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Retention characteristics of octadecylsiloxane-bonded silica and porous polymer particle-loaded membranes for solid-phase extraction

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Abstract

Forced-flow planar chromatography was used to determine the kinetic and retention properties of an octadecylsiloxane-bonded, silica-based, particle-loaded membrane used for solid-phase extraction. The sorbent was heavily loaded with bonded phase resulting in a small intraparticle porosity. The large plate height and flow resistance indicates a heterogeneous particle size distribution for the membrane with a significant fraction of below average size particles. The hydrophobicity and silanophilic indexes and system constants in the solvation parameter model indicate similar retention properties to a common octadecylsiloxane-bonded silica cartridge sorbent under identical mobile phase conditions. The dimensional instability of a porous polymer particle-loaded membrane prevented its evaluation by forced-flow planar chromatography using the overpressured development chamber. Breakthrough volumes were determined for the porous polymer membrane under typical sample processing conditions for a number of solutes with varied properties and fitted to a solvation parameter model. A comparison to data previously obtained for an octadecylsiloxane-bonded, silica-based, particle-loaded membrane (Bakerbond) indicated that ease of cavity formation favors retention by the octadecylsiloxane-bonded silica particle-loaded membrane for non-polar and weakly polar analytes compared to the porous polymer particle-loaded membrane. Significantly larger breakthrough volumes, however, are obtained on the porous polymer particle-loaded membrane for polar analytes. The porous polymer sorbent competes more effectively with water in dipole-type interactions and as a hydrogen-bond acid. A solvent effect is speculatively suggested as the origin of the porous-polymer sorbent's favorable retention of hydrogen-bond bases compared to the octadecylsiloxane-bonded, silica-based, material.

1. Introduction

Solid-phase extraction (SPE) using sorbent cartridges is a widely accepted technique for the concentration and isolation of analytes from solution prior to chromatographic analysis [1–4].

In 1990 Hagen et al. [5] described a new approach to SPE employing particle-loaded membranes consisting of sorbent particles of about 8 μm diameter immobilized in a web of poly(tetrafluoroethylene) microfibrils. These membranes, in the form of flexible disks of various diameters and 0.5 mm thickness, are now commercially available. The practical advantages claimed for the disk format are related to the improved packing homogeneity of the membrane and its

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shorter height and greater cross-sectional area compared to typical cartridge devices. In turn these lead to shorter sample processing times, decreased plugging by particles, reduced channeling, and reduced non-specific matrix adsorption. There has been considerable interest in this new technology resulting in a significant number of reported applications to environmental, industrial and pharmaceutical samples. The literature is now too great to review in its entirety and we direct the reader to a few recent articles and reviews for a complete bibliography [6–10].

The physicochemical basis of the extraction mechanism using particle-loaded membranes is not well understood. The kinetic properties of an octadecylsiloxane-bonded silica particle-loaded membrane were studied by forced-flow planar chromatography [11]. From a consideration of kinetic and thermodynamic factors it was shown that the most important parameter in determining breakthrough volumes was retention. This led to the development of a solvation parameter model to characterize retention in terms of solute and sorbent characteristics based on Eq. 1 [12],

$$\log V_B = c + mV_X/100 + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H \quad (1)$$

where V_B is the breakthrough volume, V_X 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 coefficients m , r , s , a , b and c are solute independent and are characteristic of the sampling system (sorbent and sample solvent). These parameters are evaluated by multiple linear regression analysis by determining the breakthrough volume for a series of solutes with known explanatory variables. Once established, the breakthrough volume can be estimated for any solute in the same sampling system for which the solute explanatory variables are known or can be reasonably estimated from empirical

combining rules. The solvation parameter model has been applied with great success to explain other solubility-related properties including retention in gas and liquid chromatography, octanol–water partition coefficients, and to characterize coatings for sensors [13–16].

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. The Impress II sealant was obtained from Factory for Laboratory Instruments (Budapest, Hungary). Empore sheets cut to 20 × 10 cm, containing octadecylsiloxane-bonded silica particles and poly(styrene)–divinylbenzene porous polymer particles of the same composition used to prepare Empore extraction disks from Varian Sample Preparation Products (Harbor City, CA, USA) and J.T. Baker (Phillipsburgh, NJ, USA), respectively, were a gift from 3M Co. (St. Paul, MN, USA). Empore extraction disks, 47 mm diameter, containing poly(styrene)–divinylbenzene porous polymer particles were obtained from J.T. Baker.

