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Sampling characteristics of octadecylsiloxane-bonded silica particle-embedded glass fiber discs for solid-phase extraction

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Abstract

Forced flow planar chromatography was used to characterize the physical and retention properties of an octadecylsiloxane-bonded particle-embedded glass fiber medium used for solid-phase extraction. The carbon loading, intraparticle porosity, binding capacity, and hydrophobicity index indicate that the medium has a large volume of bonded phase essentially filling the pore volume. The interparticle porosity and specific permeability indicate favorable flow characteristics. The flow resistance parameter and the diameter of the largest pore by the bubble method are consistent with a macroscopic homogeneous medium structure free of holes and channels. The silanophilic index indicates a significant concentration of accessible silanol groups and/or other strong hydrogen-bond acid sites. A comparison of retention characteristics to a common cartridge sorbent using the solvation parameter model indicated that the cartridge sorbent had a more favorable cavity term for retention but the particle-embedded glass fiber medium was more competitive with the sample solvent, water–methanol (99:1), for the retention of polar compounds with significant dipole-type interactions and those behaving as hydrogen-bond bases. The physical and retention properties of the particle-embedded glass fiber medium confirm its suitability for use in solid-phase extraction.

1. Introduction

The conventional approach to solid-phase extraction takes advantage of the sampling characteristics of short chromatographic columns, generally referred to as cartridges [1]. New developments in solid-phase extraction for water analysis include the introduction of particle-loaded membranes [2–4], particle-embedded glass fiber discs [5,6], and solvent free microextractions using polymer coated fibers [7]. Rigid discs containing sorbent particles embedded in a glass fiber supporting matrix for solid-phase extraction were introduced in 1990. It is claimed that these low-bed-mass extraction discs offer a number of advantages over conventional solid-phase extraction cartridge devices, such as elimination of channeling, cleaner extracts, reduced sample and solvent requirements, and ease of in situ derivatization.

Inadequate control of the packing density of conventional solid-phase extraction cartridge devices results in channeling during sample applica-

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tion and is the principle cause of poor sampling performance and, under some circumstances, results in poor reproducibility [8]. A further consequence of channeling is that cartridge sorbent beds are larger than they need be to avoid premature breakthrough resulting in increased non-specific sorption of the sample matrix and recovered extracts that are more complex than is desirable for trace analysis. These problems are avoided in a rigid matrix of low bed mass. Use of the disc format increases the cross-sectional area available to the sample compared to cartridge columns, increasing sample processing rates.

Forced flow planar chromatography provides a unique approach to study the physical and retention characteristics of particle-loaded membranes under conditions similar to those used in solid-phase extraction [9,10]. A wide range of physical characteristics relevant to their function as sorbents are easily and quantitatively obtained providing a framework to establish the general range of optimum sampling conditions and to evaluate specific conditions that affect the recovery of individual analytes. An extension of these studies to particle-embedded glass fiber discs is the purpose of this paper.

2. Experimental

Organic solvents and water were Omnisolv grade from EM Science (Gibbstown, NJ, USA). Other chemicals were reagent grade or better and obtained from several sources. Glass fiber sheets containing embedded octadecylsiloxane-bonded silica particles of the same composition used to prepare SPEC®-47-C18AR (cat. nos. 747-19), a 47-mm extraction disc used for environmental applications, were provided by ANSYS (Irvine, CA, USA).

The glass fiber sheets were cut to 20×10 cm pieces and supported by an identical sized sheet of aluminum of a similar thickness to that used in the preparation of aluminium backed TLC plates. All four edges of the glass fiber sheets were sealed with paraffin wax and two narrow channels cut through the medium with a scalpel at positions corresponding to the inlet and outlet troughs in the cushion insert used to direct the eluent flow. The glass fiber medium was installed in the overpressured development chamber without using a mask around the medium and its support.

2.1. Forced flow chromatography

The apparatus used to determine the physical and retention properties of the particle-embedded glass fiber medium is described in detail elsewhere [9,11]. It consists of a Chrompres 25 overpressured development chamber (Factory of Laboratory Instruments, Budapest, Hungary) operated at a cushion pressure of 20 bar, a Model 2350 reciprocating-piston pump (ISCO, Lincoln, NE, USA), a Supco DPG-500 high-pressure transducer (Cole-Parmer, Chicago, IL, USA), a Rheodyne 7125 valve injector with a 20-μl sample loop (Anspec, Ann Arbor, MI, USA), and a UV-50 variable-wavelength detector (Varian Instruments, Walnut Creek, CA, USA) operated at $\lambda = 270$ nm and 0.1 AU full scale. A Nelson Analytical 9000 series A/D interface (PE Nelson, Cupertino, CA, USA) and an Epson Apex 200 computer running under PE Nelson 2100 PC integrator software (revision 5.1) were used for data acquisition. A microburette was used to accurately calibrate the flow-rate.

