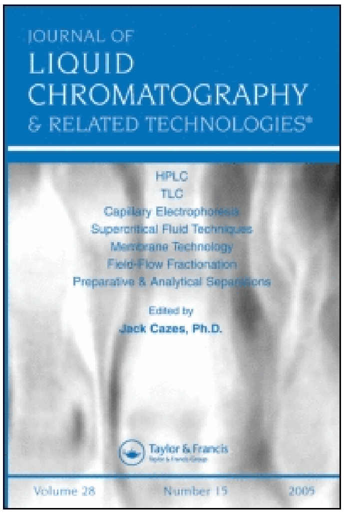

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RETENTION CHARACTERISTICS OF TITANIUM DIOXIDE AND POLYETHYLENE-COATED TITANIUM DIOXIDE AS REVERSED-PHASE SUPPORTS

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ABSTRACT

The retention of 19 solutes markedly differing in their physicochemical characteristics was determined on titanium dioxide and polyethylene-coated titanium dioxide columns in water and water-methanol eluent mixtures. Principal component analysis was used for the elucidation of the relationship between retention behavior and physicochemical parameters. Polyethylene-coated titanium dioxide showed stronger retention than titanium dioxide did, proving the retention increasing effect of polyethylene coating. Retention parameters formed a loose cluster with the excess molar refraction and the effective hydrogen bond acidity of solutes on the two-dimensional nonlinear map of principal component loadings, indicating the involvement of steric conditions and electronic interactions in the retention.

INTRODUCTION

The majority of high performance liquid chromatographic (HPLC) analyses is carried out in reversed-phase (RP) separation mode.[1] The widespread application of RP-HPLC may be due to its versatility and the environmental and toxicological safety of the eluent components.[2] Silica supports with covalently bonded hydrophobic ligands are extensively used in RP-HPLC,[3] however, the successfull application of silica-based supports in RP-HPLC is limited by the low stability of silica at high pH values,[4] and by the undesirable electrostatic interactions between the polar substructures of solutes and the free silanol groups not covered by the hydrophobic ligand.[5,6] To increase the pH range of application, many other supports have been developed, such as alumina,[7,8] zirconia,[9,10] and various polymer-based supports.[11,12]

More recently, polymer-coated supports have become popular since they combine the advantageous mechanical properties of support with the dynamic chemical properties of polymers.[13,14] Polymer coating improves not only selectivity but also the chemical stability of stationary phases.[15] The study of the retention behavior of barbituric acid derivatives[16] and nonionic surfactants[17,18] on polyethylene-coated supports have recently been reported. Due to its advantageous mechanical properties and high stability of extreme pH values,[19] titanium dioxide is a promising substitute for silica, specially, in the separation of basic compounds.[20] Octadecyl-coated titanium dioxide was also prepared,[21] and its retention characteristics was compared with those of other reversed-phase supports.[22] It was established, that, the separation capacity of octadecyl-coated titanium dioxide for basic compounds is superior to that of octadecyl-coated silica.[23]

Principal component analysis (PCA)[24] has been frequently used in chromatography for the evaluation of retention data matrices of considerable dimensions.[25] The main advantages of PCA in chromatography are as follows:

a) Clustering of variables according to their relationship (clustering chromatographic systems or solutes according to their retention characteristics),

b) The possibility of extraction of one or more background variables having concrete physicochemical meaning for the theory and practice of chromatography,

c) Reduction in the number of variables (a reduction in the number of chromatographic systems or solutes to the minimum necessary for solution of a problem),

d) Combination with nonlinear mapping or cluster analysis facilitates the visual evaluation of the resulting multidimensional matrices of PC loadings and variables.

PCA has been successfully used in chromatography for the characterization of hydrophobic interaction chromatography media,[26] the clustering of solutes,[27] the elucidation of the role of various molecular parameters in the retention,[28] the classification of antihistamine drugs in various HPLC systems,[29] etc.

The objectives of our investigations were to determine the retention behavior of solutes with widely different physicochemical parameters on a titanium dioxide and a polyethylene-coated titanium dioxide column, and to elucidate the relationship between retention characteristics and physicochemical parameters of solutes by means of principal component analysis.

