the investigation of its main interaction mechanism, hydrophobic selectivity in this journal.[18] However, as an octadecyl-bonded stationary phase, there is a large amount of information about the stationary phase effects on retention, including the effects of surface hydroxyl, surface coverage, and ion exchange sites on the packing surface. It is usually thought that the hydroxyl and negatively charged ion exchange sites could work separately via hydrogen bonding and electrostatic interactions, respectively, resulting in poor performance for hydrogenbond acceptors and protonated amines. Therefore, in this paper the chromatographic performance of octadecyl-bonded TiO_2/SiO_2 stationary phase was evaluated with Engelhardt and Tanaka test mixtures, which have been proposed by Engelhardt and Tanaka[19,20] to get a overall evaluation of the octadecyl-bonded stationary phase and have been used in many papers.[21–23]

EXPERIMENTAL

Chemicals and Materials

Tetrabutyl titanate was purchased from Shanghai Sanyou Reagent Factory (Shanghai, China). Acetic acid was purchased from Jiangsu Sanmu Group Chemical Factory (Jiangsu, China) and sodium dodecyl sulfate (SDS) from Xi'an Chemical Reagent Co. (Xi'an, China). Trichlorooctadecylsilane was purchased from Aldrich (Lancaster, UK). All of the above are chemical grade. Methanol, toluene, hexane, ethanol, and acetone were purchased from Tianjin No. 2 Chemical Reagent Plant (Tianjin, China), analytical grade.

TiO_2/SiO_2 Particles and Octadecyl-Bonded TiO_2/SiO_2 Stationary Phase

TiO_2/SiO_2 spheres were synthesized in our laboratory.[18] The average particle size was 6 μm. The specific surface area, pore volume, and pore diameter were 202 m^2/g, 0.36 cm^3/g and 7.0 nm, respectively. The preparation process of octadecyl-bonded TiO_2/SiO_2 stationary phase has been described in.[18] The packing was filled into a 150 × 4.6 mm i.d. stainless steel column at 40 Mpa pressure.

Chromatographic Conditions

The HPLC system consisted of a Waters 515 HPLC pump, 2487 absorbance detector, and a Rheodyne injection valve with a 10 μL loop. Chromatograms were recorded with a SePu 3000 workstation. The pH of the mobile phase was adjusted with the corresponding hydroxide using a calibrated pH meter before addition of methanol. All of the mobile phases were degassed in an ultrasonic bath before use. Column temperature was maintained with a thermostatted water bath.

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RESULTS AND DISCUSSION

Separation of Tanaka Test Mixtures

The first evaluation was performed similar to the Tanaka test protocol at 40°C.[20] The methylene selectivity α_{CH2} ($k_{butylbenzene}/k_{isopropylbenzene}$) and steric or shape selectivity $\alpha_{T/O}$ ($k_{triphenylene}/k_{o\text{-}terphenyl}$) were calculated from the separation of butylbenzene, isopropylbenzene, triphenylene and o-terphenyl, using MeOH–water (80:20,v/v) as mobile phase. The hydrogen bonding capacity $\alpha_{C/P}$ ($k_{caffeine}/k_{phenol}$) was determined from the separation of caffeine and phenol using MeOH–water (30:70, v/v). The ion exchange capacities $\alpha_{B/P}$ ($k_{benzylamine}/k_{phenol}$) were calculated for the separation of benzylamine and phenol, using a mobile phase composed of MeOH–20 mmol l−1 phosphate buffer (30:70, v/v) at pH 7.60 and 2.70.

Figure 1, Figure 2, and Table 1 are the results obtained with Tanaka test mixtures. The value of methylene selectivity (α_{CH2}) is 1.58. According to Kimata et al.,[20] the methylene selectivity increases with the surface coverage and with the length of the alkyl chain attached to the surface. The value of methylene selectivity (α_{CH2}) obtained from the Engelhardt test mixtures is 1.56, calculated from the capacity factor of toluene and ethylbenzene. Both of the values of α_{CH2} indicate a comparatively good methylene selectivity of the C_{18} bonded TiO_2/SiO_2. A steric selectivity ($\alpha_{T/O}$) is 1.55, which suggests that similar compounds with different steric structures, such as triphenylene and o-terphenyl could be well separated. The hydrogen bonding capacity ($\alpha_{C/P}$) of 0.44 indicated a comparatively low amount of hydroxyl and a high surface coverage. The ion exchange capacity ($\alpha_{B/P}$) is 2.01 at pH 2.70 and 1.91 at pH 7.6. With the different mobile phase, MeOH–20 mmol l^{-1} phosphate buffer (30:70, v/v) at pH 7.60 and at pH