The theoretical basis and experimental protocol for the methods used to calculate the porosity, permeability, apparent particle diameter, and flow resistance of the particle-loaded membranes by forced flow planar chromatography are outlined elsewhere [8,9,12]. The same procedures were used in these studies for the particle-embedded glass fiber medium. The hydrophobicity index, based on the ratio of the capacity factors of *n*-pentylbenzene and *n*-butylbenzene in methanol–water (4:1), and the silanophilic index, from the ratio of the capacity factors of caffeine and phenol in methanol–water (3:7), were determined according to the scales described by Kimata et al. [13]. A second estimate of the hydrophobicity index, based on the ratio of the capacity factors for anthracene and benzene in acetonitrile–water (65:35), and the

silanophilic index, from the ratio of the capacity factors for N,N-diethyl-*m*-toluamide and anthracene in acetonitrile, were determined as described by Walters [14].

2.2. Flow-through porosity and binding capacity

Measurement of flow-through porosity by the bubble point method was made by retaining an 8-mm disc of the C18AR medium in an ANSYS solid-phase extraction device. Isopropanol was the wetting solvent and nitrogen was applied to the bottom of the disk until the gas just broke through to form a bubble. Eq. 1 was used to calculate the diameter of the largest pore.

$$d = C(\gamma/P) \quad (1)$$

where d is the pore diameter (μm), γ the surface tension (dynes/cm), P pressure in p.s.i. and C is a constant equal to 0.415 when the above units are used.

Binding capacities of the C18AR medium were determined by pumping solutions of a well-retained compound through a disc of known mass, until breakthrough occurred. The quantity bound under these conditions is expressed as a percentage by weight of the total disc mass.

2.3. Calculation of medium properties from the breakthrough model

In previous studies it was demonstrated that a breakthrough model proposed by Lovkvist and Jonson [15] provides a reasonable description of the sampling characteristics of particle-loaded membrane and cartridge sampling devices, Eq. 2 [8,9,16]

$$V_B = (a_0 + a_1/n + a_2/n^2)^{-1/2}(1 + k_s)V_m \quad (2)$$

where a_0, a_1 and a_2 are constants determined for a particular breakthrough level, n the number of theoretical plates for the sampling device, k_s the solute capacity factor with the sample solvent as the mobile phase, and V_m the holdup volume of the sampling device. Under normal sampling conditions n is small (usually < 20) and does not vary strongly with flow-rates in the normal operating range. The quotient in Eq. 2 containing n varies over a narrow numerical range and V_m is fixed by the design of the device. Thus the most important factor for determining the breakthrough volume under normal sampling conditions is the solute capacity factor.

Poole and co-workers [8,10,16,17] have shown that the retention characteristics of a sorbent under solid-phase sampling conditions can be predicted for a wide range of solutes using a solvation parameter model set up as indicated below

$$\log SP = c + mV_X/100 + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H \quad (3)$$

where SP is the correlated solute property, in this case either the capacity factor at a fixed mobile phase composition or the breakthrough volume determined for the sample solvent, V_X is the solute's characteristic volume, R_2 the solute's excess molar refraction, π_2^H is a measure of the solute's ability to stabilize a neighboring dipole by virtue of its capacity for orientation and induction interactions, and α_2^H and β_2^H are parameters characterizing the solute's hydrogen-bond acidity and hydrogen-bond basicity, respectively. The system constants m, r, s, a, b and c are solute independent and characteristic of the sampling system (sorbent and sample solvent). These parameters are evaluated by multiple linear regression analysis by determining the property SP for a series of solutes with known explanatory variables. Once established, the property SP can be estimated for any solute under the same conditions provided that the solute's explanatory variables are known or can be reasonably estimated from empirical combining rules [18].