MATERIALS AND METHODS

The chemical name of solutes are compiled in Table 1. They were selected to minimize the intercorrelations between their physicochemical parameters included in PCA: excess molar refraction (further parameter I), dipolarity/polarizability (II), effective hydrogen bond acidity (III), effective hydrogen bond basicity (IV), the characteristic volume of McGovan (V), total dipole moment (VI), maximum electron access charge (electron deficiency) on an atom (VII), and a solvent (water) accessible molecular volume (VIII). Titanium dioxide support was prepared by the research group of Dr.M. Zaharescu (Institute of Physical Chemistry "I.G.Murgulescu", Romanian Academy, Bucharest, Romania). Polyethylene-coated titanium dioxide was prepared as described earlier.[16] Columns of 250 x 4 mm I.D. was filled with titanium dioxide and polyethylene-coated titanium dioxide using a Shandon (Pittsburgh, PA, USA) analytical pump. The eluents were the eluent systems proposed for the filling of adsorption and reversed-phase columns, respectively.[30]

The HPLC system consisted of a Merck-Hitachi apparatus (Model L-6000A pump, L-4000A UV detector and D-2500A integrator, Merck, Darmstadt, Germany). Detection wavelength varied between 210 and 254 nm, depending on the absorption maximum of the solute. Water and water-methanol mixtures were used as eluent, the flow-rate being 1 mL/min. Columns were not thermostated, each determination being run at room temperature (22±2° C). Dead volumes were determined by injecting 1 % $NaNO_3$. The use

Table 1

Chemical Name, Log k_0', and Relative Standard Deviation (R.S.D.%) of Solutes on Titanium Dioxide (TiO_2) and Polyethylene-Coated Titanium Dioxide (PE-TiO_2) Supports

No.	Chemical Name	TiO_2		PE-TiO_2	
		Average	R.S.D. %	Average	R.S.D. %
1	n-Hexylbenzene	-0.114	1.28	0.544	0.85
2	1,3,5-Triisopropylbenzene	-0.126	0.43	1.212	1.36
3	1,4-Dinitrobenzene	-0.101	0.76	0.038	1.39
4	3,5-Dichlorophenol	0.221	0.84	1.347	0.58
5	4-Iodophenol	-0.234	1.08	0.389	0.70
6	Benzamide	-0.291	0.87	0.179	1.41
7	Benzene	-0.017	1.32	0.823	0.86
8	Chlorobenzene	-0.223	0.92	0.749	0.74
9	Cyclohexanone	-0.184	1.53	0.349	0.83
10	Phenol	0.604	0.66	0.023	1.27
11	Hexachlorobutadiene	0.041	1.37	1.672	1.53
12	Indazol	-0.345	1.19	0.690	0.89
13	Caffeine	-0.057	0.96	1.187	1.34
14	4-Nitrobenzoic acid	-0.136	0.81	1.190	0.98
15	N-Methyl-2-pyrrolidinone	-0.237	1.04	0.402	0.92
16	Naphtalene	0.195	1.11	1.215	0.78
17	4-Chlorophenol	0.293	1.42	1.049	1.04
18	Piperidine	-0.132	0.91	-0.889	0.59
19	Benzonitrile	0.014	1.387	-0.562	1.21

of titanium dioxide as reversed-phase support was motivated by the finding that it showed negligible retention capacity in adsorption separation mode, even in n-hexane eluent. Solutes were dissolved in the eluent at a concentration of 0.1 mg/mL.

Each determination was run in quadruplicate and the capacity factor in water (log k_0') or extrapolated to water in the case of more hydrophobic compounds and its relative standard deviation (R.S.D.%) was calculated.

PCA was applied to find the similarities and dissimilarities between the retention capacity of titanium dioxide and polyethylene-coated titanium dioxide columns and the physicochemical parameters of solutes listed above. The logarithm of the capacity factor, determined in water or extrapolated to water (log k_0'), of solutes determined on titanium dioxide and on polyethylene-coated titanium dioxide and the physicochemical parameters listed above were the variables (altogether 10 variables) and the solutes the observations. The limit of the variance explained was set to 99.9%.

As the visual evaluation of the multidimensional matrices of PC loadings and variables is difficult, their two-dimensional nonlinear maps were also calculated.[31] The iteration was carried out to the point when the difference between the two last iterations was lower than 10^{-8}. Softwares for PCA and two-dimensional nonlinear mapping was prepared by Dr. Barna Bordás (Plant Protection Institute of Hungarian Academy of Sciences, Budapest, Hungary) and were run on an IBM AT computer.