2.1. Forced-flow chromatography

The apparatus used to determine the kinetic and thermodynamic properties of the particle-loaded membranes is described in detail elsewhere [11,17]. It consists of a Chrompres 25 overpressured development chamber (Factory of Laboratory Instruments) 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- μ l sample loop (Anspec, Ann Arbor, MI, USA), and a UV-50 variable-wavelength detector (Varian Instruments, Walnut Creek, CA, USA) operated at 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 and calculation of peak variance using the Dorsey–Foley peak shape model. A microburette was used to accurately calibrate the flow-rate.

The Empore sheets were supported by and immobilized onto a sheet of 20 × 10 cm aluminum using a light coating of Impress II sealant. The edges of the membrane were sealed with paraffin wax. A scalpel was used to cut inlet and outlet troughs in the Empore sheets at positions corresponding to the troughs in the cushion insert used to direct the eluent flow.

2.2. Direct measurement of breakthrough volumes

The porous polymer particle-loaded membrane disks were mounted in the usual way on the fritted glass support of a standard vacuum filtration apparatus (Millipore, Bedford, MA, USA) connected to a water aspirator via a flow metering valve as described previously [5,6,12]. Prior to use the membranes were washed by sucking 10 ml of acetonitrile through them and subsequently dried by pulling air through the membrane for about 10 min. The disk was then conditioned with methanol, 10 ml, by allowing the solvent to permeate the disk for a few minutes, followed by sucking the solvent through the membrane and releasing the vacuum before the last drop of methanol had passed through the membrane. The disk was then washed with water, 10 ml, followed by application of the sample without allowing the disk to become dry. The samples were sucked through the membrane at a flow-rate of 40 ± 3 ml/min. After the sample had been processed, the receiver was changed for elution of the standards with two 5-ml volumes of acetonitrile. Prior to elution of the standards the disk was allowed to dry for about 30 s under suction. The combined aliquots of acetonitrile were then transferred to a 10-ml volumetric flask, an internal standard added, and the solution adjusted to the mark. The internal standard was used to correct for injection volume differences in gas chromatography and was

selected to have similar volatility to the analytes in solution and to be easily separated from them on the column. Suitable internal standards are 2-alkanones and fatty acid methyl esters.

Standard compounds selected to represent a varied range of intermolecular interactions and acceptable water solubility, taken from Table 1, were prepared in methanol and added to water containing 0.5% (v/v) methanol to give a known amount of standard, 10–20 μ g, in an aqueous solution containing a total of 1% (v/v) methanol. Standards were processed in groups of three to five components per experiment (with representative compounds run in different mixtures to ensure that there was no significant interactions between compounds that affected the breakthrough volume measurements). Initially, samples were screened using decade changes in the sample volume to estimate the approximate breakthrough volumes, followed by a more systematic experimental design. For compounds with a breakthrough volume between 0 and 50 ml, measurements were made at 2.5-ml volume increments, 50 and 100 ml at 5-ml increments, 100 and 1000 ml at 10-ml increments, and greater than 1000 ml at 100-ml increments. The data were subsequently plotted as breakthrough curves. Since it is impossible to interpolate between experimental points to find the breakthrough volume, the difference between the amount of analyte recovered between two points and the general trend in the experimental breakthrough curves was used to establish the breakthrough volume.

2.3. Calculation of membrane properties

The experimental protocol and theoretical relationships used to calculate porosity, specific permeability, flow resistance, apparent particle size, plate height as a function of solvent velocity, hydrophobicity index, silanophilic index, and solute capacity factors in methanol–water mixtures were as reported previously [11,17–19].