The retention properties of the particle-embedded glass fiber medium were determined as the capacity factors for a series of varied solutes as a function of mobile phase composition over the range methanol to methanol–water (3:7). The data were fitted to a linear or second order polynomial equation of the type

$$\log k_s = z_0 + z_1\Theta + z_2\Theta^2 \quad (4)$$

where Θ is the volume fraction of methanol in water (% v/v). The coefficients z_0, z_1, and z_2 and the statistics for the fit of the experimental data to Eq. 4 are summarized in Table 1. The values of k_s in water–methanol (99:1) were obtained by extrapolation using Eq. 4. The extrapolated capacity factors contain additional uncertainty over the experimental values. This was unavoidable because of the excessively long retention times and difficult to detect broad and distorted peaks observed at low methanol concentrations for the solutes which made direct measurements impossible to obtain. The experimental values of $\log k_s$ and the extrapolated values for $\log k_s$ in water–methanol (99:1) were used to determine the system constants in Eq. 3. The explanatory variables for the solutes used in Eq. 3 were taken from refs. [18–20]. For convenience they are assembled in Table 2. The characteristic molecular volumes were calculated from incremental constants using the method described by Abraham and McGowan [21]. Multiple linear regression analysis was performed using the program SPSS V4.0 (SPSS, Chicago, IL, USA) on an Epson Apex 200 personal computer.

3. Results and discussion

3.1. Physical characteristics of the glass fiber medium

Forced flow planar chromatography enabled the determination of a number of physical and chemical properties of the particle-embedded glass fiber medium to be made that would have been difficult by other means. These are summa-

Table 1
Coefficients for the variation of retention for the particle-embedded glass fiber medium with methanol–water composition, Eq. 4

Solute	z_0	z_1 $\times 10^2$	z_2 $\times 10^4$	r	Range (% v/v methanol)
Benzene	2.172	−2.70		1.00	100–50
Toluene	4.936	−9.10	4.029	1.00	100–50
n-Propylbenzene	4.459	−4.80		1.00	100–70
Naphthalene	3.179	−3.50		1.00	100–60
Anthracene	4.628	−4.80		1.00	100–70
Chlorobenzene	2.948	−3.40		1.00	100–60
1,2-Dichlorobenzene	3.441	−3.90		0.99	100–70
1,2,4-Trichlorobenzene	3.943	−4.20		1.00	100–70
Bromobenzene	2.806	−3.10		1.00	100–60
1,2-Dibromobenzene	3.531	−3.80		1.00	100–70
Pentan-2-one	1.531	−3.00	0.884	1.00	100–30
Hexan-2-one	1.621	−2.30		0.99	100–30
Nitrobenzene	2.098	−2.70		1.00	100–30
Anisole	2.399	−3.00		1.00	100–30
Benzaldehyde	1.749	−2.50		1.00	100–30
Benzonitrile	2.219	−4.20	1.461	1.00	100–30
Acetophenone	2.325	−4.20	1.280	1.00	100–40
Benzyl alcohol	1.659	−3.40	1.027	1.00	100–30
1-Phenylethanol	2.198	−4.50	1.601	1.00	100–30
Benzamide	1.492	−4.30	1.821	1.00	100–30
Acetanilide	2.029	−4.70	1.905	1.00	100–30
Phenol	1.251	−2.20		1.00	100–30
2-Chlorophenol	1.927	−2.80		1.00	100–30
2-Methylphenol	1.959	−2.90		1.00	100–30
4-Methylphenol	1.824	−2.70		1.00	100–30

Table 2
Explanatory variables for the solvation parameter model, Eq. 3

Solute	V_x/100	R_2	π_2^H	α_2^H	β_2^H
Naphthalene	1.085	1.340	0.92		0.20
Anthracene	1.454	1.340	0.92		0.20
Benzene	0.716	0.610	0.52		0.14
Toluene	0.857	0.601	0.52		0.14
n-Propylbenzene	1.139	0.604	0.50		0.15
Chlorobenzene	0.839	0.718	0.65		0.07
1,2-Dichlorobenzene	0.961	0.872	0.78		0.04
Bromobenzene	0.891	0.882	0.73		0.09
1,2-Dibromobenzene	1.066	1.190	0.96		0.04
1,2,4-Trichlorobenzene	1.083	0.980	0.81		
Pentan-2-one	0.828	0.143	0.68		0.51
Hexan-2-one	0.969	0.136	0.68		0.51
Nitrobenzene	0.891	0.871	1.11		0.28
Acetophenone	1.014	0.818	1.01		0.48
Anisole	0.916	0.708	0.75		0.29
Benzonitrile	0.871	0.742	1.11		0.33
Benzaldehyde	0.873	0.820	1.00		0.39
Benzyl alcohol	0.916	0.803	0.87	0.33	0.56
1-Phenylethanol	1.057	0.784	0.83	0.30	0.66
Acetanilide	1.113	0.870	1.40	0.50	0.67
Benzamide	0.973	0.990	1.50	0.49	0.67
Phenol	0.775	0.805	0.89	0.60	0.30
2-Chlorophenol	0.898	0.853	0.88	0.32	0.31
2-Hydroxytoluene	0.916	0.840	0.86	0.52	0.30
4-Hydroxytoluene	0.916	0.820	0.87	0.57	0.31