In order to compare the retention characteristics of titanium dioxide and polyethylene-coated titanium dioxide with those of other polyethylene-coated supports, linear correlations were calculated between the log k_0' values in Table 1 and the similar values determined on polyethylene-coated silica and polyethylene-coated zirconia. The corresponding log k' values were taken from Ref. 32.

RESULTS AND DISCUSSION

Chromatogram of some solutes on polyethylene-coated titanium dioxide is shown in Fig.1. The peaks are symmetric, even at the higher retention times, indicating that this support can be successfully used for the separation of these class of solutes without buffering the eluent.

The logarithm of the capacity factors and the relative standard deviations are compiled in Table 1. The low values of the relative standard deviation indicate the good stability of the HPLC system and that of the polyethylene-coating.

The data in Table 1 clearly show that titanium dioxide support has a low retention capacity, even in aqueous eluent, indicating that the binding strength of the adsorption centers on the surface of titanium dioxide is fairly low. This finding suggests, that, in the case of any reversed-phase support prepared from titanium dioxide, the undesirable side effect of the original adsorption centers on the retention is negligible.

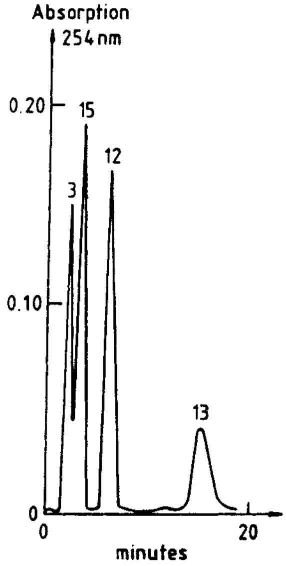

Figure 1. Separation of some solutes on polyethylene-coated titanium dioxide. Eluent: water. Number refer to solutes in Table 1.

The results of PCA are compiled in Table 2. The overwhelming majority of the information contained in the original data matrix can be described by three background variables. In other words, a few theoretical variables are sufficient to describe the relationship between the physicochemical parameters and retention characteristics of these solutes. Unfortunately, PCA does not define these variables as concrete physical or physicochemical entities, only indicates their mathematical possibility.

The retention parameters of solutes have high loadings in different PC components, indicating that titanium dioxide and polyethylene-coated titanium dioxide expose different retention characteristics. The fact that the majority of physicochemical parameters, but not the log k_0' values, have high loadings in the first PC, suggests that the correlation between the two groups of variables is not strong enough for the reliable prediction of the retention of solutes in these RP-HLPC systems. It can be further assumed, that other molecular parameters not included in the calculation may also have a considerable impact on the relationship between retention and molecular characteristics.

Table 2

Similarities and Dissimilarities Between the Physiochemical Parameters and Retention Characteristics of Various Solutes on Titanium Dioxide (log k_0' TiO_2) and Polyethylene-Coated Titanium Dioxide (log k_0' PE-TiO_2) Supports[a]

No of Principal Component	Eigenvalues	Variance Explained %	Total Variance Explained %
1	3.16	31.55	31.55
2	2.35	23.46	55.01
3	1.86	18.62	73.63
4	0.70	7.00	80.62
5	0.67	6.70	87.33
6	0.58	5.81	93.13

Principal Component Loadings

Variables	No. of Principal Component					
Retention parameters:	1	2	3	4	5	6
log k_0' TiO_2:	-0.22	-0.18	**0.64**	**0.68**	-0.21	-0.06
log k_0' PE-TiO_2'	-0.33	**0.62**	0.37	-0.04	0.08	**0.52**
Physiocochemical Parameter						
I	0.31	**0.62**	**0.52**	-0.17	-0.30	0.06
II	**0.84**	0.35	0.15	-0.05	-0.21	0.02
III	0.31	0.03	**0.73**	-0.01	**0.56**	-0.18
IV	**0.69**	0.21	**-0.52**	0.34	-0.09	0.10
V	**-0.52**	**0.78**	-0.26	0.13	0.12	-0.14
VI	**0.78**	0.01	-0.27	0.23	0.37	0.28
VII	**0.71**	0.42	0.06	-0.05	-0.04	-0.37
VIII	**-0.50**	**0.77**	-0.29	0.15	0.13	-0.16

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[a] Results of principal component analysis. For symbols see **MATERIALS AND METHODS.**