The explanatory variables used in the solvation parameter model, Eq. 1, were taken from Refs. [13,14,20,21]. For convenience they are

Table 1
Explanatory variables for use in the solvation parameter model (Eq. 1)

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
<i>n</i> -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
1,4-Dichlorobenzene	0.961	0.825	0.75		0.02
Bromobenzene	0.891	0.882	0.73		0.09
1,2-Dibromobenzene	1.066	1.190	0.96		0.04
Iodobenzene	0.975	1.188	0.82		0.12
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
Heptan-2-one	1.111	0.123	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
1-Nitropentane	1.057	0.212	0.95		0.29
4-Chloroacetophenone	1.136	0.955	1.09		0.44
Heptanal	1.111	0.140	0.65		0.45
Methyl benzoate	1.073	0.733	0.85		0.46
Phenyl acetate	1.073	0.661	1.13		0.54
3-Nitrotoluene	1.032	0.874	1.10		0.25
1,1,2,2-Tetrachloroethane	0.880	0.595	0.76	0.16	0.12
1,1,2-Trichloroethylene	0.715	0.524	0.37	0.08	0.03
Hexan-1-ol	1.013	0.210	0.42	0.37	0.48
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
4-Chlorophenol	0.896	0.915	1.08	0.67	0.20
2-Hydroxytoluene	0.916	0.840	0.86	0.52	0.30
3-Hydroxytoluene	0.916	0.820	0.88	0.57	0.34
4-Hydroxytoluene	0.916	0.820	0.87	0.57	0.31

assembled in Table 1. The characteristic molecular volumes were calculated using the incremental constants and method described by Abraham and McGowan [22]. 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

An earlier report provided a series of values for the kinetic and thermodynamic properties of octadecylsiloxane-bonded silica Bakerbond Empore membranes [11]. These can be compared to the values for a similar material using octa-

Table 2
Characteristic properties of octadecylsiloxane-bonded silica particle-loaded membranes

Property	Bakerbond	Varian Sample Preparation Products
Total porosity	0.52	0.54
Interparticle porosity	0.37	0.48
Intraparticle porosity	0.15	0.06
Specific permeability ($\text{m}^2 \times 10^{12}$)	2.50	2.21
Flow resistance parameter	1000–1250	1040
Apparent particle size (μm)	7.7	5.8
Minimum plate height (μm)	56	<120
Optimum velocity (mm/s)	0.13	<0.045
Hydrophobicity index	1.55	1.51
Silanophilic index	1.34	1.14

decylsiloxane-bonded silica from Varian Separation Products determined in this study (Table 2). Notionally, both membranes contain irregular 8- μm diameter particles with an average pore diameter of 6 nm. Their total porosity values are similar but the Varian product has a higher interparticle porosity and a lower intraparticle porosity than the Bakerbond material. For the Varian material most of the pore volume is either filled or the pore entrances blocked by the bonded phase. Given the intended use of the material in SPE this need not be detrimental. The larger interparticle porosity would suggest a more heterogeneous structure for the membrane compared to the Bakerbond material. The apparent particle size for the Varian product at 5.8 μm is significantly below the value indicated by the manufacturer. This combined with the poor plate height values for the Varian product compared to the Bakerbond material suggest a broader particle size distribution with a larger fraction of fine particles. A considerably higher pressure was required to obtain a given mobile phase velocity through the layer for the Varian membrane than was needed for the Bakerbond material. The overpressured development chamber is restricted to a maximum inlet pressure of about 20 bar so that the range of interparticle mobile phase velocities that could be used to study the kinetic properties of the

Varian material was limited to 0.2 to 0.04 mm/s, corresponding to sample flow-rates for a 47-mm disk with a 38-mm active sampling area of about 3 to 16 ml/min. Within this flow-rate range the plate height for the membrane is controlled by the rate of mass transfer and a linear relationship between the plate height (H , μm) and the interparticle mobile phase velocity (u_e , mm/s) was observed:

$$H = 81.2 + 905u_e \quad R^2 = 1.000, n = 6$$

The minimum plate height for the Bakerbond material was 56 μm obtained at an optimum interparticle mobile phase velocity of 0.13 mm/s [11]. The optimum mobile phase velocity for the Varian product is at least an order of magnitude smaller and corresponds to a sample flow-rate that would not be useful in practice. The membrane is more likely to be used within the flow-rate range of the experiments or at higher values in which the chromatographic efficiency of the membrane is limited by contributions from the resistance to mass transfer and flow anisotropy. In terms of their kinetic characteristics the Bakerbond material is clearly superior but, as demonstrated elsewhere [12,19], the most important property of a particle-loaded membrane in judging its effectiveness for SPE is its retention characteristics. It is probable that a

minimum chromatographic efficiency is needed for the device to function without instantaneous breakthrough, but once this requirement is met, breakthrough is only weakly dependent on the chromatographic efficiency, at least for the low plate numbers associated with SPE devices.