rized in Table 3 along with some representative values obtained for an octadecylsiloxane-bonded silica particle-loaded membrane. The total porosity of the particle-embedded medium is similar to that of the particle-loaded membrane (both of which are similar to typical values for slurry-packed HPLC columns). This is an indication of a good packing structure. The particle-embedded glass fiber medium, and to a lesser extent the particle-loaded membrane, posses very little intraparticle porosity. This results from the dense loading of octadecylsiloxane groups essentially filling the pore volume and is confirmed by the relative weight of bonded phase as a fraction of the disc weight, the high binding capacity of the discs, and the high values for the hydrophobicity indexes. Given the intended use of the particle-embedded medium for solid-phase extraction such large volumes of octadecylsiloxane groups are advantageous in promoting retention and favorable breakthrough volumes.

The silanophilic indexes are consistent with a significant concentration of accessible silanol groups and/or other strong hydrogen-bond acid sites. The high hydrophobicity index and silanophilic index, taken together, are typical of polymeric octadecylsiloxane-bonded phases formed from multifunctional silanes in the presence of water. Such phases show greater resistance to acid hydrolysis for sampling aqueous solutions at low pH because of their abundant surface and polymer cross-links.

The interparticle porosity and high specific permeability of the particle-embedded medium indicate favorable flow characteristics. The glass fiber medium is a heterogeneous mixture of glass fibers and embedded sorbent particles with flow properties that can be represented by an optimum particle bed with an average particle

Table 3
Characteristic properties of the SPEC-C18AR particle-embedded glass fiber medium and a J.T. Baker ODS particle-loaded membrane

Property	Value	
	Particle-embedded medium	Particle-loaded membrane [9]
Total porosity, ϵ_T	0.51	0.52
Interparticle porosity, ϵ_o	0.47	0.37
Intraparticle porosity, ϵ_i	0.04	0.15
Apparent average particle diameter, d_p (μm)	15.3	7.7
Specific permeability, B (10^{14} m^2)	8.38	2.5
Flow resistance parameter, ϕ	971	1000–1250
Diameter of largest pore (μm)	5	
Media density (g/ml)	0.49	
Weight of media that is carbon (% w/w)	9.1	
Media surface area (m^2/g)	250	
Average pore diameter of silica before bonding (nm)	8	6
Binding capacity of media (% w/w)	12	
Hydrophobicity index		
Kimata[1]	1.52	1.55
Walters[2]	4.81	5.38
Silanophilic index		
Kimata[3]	0.72	0.64
Walters[4]	1.74	1.34

[1] Normal range of values characterized as low to high 1.3 to 1.52 [13].
[2] Values >4.0 characterized as highly loaded [14].
[3] Values 0.42 to 0.66 characteristic of bonded phases formed with trifunctionalsilanes [13].
[4] Values >1.2 characterized as high [14].

diameter of 15.3 μm. The favorable flow resistance parameter and the diameter of the largest pore by the bubble method, 5 μm, are consistent with a macroscopic homogeneous structure free of holes and channels.

3.2. Retention characteristics of the glass fiber medium

The system constants for the solvation parameter model as a function of mobile phase composition are summarized in Table 4. The statistics of the fit for the measured values to Eq. 3 are within normal expectations and the estimated values for water–methanol (99:1) are acceptable for the estimation of safe sampling volumes. Clearly, the estimated system constants for water–methanol (99:1) are not as good as the experimental values for the middle range of solvent compositions where the capacity factors are most accurately determined. Some deviation from the extrapolated values for k_s in water–methanol (99:1) can be anticipated due to the irregular changes in k_s normally observed at low modifier concentrations.