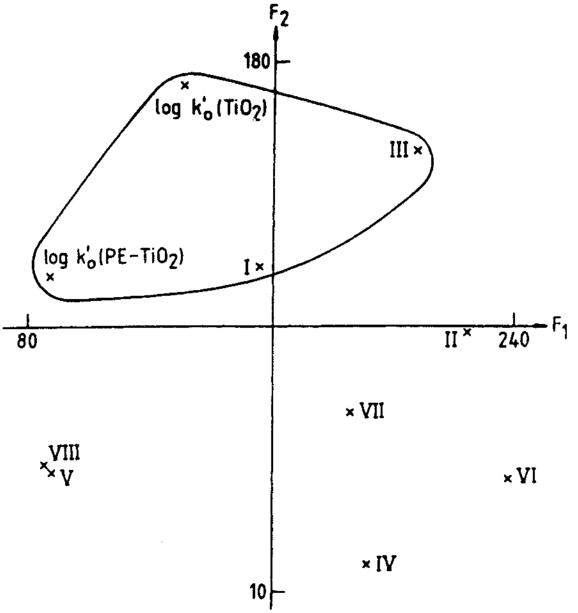

Figure 2. Relationship between the various physicochemical parameters of solutes and their retention behaviour on tita- nium dioxide and polyethylene-coated titanium dioxide supports. Two-dimensional nonlinear map of principal component loadings (number of iterations: 234, maximum error: $4.21.10^{-2}$). For symbols see **MATERIALS AND METHODS**.

The two-dimensional nonlinear map of principal component loadings is shown in Fig 2. Chromatographic parameters form a loose cluster with the excess molar refraction (I) and with the effective hydrogen bond acidity (III), indicating that more than one physicochemical parameter influences the retention of solutes on both titanium dioxide and polyethylene-coated titanium dioxide supports in reversed-phase separation mode. The cluster formation of excess molar refraction and effective hydrogen bond acidity with the retention characteristics suggests that steric correspondence between solutes and the surface of the support, as well as the electronic interactions between them, exert the highest impact on the retention. Solutes do not form separate clusters on the two-dimensional nonlinear map of principal component variables (Fig. 3). This finding supports our previous conclusions that the physicochemical parameters of the solutes are really different, resulting in different retention.

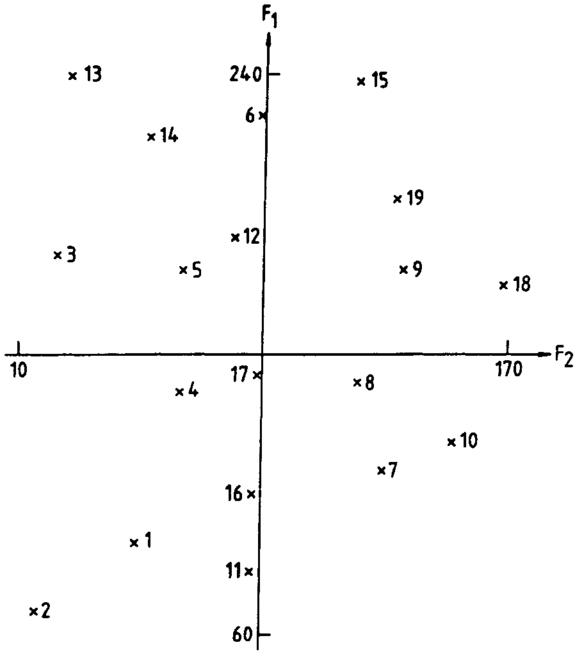

Figure 3. Distribution of solutes according to their retention behaviour on titanium dioxide and polyethylene-coated titanium dioxide supports. Two-dimensional non-linear map of principal component variables (number of iterations: 208, maximum error: $5.55.10^{-2}$). Numbers refer to solutes in Table 1.

The coefficients of linear correlations between the various log k values were not significant (titanium dioxide - polyethylene-coated silica: r = 0.0235; titanium dioxide -polyethylene-coated zirconia: r = 0.0264; polyethylene-coated titanium dioxide - polyethylene-coated silica: r = 0.3688; polyethylene-coated titanium dioxide - polyethylene-coated silica: r = 0.4245). These finding indicates that the retention behavior of titanium dioxide based supports may be different from those of other polymer-coated supports, which advocates their future use in both pharmaceutical and environmental analysis.

It can be concluded from the data, that the retention capacity of titanium dioxide and polyethylene-coated titanium dioxide differ considerably under reversed-phase conditions. Titanium dioxide shows negligible retention strength, which makes it a promising support in reversed-phase chromatography. Principal component analysis suggested that steric conditions and electronic interactions exert the highest impact on the retention.

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