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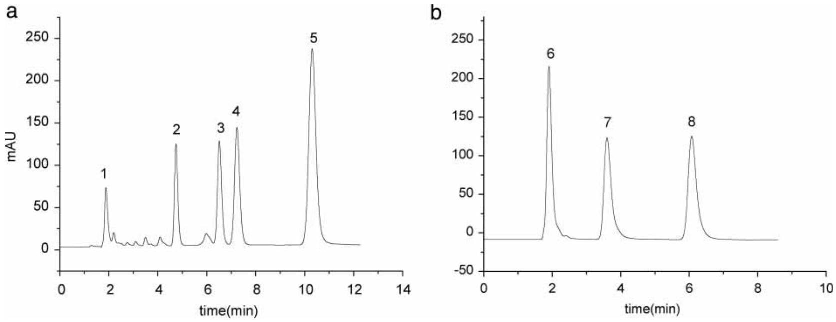

Figure 1. Chromatograms of the Tanaka test mixture. Detection: UV at 254 nm, temperature of 40°C. Mobile phase: (a) MeOH–water (80:20, v/v), (b) MeOH–water (30:70, v/v). Peaks: Uracil (1), Isopropylbenzene (2), Butylbenzene (3), o-Terphenyl (4), Triphenylene(5), Uracil (6), Caffeine (7), Phenol (8).

2.70, the peak of benzylamine changed dramatically. The asymmetry factor (T_f) at 7.60 is 6.25 times of that at pH 2.70. The P_{zc} of titania is about 5; at pH 7.6 titania should act as a cation ion exchange sorbent. The pK_a of benzylamine is 9.3, which indicates benzylamine is protonated at pH 7.6. Thus, the serious tailing of benzylamine at pH 7.6 should be the result of the strongly electrostatic interaction between the cation ion exchange sites of the stationary phase and the protonated benzylamine. When at pH 2.70, benzylamine is still protonated, but the surface of the stationary phase is not positively charged but negatively charged, so the peak of benzylamine improved.

Separation of Engelhardt Test Mixtures

Another set of experiments was performed using compounds from the Engelhardt test mixtures.[19] This mixture, containing uracil, aniline, phenol, *N,N*-dimethylaniline (*N,N*-DMA), toluene, and ethylbenzene, was separated using MeOH–water (60:40, v/v) or MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v) as mobile phase. The results are shown in Figure 3. Six compounds were well separated under two mobile phase conditions. For the neutral compounds, the peaks are symmetrical; but for the basic compounds, a little tailing is observed.

The efficiency (N), tailing factor (T_{f},), and capacity factor of the compounds are shown in Table 2. We can see that with the addition of 20 mmol L^{-1} phosphate buffer in the mobile phase, the peaks of aniline improved greatly, and for others the change is only a little. Possible mechanisms are the ionization suppression of the base as well as the acid–base interactions of the phosphate Lewis base with acidic residual groups on the titanized surface. Although aniline and *N,N*-dimethylaniline both are basic

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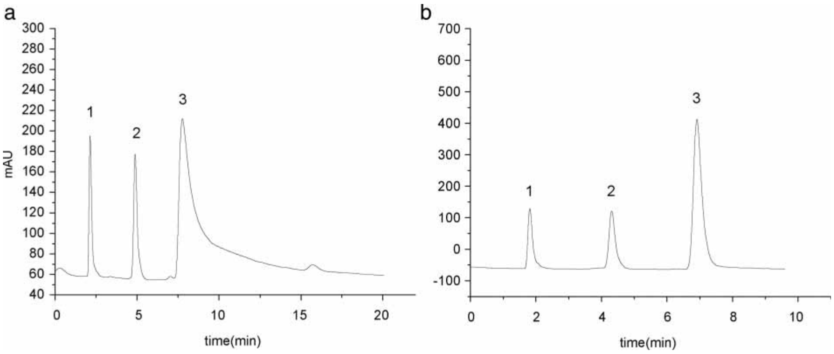