For evaluation the system constants as a function of mobile phase composition are plotted in Fig. 1. Only the cavity term (m-constant) and interactions with n- and π-electron pairs (r-constant) have positive values and favor extraction by the solvated sorbent. The m-constant increases with decreasing methanol concentration indicating that collapsing the solute cavity in the mobile phase becomes increasingly more favorable as the water structure builds up in the mobile phase. By comparison the r-constant is much less significant and not a major contributing factor to retention. All polar interactions

Table 4
System constants and statistics for the fit to the solvation parameter model for the data obtained by forced flow planar chromatography

Mobile phase composition (% v/v methanol)	System coefficients[a]						Statistics[b]			
	m	*r*	*s*	*a*	*b*	*c*	*R*	*S.E.*	*F*	*n*
100	0.58			−0.63	−0.42	−0.91	0.954	0.08	68	25
	(0.11)			(0.08)	(0.09)	(0.11)				
90	0.89	0.11	−0.18	−0.62	−0.72	−0.78	0.991	0.05	204	25
	(0.09)	(0.07)	(0.07)	(0.06)	(0.06)	(0.07)				
80	1.27	0.12	−0.39	−0.48	−1.07	−0.61	0.990	0.06	186	25
	(0.12)	(0.09)	(0.10)	(0.07)	(0.12)	(0.10)				
70	1.63	0.11	−0.36	−0.52	−1.40	−0.61	0.992	0.07	210	24
	(0.14)	(0.10)	(0.11)	(0.08)	(0.13)	(0.11)				
60	1.75	0.27	−0.45	−0.63	−1.49	−0.44	0.992	0.06	163	20
	(0.21)	(0.09)	(0.09)	(0.07)	(0.15)	(0.15)				
50	1.93	0.19	−0.50	−0.53	−1.57	−0.21	0.988	0.05	84	17
	(0.23)	(0.09)	(0.09)	(0.07)	(0.16)	(0.16)				
40	2.13	0.30	−0.39	−0.56	−1.84	−0.22	0.983	0.07	52	15
	(0.31)	(0.12)	(0.12)	(0.09)	(0.20)	(0.23)				
30	2.75	0.37	−0.48	−0.71	−1.65	−0.48	0.996	0.03	180	14
	(0.16)	(0.07)	(0.06)	(0.05)	(0.06)	(0.12)				
1	4.27		−0.37	−0.58	−2.45	−0.49	0.968	0.26	71	20
	(0.38)		(0.29)	(0.28)	(0.32)	(0.38)				

[a] Values in parentheses represent standard deviations.
[b] R = multiple linear regression coefficient, $S.E.$ = standard error in the estimate, F = Fischer F-statistic, and n = number of solutes.

favor retention in the mobile phase. The hydrogen-bond acidity of water dominates the polar interactions indicating that the solvated sorbent is unable to compete effectively with water for the retention of hydrogen-bond bases. The mobile phase is a stronger hydrogen-bond base than the solvated sorbent but changes in the hydrogen-bond base character of the system (a-constant) are not a strong function of the mobile phase composition.

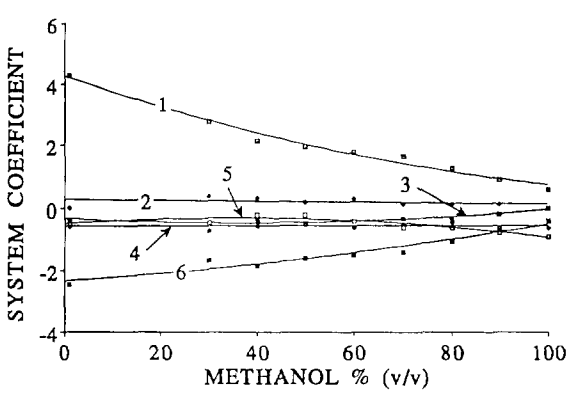

Fig. 1. Variation of the system coefficients as a function of the mobile phase composition for the octadecylsiloxane-bonded silica particle-embedded glass fiber medium. Identification: 1 = m; 2 = r; 3 = s; 4 = a; 5 = c; and 6 = b.