An indication of the retention properties of the sorbent can be obtained from the relative retention of test solutes determined under specified conditions. A hydrophobicity index [23] and a silanophilic index [24] have been developed for the comparison of the retention characteristics of reversed-phase column packings in high-performance liquid chromatography and can be usefully applied to the comparison of SPE sorbents [11,19]. The normal range observed for the hydrophobicity index for column packings is 1.3 to 1.52 indicating that both the Bakerbond material (1.55) and the Varian material (1.51) are synthesized with a high volume of bonded phase material. Given their intended use in extraction this is desirable and there is little to choose between the two materials in this respect. The silanophilic index has values of 0.9 to 1.2 for intermediate activity and a value > 1.2 for high activity. On this scale the Bakerbond material has a high silanophilic activity (1.34) while the Varian product is in the intermediate range (1.14). The difference in the silanophilic index between the two materials will be important in the relative retention of hydrogen-bonding solutes but should not significantly influence the retention of neutral solutes.

Particle-loaded membranes containing octadecylsiloxane-bonded silica particles are used predominantly with aqueous solutions containing 1% (v/v) methanol to ensure adequate wetting of the membrane, reasonable flow-rates, and useful breakthrough volumes for low-molecular-weight analytes [6]. Breakthrough volumes can be measured directly for use in Eq. 1 but this is a slow process. Alternatively, retention measurements can be made at more convenient mobile phase compositions and the value of the capacity factor at 1% (v/v) methanol obtained by a short extrapolation [19]. This process is generally faster when information for a large number of varied solutes is required to determine the sys-

tem coefficients in Eq. 1. Data for the first-order or second-order fit of $\log k$, where k is the capacity factor, against the volume fraction of methanol in the mobile phase (% v/v) for the Varian material are given in Table 3. Data were generated in the range 100 to 50% (v/v) methanol. Increasing mobile phase viscosity combined with the poor chromatographic efficiency of the membrane restricted the measurements to a less than desirable range of mobile phase compositions. This range is not as wide as that available for the Bakerbond material [11]. The system coefficients for the experimental data, the extrapolated data for 1% (v/v) methanol, and the statistics for the fits are summarized in Table 4. There is a smooth change in the system coefficients as a function of mobile phase composition (Fig. 1), in line with expectations from previous studies. The results obtained by extrapolation of the capacity factor values to 1% (v/v) methanol provide a poor fit to Eq. 1. Consequently the system constants obtained are unreliable and should be considered no better than qualitative values and used accordingly.

For the present purposes a direct comparison of the retention properties of the Varian material can be made to a Bakerbond sorbent used in SPE cartridges at a composition of 70% (v/v) methanol in water [19]. The system constants for the Bakerbond cartridge sorbent for these conditions are: $m = 2.12 (\pm 0.23)$, $r = 0.16 (\pm 0.13)$, $s = -0.44 (\pm 0.14)$, $a = -0.32 (\pm 0.11)$, $b = -1.59 (\pm 0.18)$ and $c = -0.71 (\pm 0.21)$. The system constants, in this case, represent the contribution of defined intermolecular interactions to the transfer of a solute from a solution of 30% (v/v) water in methanol to an octadecylsiloxane-bonded silica sorbent in equilibrium with the solvent. Only the m and the r coefficients are positive and therefore favor transfer to the solvated sorbent. The r coefficient is barely significant so the most important contribution to retention is the cavity contribution represented by the m coefficient. The m coefficient is larger for the Bakerbond cartridge sorbent indicating that forming a cavity for the solute is easier for this material than for the Varian product. Neutral polar molecules have

Table 3
Relationship between the capacity factor and the volume fraction of methanol (φ) in the mobile phase determined by forced-flow planar chromatography