Figure 2. Chromatograms of the Tanaka test mixture. Detection: UV at 254 nm, temperature of 40°C. Mobile phase: (a) MeOH−0.020 mol L^{-1} phosphate buffer at pH 7.6 (30:70, v/v), (b) MeOH−0.020 mol L^{-1} phosphate buffer at pH 2.70 (30:70, v/v), Peaks: Uracil (1), Phenol (2), benzylamine (3).

compounds, their basic strength are different. The pKa of aniline is 4.6, smaller than the pKa of *N,N*-dimethylaniline of 5.15, indicating a slightly basic property. In the MeOH−20 mmol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v) mobile phase, the ionization suppression of aniline is stronger than that of *N,N*-dimethylaniline. So the peak of aniline improved more obviously. The capacity factor k almost did not change and the efficiency (N) decreased a little with the addition of phosphate buffer.

Table 1. Chromatographic parameters obtained for the separation of some compounds of the Tanaka test mixtures on the octadecyl-bonded TiO_2/SiO_2 stationary phase

Compounds	k	T_f	N (N/m)
Isopropylbenzene[a]	1.78	1.20	6110
Butylbenzene[a]	2.82	1.16	7350
o-Terphenyl[a]	3.24	1.13	6210
Triphenylene[a]	5.03	1.17	6620
Caffeine[d]	1.11	1.63	1550
Phenol[d]	2.55	1.45	3320
Phenol[b]	1.52	1.47	2720
Phenol[c]	1.86	1.59	2910
Benzylamine[b]	3.05	1.52	3900
Benzylamine[c]	3.55	9.50	524

[a] MeOH−water (80:20,v/v) as mobile phase.
[b] MeOH−water (30:70, v/v) at pH 2.70.
[c] MeOH−20 mmol l− 1 phosphate buffer (30:70, v/v) at pH 7.60.
[d] MeOH−water (30:70, v/v).

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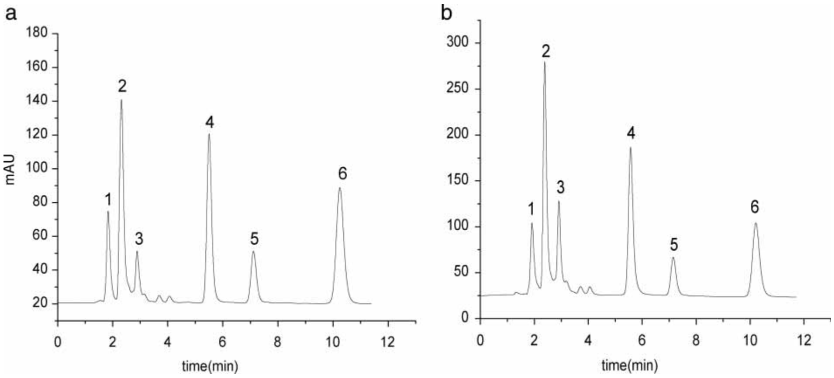

Figure 3. Separation of some components of the Engelhardt test mixture. Conditions: 150 mm × 4.6 mm HPLC columns, mobile phase: (a) MeOH–water (60:40, v/v), (b) MeOH–0.020 mol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v), detection: UV at 254 nm, Peaks: Uracil (1), Aniline (2), Phenol (3), *N,N*-DMA (4), Toluene (5) and Ethylbenzene (6).