3.3. Comparison of retention characteristics of different extraction media

A comparison of the extraction properties of the octadecylsiloxane-bonded silica particle-embedded medium, particle-loaded membranes [10,16] and a typical cartridge sorbent [8] is summarized in Table 5. Differences in the system constants with the same bulk sample solvent composition are due to differences in the extraction properties of the solvated sorbent. The extraction properties of the Varian Sample Preparation Products particle-loaded membrane and the ANSYS particle-embedded medium, coincidentally, are virtually identical, with both being similar to the extraction properties of the

Table 5
Comparison of system constants for different octadecylsiloxane-bonded silica (ODS) sorbents used in solid-phase extraction

(i) Sample solvent 70% (v/v) methanol in water ($\log k$)

System constants	ANSYS ODS media	Varian ODS membrane	J.T. Baker ODS cartridge
m	1.63	1.63	2.12
r	0.11	0.11	0.16
s	−0.36	−0.37	−0.44
a	−0.52	−0.52	−0.32
b	−1.40	−1.40	−1.59
c	−0.61	−0.61	−0.71

(ii) Sample solvent 1% (v/v) methanol in water

	Extrapolation method ($\log k$)		Direct method ($\log V_B$)
	ANSYS ODS media	J.T. Baker ODS cartridge	J.T. Baker ODS membrane
m	4.27	5.65	5.14
r		0.70	
s	−0.37	−0.76	−0.92
a	0.58	−0.40	−1.05
b	−2.45	−3.26	−2.24
c	−0.49	−1.18	−1.23

J.T. Baker cartridge sorbent with methanol–water (7:3, v/v) as the sample solvent. The choice of methanol–water (7:3) as the mobile phase for comparison was dictated by the high flow resistance of the Varian Sample Preparation Products membrane, which prevented useful measurements by forced flow planar chromatography from being made in predominantly aqueous mobile phases [10]. The results serve the purpose of indicating that the extraction properties of the particle-embedded medium are in no way atypical of expected sorption interactions for more familiar solid-phase extraction sorbents.

Also compiled in Table 5 are estimated system constants for the ANSYS particle-embedded fiber glass medium and the J.T. Baker cartridge sorbent [8] obtained by the extrapolation method as well as system constants determined by the direct method for a J.T. Baker particle-loaded membrane [16] for more typical solid-phase extraction conditions with water–methanol (99:1) as the sample solvent. The most noticeable difference between the three materials is the greater difficulty of cavity formation in the particle-embedded glass fiber medium (*m*-constant), which result in a decrease in general retention, accompanied by a more favorable capacity for dipole-type interactions (*s*-constant), which leads to a relative increase in the retention of dipolar and polarizable compounds. The particle-embedded medium and the particle-loaded membrane have a similar hydrogen-bond acidity (*b*-constant) and are more competitive with water for the retention of hydrogen-bond base solutes than is the cartridge sorbent. The cartridge and particle-embedded medium have similar hydrogen-bond basicity (*a*-constant) and are more competitive with water than the particle-loaded membrane sorbent for the retention of

hydrogen-bond acids. As a group the three sampling devices show similar trends in their retention characteristics with individual differences in the capacity for specific intermolecular interactions that are not unexpected for bonded phases of the octadecylsiloxane type.

3.4. Contribution of solute properties to retention

The difference in estimated retention properties of the particle-embedded glass fiber medium and the cartridge sorbent can be highlighted by considering the contribution of individual intermolecular interactions to the retention of a few solutes with varied properties, Table 6. These are broken out as the contribution of solute size and non-polar interactions represented by $(mV_x/100)$ with possibly a contribution from the c term in Eq. 3, and individual polar interactions represented by rR_2, $s\pi_2^H$, $a\alpha_2^H$, and $b\beta_2^H$. For non-polar and weakly polar solutes like n-propylbenzene the cartridge sorbent is more retentive because of its more favorable cavity term supplemented by a small contribution from the rR_2 term. For polar compounds the difference in retention properties is less marked due to the more favorable dipole–dipole, dipole–induced dipole and solute hydrogen-bond base interactions of the particle-embedded media compared to those of the cartridge sorbent. Most dipolar compounds are also hydrogen-bond bases and the difference in retention for compounds like benzonitrile, acetophenone, anisole, hexan-2-one, and heptanal is not as great as for solutes lacking significant polar interactions. The difference in the sum of the polar interactions does not completely offset the difference in ease of cavity formation so that the cartridge sorbent shows greater retention overall. When the $a\alpha_2^H$ term is considered it favors retention by the cartridge sorbent for compounds like phenol, 1-phenylethanol, and hexan-1-ol, but this advantage is offset by the more favorable dipole and solute hydrogen-bond base interactions with the particle-embedded media.