Solute	a_0	a_1 $\times 10^2$	a_2 $\times 10^4$	Composition range (%, v/v. methanol)
Naphthalene	2.070	-2.11		100–60
Benzene	1.887	-2.21		100–50
Toluene	2.523	-2.92		100–50
Anthracene	6.645	-1.271	6.35	100–70
Chlorobenzene	2.049	-2.22		100–50
Pentan-2-one	1.548	-1.96		100–50
Hexan-2-one	4.813	-1.002	4.82	100–50
4-Hydroxytoluene	2.550	-3.07		100–60
2-Hydroxytoluene	2.214	-3.85	1.28	100–50
Acetanilide	2.612	-5.53	2.53	100–50
Benzamide	0.597	-1.03		100–50
1,2-Dibromobenzene	2.803	-2.90		100–70
2-Chlorophenol	2.508	-4.29	1.40	100–50
1-Phenylethanol	2.664	-5.45	2.41	100–50
Benzyl alcohol	1.409	-1.86		100–50
Phenol	1.477	-2.08		100–50
Nitrobenzene	2.153	-2.45		100–60
<i>n</i> -Propylbenzene	2.703	-2.83		100–60
Anisole	2.138	-2.38		100–60
Acetophenone	1.473	-1.83		100–50
Benzonitrile	2.359	-4.42	1.75	100–50
Bromobenzene	2.268	-2.45		100–60
Benzaldehyde	2.257	-5.08	2.47	100–50
1,2-Dichlorobenzene	4.487	-7.64	3.09	100–60

Log $k_s = a_0 + a_1\varphi + a_2\varphi^2$ (in all cases $R^2 = 1.000$ for the fit). k_s = capacity factor for solute *s*.

about the same dipole type interactions with both sorbents and hydrogen-bond bases are marginally better retained on the Bakerbond sorbent and hydrogen-bond acids on the Varian sorbent. The difference in properties between the two sorbents are not large enough to reach any substantive conclusions about one material being superior to the other. They are slightly different in retention properties and both sorbents should function acceptably in SPE.

Particle-loaded membranes containing porous polymer sorbents were recently introduced to obtain improved retention of weak acids like phenols and to eliminate undesirable ion-exchange interactions of the silanol groups present in silica-based bonded phases with bases, such as amines [25]. The porous polymer particle-loaded membranes, unfortunately, were too dimensionally unstable to allow measurements to be made

by forced-flow planar chromatography. Even after applying an overpressure of only 10 bar the membranes visibly changed shape and lifted from its aluminum support. It was impossible to obtain any useful information concerning the kinetic properties of these membranes and the direct method of determining breakthrough volumes had to be used to characterize their retention properties.

The breakthrough volumes for a series of solutes with a wide variation in solute properties for a sample solvent containing 1% (v/v) methanol in water are summarized in Table 5. The fit to Eq. 1 is as follows: $m = 3.520 (\pm 0.2)$, $r = 0.336 (\pm 0.09)$, $s = -0.265 (\pm 0.11)$, $a = -2.306 (\pm 0.08)$, $b = -0.761 (\pm 0.12)$ and $c = -0.400 (\pm 0.19)$. Statistically the fit to the data is good with a multiple correlation coefficient = 0.994, standard error = 0.08, and F -statistic =

Table 4

System coefficients 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						Statistics			
	<i>m</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>R</i>	S.E.	<i>F</i>	<i>n</i>
100	0.343 (0.11)	0.120 (0.09)		-0.711 (0.10)	-0.379 (0.12)	-0.785 (0.09)	0.958	0.079	47	22
90	0.888 (0.09)	0.108 (0.07)	-0.183 (0.07)	-0.624 (0.06)	-0.717 (0.09)	-0.779 (0.07)	0.991	0.048	204	26
80	1.270 (0.12)	0.119 (0.09)	-0.391 (0.10)	-0.478 (0.07)	-1.072 (0.12)	-0.609 (0.10)	0.990	0.064	186	24
70	1.632 (0.14)	0.114 (0.10)	-0.365 (0.11)	-0.523 (0.08)	-1.402 (0.13)	-0.605 (0.11)	0.992	0.070	210	25
60	1.747 (0.21)	0.268 (0.09)	-0.454 (0.09)	-0.629 (0.07)	-1.491 (0.15)	-0.437 (0.15)	0.992	0.058	163	18
50	1.931 (0.23)	0.193 (0.09)	-0.504 (0.09)	-0.526 (0.07)	-1.567 (0.16)	-0.207 (0.16)	0.988	0.052	84	17
1	2.930 (0.57)	-1.702 (0.60)	-1.557 (0.57)	-0.681 (0.40)	-3.365 (0.79)	-0.313 (0.47)	0.830	0.079	6	20

R = Multiple linear regression coefficient; S.E. = standard error in the estimate; *F* = Fischer *F*-statistic; *n* = number of solutes. Values in parentheses are the uncertainty values (standard deviation) in the identified coefficient.