Collins and collaborators prepared C_{18} bonded doubly-titanized silica (SiTi2C_{18}) and also evaluated the packing made in their paper with the Engelhardt test mixtures. Their results are shown in Table 2 and Table 3. The most obvious difference is the chromatography for the basic compounds. C_{18} bonded TiO_2/SiO_2 almost gave more symmetrical peaks for the compounds, except for *N,N*-DMA with MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v) as mobile phase, 1.29 for C_{18} bonded TiO_2/SiO_2 and 1.28 for SiTi2C_{18}. Another obvious difference is that with MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v) as mobile phase, the symmetry of the basic compounds greatly improved on the SiTi2C_{18} column but only a little on C_{18} bonded TiO_2/SiO_2. We attribute this to the more complete cover of silica by titania on the TiO_2/SiO_2 surface than that of $SiTi_2C_{18}$. $\alpha_{P/T}$ ($k_{phenol}/k_{toluene}$) obtained from C_{18} bonded TiO_2/SiO_2 is higher than that obtained from $SiTi_2C_{18}$, indicating more hydroxyl on the C_{18} bonded TiO_2/SiO_2, which is usually thought to cause more bad peaks for basic compounds. Fortunately, the chromatography of C_{18} bonded TiO_2/SiO_2 for basic compounds proved that the situation for TiO_2/SiO_2 is different. The case may be as follows: there is actually more hydroxyl on the C_{18} bonded TiO_2/SiO_2 than on the $SiTi_2C_{18}$ as the $\alpha_{P/T}$ indicated, but these hydroxyls on the surface of TiO_2/SiO_2 are mostly bonded to titania other than silica, showing much weaker acidic than the silanols, and they do not cause the tailing of the basic compounds as seriously as the silanols do. For the $\alpha_{E/T}$ ($k_{ethylbenzene}/k_{toluene}$), $SiTi_2C_{18}$ gave a higher value than the C_{18} bonded TiO_2/SiO_2, which indicates a higher surface coverage. This may be the result of a higher surface area of 280 ± 10 m^2/g of $SiTi_2$, which promises a higher bonded amount.

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Table 2. Chromatographic parameters obtained for the separation of some compounds of the Engelhardt test mixtures on the octadecyl-bonded TiO_2/SiO_2 stationary phase

Compounds	K	N (N/m)		T_f	
Aniline	0.39^a; 0.36^b	1840^a; 1190^b	(490^a, 1570^b)	1.49^a; 1.29^b	(2.37^a, 1.36^b)
Phenol	0.70^a; 0.69^b	2960^a; 2310^b	(1930^a, 1950^b)	1.15^a; 1.12^b	(1.27^a, 1.33^b)
N,N-DMA	2.26^a; 2.22^b	5500^a; 5310^b	(2840^a, 4210^b)	1.33^a; 1.29^b	(1.85^a, 1.28^b)
Toluene	3.19^a; 3.16^b	7100^a; 6530^b	(4290^a, 4370^b)	1.22^a; 1.21^b	(1.28^a, 1.25^b)
Ethylbenzene	4.98^a; 5.00^b	7830^a; 7250^b	(3990^a, 4090^b)	1.18^a; 1.14^b	(1.26^a, 1.19^b)

[a] MeOH–water (60:40, v/v) as mobile phase.

[b] MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v) as mobile phase.

[b] The value in parenthesis are those cited from,[21] ([a]) MeOH–water (55:45, v/v) as mobile phase. ([b]) MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (55:45, v/v) as mobile phase.

Table 3. Relative retentions compared to toluene (T) for aniline (A), phenol (P), *N*,*N*-dimethylaniline (DMA) and ethylbenzene (E) for separations on the octadecyl-bonded TiO_2/SiO_2 stationary phase

	$\alpha_{A/T}$	$\alpha_{P/T}$	$\alpha_{DMA/T}$	$\alpha_{E/T}$
This paper[a]	0.12	0.22	0.71	1.56
This paper[b]	0.11	0.22	0.70	1.58
[21][c]	0.13	0.09	0.71	1.91
[21][d]	0.07	0.09	0.65	1.91

[a] MeOH–water (60:40, v/v) as mobile phase.

[b] MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (60:40, v/v) as mobile phase.

[c] MeOH–water (55:45, v/v) as mobile phase.

[d] MeOH–20 mmol L^{-1} phosphate buffer at pH 7.0 (55:45, v/v) as mobile phase.

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CONCLUSION

Octadecyl-bonded TiO_2/SiO_2 stationary phase was used as RPLC with the phosphate buffered mobile phase and unbuffered mobile phase. Neutral, basic and acidic compounds were separated. The octadecyl-bonded TiO_2/SiO_2 stationary phase also shows comparatively good methylene selectivity and good steric selectivity. The high symmetry of basic compounds and the little symmetry difference under the mobile phase with and without phosphate buffer, suggests that the coating method used to prepare TiO_2/SiO_2 is successful and this titania coated silica is fit for the separation of basic compounds.

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