Table 6
Contribution of different intermolecular interactions to retention for octadecylsiloxane-bonded silica particle-embedded glass fiber media and a cartridge sorbent

Solute	Sorbent type	Intermolecular interactions						Estimated log k_s
		$mV_x/100$	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$b\beta_2^H$	c	
n-Propylbenzene	Cartridge	6.44	0.42	−0.38		−0.49	−1.18	4.8
	Glass fiber	4.86		−0.19		−0.37	−0.49	3.8
Benzonitrile	Cartridge	4.92	0.52	−0.84		−1.08	−1.18	2.3
	Glass fiber	3.72		−0.41		−0.81	−0.49	2.0
Acetophenone	Cartridge	5.73	0.49	−0.77		−1.56	−1.18	2.8
	Glass fiber	4.33		−0.37		−1.18	−0.49	2.2
Phenol	Cartridge	4.38	0.56	−0.68	−0.24	−0.98	−1.18	1.9
	Glass fiber	3.31		−0.33	−0.35	−0.74	−0.49	1.4
1-Phenylethanol	Cartridge	5.97	0.55	−0.63	−0.12	−2.15	−1.18	2.4
	Glass fiber	4.51		−0.31	−0.17	−1.62	−0.49	1.9
Anisole	Cartridge	5.18	0.50	−0.57		−0.95	−1.18	3.0
	Glass fiber	3.91		−0.28		−0.71	−0.49	2.4
Hexan-2-one	Cartridge	5.47	0.10	−0.52		−1.66	−1.18	2.2
	Glass fiber	4.14		−0.25		−1.25	−0.49	2.2
Hexanal	Cartridge	5.48	0.10	−0.49		−1.47	−1.18	2.4
	Glass fiber	4.14		−0.24		−1.25	−0.49	2.2
Hexan-1-ol	Cartridge	5.72	0.15	−0.32	−0.15	−1.56	−1.18	2.7
	Glass fiber	4.32		−0.16	−0.21	−1.18	−0.49	2.3

4. Conclusions

Forced flow planar chromatography provides a versatile approach to study the characteristic physical and retention properties of glass fiber media and particle-loaded membranes intended for use in solid-phase extraction. In this way it is demonstrated that the octadecylsiloxane-bonded, particle-embedded, glass fiber media are macroscopically homogeneous with favorable flow characteristics for solid-phase extraction. The high loading of bonded phase results in retention characteristics for the particle-embedded glass fiber media which are similar to those of particle-loaded membranes and conventional cartridge sorbents.

The solvation parameter model provides insight into the composition of fundamental interactions that are responsible for the retention of individual solutes. The model provides a good description of the experimental data for those regions of the mobile phase composition where accurate capacity factor measurements can be made. For the case most relevant to practical applications of solid-phase extraction, a sample solvent of water–methanol (99:1), the fit is not as good because excessive retention times prevent direct measurement of the capacity factor values. Estimated values obtained by polynomial extrapolation are only approximate because of the length of the extrapolation employed (from water–methanol ratios of 7:3 to 99:1) and because of the likelihood that at very low methanol compositions deviation from the results obtained at higher methanol compositions probably occur. In the only case where it has proven possible to make direct capacity factor measurements for a cyanopropylsiloxane sorbent under solid-phase extraction conditions the deviations from values predicted by extrapolation and measured experimentally are small but significant [22]. For this reason the prediction of $\log k$ values by Eq. 3 cannot be made to better than 0.26 log units from the extrapolated experimental data, which is a significantly larger uncertainty than is typical of the equation fit to experimental data of about 0.05 to 0.08 log units. Not withstanding the uncertainty with which $\log k$ can be estimated the solvation parameter model provides a useful first round prediction of the breakthrough volume of a solute using Eq. 2 given that the value for the holdup volume, V_m, is easily calculated for any extraction disc (or could be estimated from the data given in Table 3) and the kinetic component, which has a narrow numerical range for any selected level of breakthrough [8], is taken as a psuedoconstant. The complementary explanatory variables to the system constants are known for in excess of 1000 compounds [18–20], and others can be estimated from simple combining rules, making the application of Eq. 3 to the estimation of breakthrough volumes using the particle-embedded glass fiber media widely accessible for many compounds of environmental interest.

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