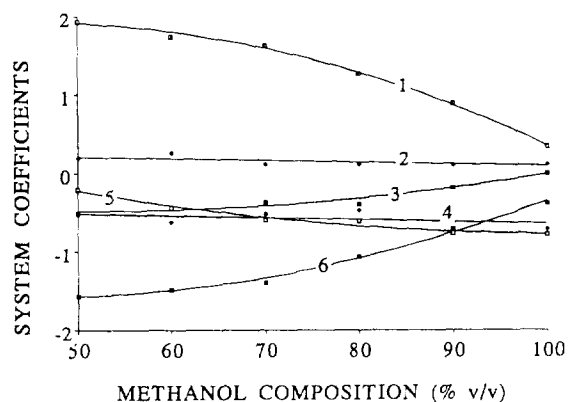


Fig. 1. Variation of the system constants as a function of the mobile phase composition for the octadecylsiloxane-bonded silica particle-loaded membrane from Varian Sample Preparation Products. Identification: 1 = *m*; 2 = *r*; 3 = *s*; 4 = *a*; 5 = *c*; 6 = *b*.

360. The system constants are reliable and can be quantitatively compared with the results for the Bakerbond octadecylsiloxane-bonded, silica-based, particle-loaded membranes [12] for which $m = 5.14 (\pm 0.17)$, $s = -0.92 (\pm 0.08)$, $a = -1.05 (\pm 0.08)$, $b = -2.24 (\pm 0.10)$ and $c = -1.23 (\pm 0.17)$. In making a comparison between the two membrane types it is necessary to keep in mind that the stationary phase into which the solutes are extracted is comprised of the sorbent material and those sample solvent molecules selectively localized at the sorbent surface in the stagnant solvent interface region. With some certainty we can state that the solvent composition of the interfacial region and the sample solvent are different, but it is no simple matter to assign a composition to this region [1].

There are significant differences in the system constants for the two types of particle-loaded membranes indicating different characteristic extraction properties. Cavity formation is signifi-

Table 5
Breakthrough volumes for the porous polymer particle-loaded membrane (solvent 1% v/v, methanol)

Solute	Log V_B
Heptan-2-one	3.070
1-Nitropentane	2.875
3-Nitrotoluene	2.942
Acetophenone	2.780
Anisole	2.544
Chlorobenzene	2.574
Benzaldehyde	2.477
Benzonitrile	2.477
Iodobenzene	3.130
1,2-Dichlorobenzene	3.070
Phenol	0.700
Nitrobenzene	2.477
2-Chlorophenol	1.929
4-Chloroacetophenone	3.176
1,1,2,2-Tetrachloroethane	2.146
Heptanal	2.041
1,4-Dichlorobenzene	3.079
1,1,2-Trichloroethylene	2.000
Benzyl alcohol	1.653
1-Phenylethanol	2.097
Hexan-1-ol	1.875
3-Hydroxytoluene	1.397
4-Hydroxytoluene	1.397
Methyl benzoate	3.114
Phenyl acetate	3.041
4-Chlorophenol	1.000

cantly easier for the solvated octadecylsiloxane-bonded silica sorbent than is the case for the solvated porous polymer. Since, within reason, the m coefficient can not be too large, the octadecylsiloxane-bonded silica sorbent is expected to provide larger breakthrough volumes for non-polar solutes. There is a favorable contribution from the r coefficient for extraction by the porous polymer (the r coefficient is not significant for the octadecylsiloxane-bonded silica sorbent) indicating weak selectivity for the retention of π - and n -electron acceptor solutes by the porous polymer sorbent. This effect, however, is generally small and in no way can compensate for differences in the ease of cavity formation for solutes lacking polar functional groups.

All polar interactions favor solubility in the sample solvent and result in a general decrease

in the breakthrough volume. The extent to which the polar interactions affect the breakthrough volume are significantly influenced by properties of the solvated sorbent. The greater polarizability of the aromatic rings of the porous polymer results in a more favorable interaction with dipolar compounds and larger breakthrough volumes compared to the silica-based material. Neither material is competitive with water as a reservoir of hydrogen-bonding interactions but their capacity to retain hydrogen-bond acids and bases are complementary. The large negative a coefficient for the porous polymer probably reflects the strong hydrogen-bond basicity of water and the lack of competing interactions offered by the solvated sorbent. In which case the smaller negative a coefficient for the silica-based material is an indication that it can more effectively compete with water as a hydrogen-bond base than can the porous polymer, most likely due to the lone pair electrons on the oxygen of the siloxane and silanol groups of the silica-based sorbent. The larger negative b coefficient for the silica-based material compared to the porous polymer was unanticipated. It suggests that the solvated porous polymer is a stronger hydrogen-bond acid than the solvated silica-based material. Given that the porous polymer contains no obvious hydrogen-bond acid sites that could compete with the sample solvent then the differences in properties must be due to differences in composition of the stagnant interfacial solvent associated with the sorbent. Water is a moderate hydrogen-bond acid and methanol should be able to effectively compete with it. The porous polymer is effectively hydrophobic and should take up methanol in preference to water in a more selective manner than the structurally heterogeneous silica-based sorbent with its significant proportion of polar groups. The silanol groups of the silica-based material must be effectively involved in internal hydrogen bonding and hydrogen bonding to sorbed components of the sample solvent, and are unavailable to solutes entering the sorption layer. From this we infer that the difference in relative concentration of methanol, and possibly the thickness of the sorption layer, is responsible for

the greater apparent hydrogen-bond acidity of the porous-polymer sorbent compared to the silica-based material. This we admit is speculation but no other obvious explanation seems to fit the facts.

The difference in extraction properties of the two materials can be highlighted by considering the contribution of individual intermolecular interactions to the breakthrough volume. 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 equation constant c , and individual polar interactions described by rR_2 , $s\pi_2^H$, $a\alpha_2^H$ and $b\beta_2^H$ for a few select solutes in Table 6. For non-polar compounds and weakly polar compounds like *n*-butylbenzene the octadecylsiloxane-bonded silica sorbent is preferred because of its more favorable cavity term. Most dipolar compounds are also hydrogen-bond bases and for these compounds retention on the porous polymer is more favorable. The difference in contributions from $s\pi_2^H$ and $b\beta_2^H$ between the two materials for compounds like benzonitrile, acetophenone, anisole, and hexan-2-one is sufficient to offset the more favorable cavity term for the octa-

decylsiloxane-bonded silica sorbent. Most hydrogen-bond acids are also dipolar and significant hydrogen-bond bases. When the $a\alpha_2^H$ term is considered it strongly favors retention by the octadecylsiloxane-bonded silica sorbent for compounds like phenol and 1-phenylethanol but this advantage is more than compensated for by the less favorable $s\pi_2^H$ and $b\beta_2^H$ terms. Again the porous polymer provides more favorable breakthrough volumes for these compounds.

For the retention of low-molecular-mass polar solutes the porous polymer sorbent provides larger breakthrough volumes because it more effectively competes with water in dipolar and solute hydrogen-bond base interactions. The octadecylsiloxane-bonded sorbent has a more favorable cavity term and competes more effectively with water for solutes that are hydrogen-bond acids but, in general, for polar solutes the balance of all intermolecular interactions still favors retention by the porous polymer. Since solute size and the capacity for polar interactions are not expected to be correlated this picture could change for larger solutes which might well be preferentially retained by the octadecylsiloxane-bonded silica sorbent in those

Table 6

Contribution of different intermolecular interactions to the breakthrough volume ($\log V_b$) of some typical solutes (solvent 1%, v/v, methanol)

Solute	Membrane type ^a	Intermolecular interaction					Estimated breakthrough volume	
		$mV_X/100$	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$b\beta_2^H$		c
<i>n</i> -Butylbenzene	ODS	6.579		-0.469		-0.336	-1.23	4.544
	PS-DVB	4.496	0.202	-0.135		-0.114	-0.40	4.058
Benzonitrile	ODS	4.477		-1.021		-0.805	-1.23	1.421
	PS-DVB	3.066	0.249	-0.294		-0.251	-0.40	2.370
Acetophenone	ODS	5.212		-0.929		-1.075	-1.23	1.978
	PS-DVB	3.569	0.275	-0.268		-0.365	-0.40	2.811
Phenol	ODS	3.984		-0.819	-0.630	-0.672	-1.23	0.624
	PS-DVB	2.728	0.271	-0.236	-1.384	-0.228	-0.40	0.751
1-Phenylethanol	ODS	5.433		-0.764	-0.315	-1.478	-1.23	1.646
	PS-DVB	3.721	0.263	-0.220	-0.692	-0.502	-0.40	2.170
Anisole	ODS	4.708		-0.690		-0.650	-1.23	2.138
	PS-DVB	3.224	0.238	-0.199		-0.221	-0.40	2.642
Hexan-2-one	ODS	4.981		-0.626		-1.142	-1.23	1.983
	PS-DVB	3.411	0.046	-0.180		-0.388	-0.40	2.489

^a ODS = Octadecylsiloxane-bonded silica sorbent; PS-DVB = poly(styrene)-divinylbenzene porous polymer.

cases where the more favorable cavity term exceeds the difference in contributions from the polar interaction terms.

The addition of a small amount of organic solvent to the sample to obtain adequate flow through the membrane and stable sampling conditions over time is not an optional step [6]. The above results suggest that the selectivity of the sorbent for specific intermolecular interactions is significantly influenced by the choice of organic solvent employed. Methanol is almost always used for this purpose but solvents with a contra selectivity may be capable of significant changes in breakthrough volumes. The experimental protocol in combination with the solvation parameter model provides an experimental framework to study these effects quantitatively.

References

- [1] C.F. Poole and S.K. Poole, *Chromatography Today*, Elsevier, Amsterdam, 1991, pp. 777–793.
- [2] S.K. Poole, T.A. Dean, J.W. Oudsema and C.F. Poole, *Anal. Chim. Acta*, 236 (1990) 3.
- [3] I. Liska, J. Krupcik and P.A. Leclercq, *J. High Resolut. Chromatogr.*, 12 (1989) 577.
- [4] I. Liska, *J. Chromatogr. A*, 655 (1993) 163.
- [5] D.R. Hagen, C.G. Markell, G. Schmitt and D.B. Blevins, *Anal. Chim. Acta*, 236 (1990) 157.
- [6] M.L. Mayer and C.F. Poole, *Anal. Chim. Acta*, 294 (1994) 113.
- [7] D. Barcelo, S. Chiron, S. Lacorte, E. Martinez and J.S. Salau and M.C. Hennion, *Trends Anal. Chem.* 13 (1994) 352.
- [8] J. Hodgson, J. Collins and W. Bashe, *J. Chromatogr. A*, 659 (1994) 395.
- [9] J. Beltran, F.J. Lopez and F. Hernandez, *J. Chromatogr. A*, 283 (1993) 297.
- [10] C. Markell, D.F. Hagen and V.A. Bunnelle, *LC·GC*, 9 (1991) 332.
- [11] W.P.N. Fernando, M.L. Larrivee and C.F. Poole, *Anal. Chem.*, 65 (1993) 588.
- [12] M.L. Larrivee and C.F. Poole, *Anal. Chem.*, 66 (1994) 139.
- [13] M.H. Abraham, *Chem. Soc. Rev.*, 22 (1993) 73.
- [14] M.H. Abraham, J. Andonian-Haftvan, G.S. Whiting, A. Leo and R.S. Taft, *J. Chem Soc., Perkin Trans. 2*, (1994) 1777.
- [15] C.F. Poole, T.O. Kollie and S.K. Poole, *Chromatographia*, 34 (1992) 281.
- [16] P.W. Carr, *Microchem. J.*, 48 (1993) 4.
- [17] W.P.N. Fernando and C.F. Poole, *J. Planar Chromatogr.*, 3 (1990) 389.
- [18] W.P.N. Fernando and C.F. Poole, *J. Planar Chromatogr.*, 4 (1991) 278.
- [19] K.G. Miller and C.F. Poole, *J. High Resolut. Chromatogr.*, 17 (1994) 125.
- [20] M.H. Abraham, *J. Phys. Org. Chem.*, 6 (1993) 660.
- [21] M.H. Abraham, *J. Chromatogr.*, 644 (1993) 95.
- [22] M.H. Abraham and J.C. McGowan, *Chromatographia*, 23 (1987) 243.
- [23] K. Kimata, F. Iwaguchi, S. Onishi, K. Jinno, R. Eksteen, K. Hosoya, M. Araki, and N. Tanaka, *J. Chromatogr. Sci.*, 27 (1989) 721.
- [24] M.J. Walters, *J. Assoc. Off. Anal. Chem.*, 70 (1987) 465.
- [25] L. Schmidt, J.J. Sun, J.S. Fritz, D.F. Hagen, C.G. Markell and E.E. Wisted, *J. Chromatogr.*, 641 (1993) 57.