Sorption Properties of Styrene–Divinylbenzene Macroreticular Porous Polymers

Communications

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The sorption properties of some styrene–divinylbenzene macroreticular porous polymer sorbents for solid-phase extraction are characterized using the solvation parameter model. Dispersion interactions are generally responsible for retention with a small contribution from hydrogen-bond interactions that may arise from the presence of polymer impurities. Lone pair–lone pair electron repulsion is a common mechanism reducing retention. Interactions of a dipole-type are not significant for styrene–divinylbenzene sorbents while these play a significant role in retention on Tenax sorbents, highlighting the complementary character of these two porous polymers. The solvation parameter model can also be used to characterize retention of styrene–divinylbenzene sorbents in non-aqueous solvents and to predict conditions resulting in maximum sample concentration in the recovery step in solid-phase extraction.

Macroreticular porous polymers are widely used in solid-phase extraction for the isolation of organic compounds from air and water, and in gas, liquid and supercritical fluid chromatography as stationary phases.[1] Porous polymers based on the co-polymerization of styrene and divinylbenzene are the most common type, although others based on ethylvinylbenzene, acrylonitrile, acrylic esters, vinylpyrrolidone, *etc.*, are well known. The choice of experimental conditions allows rigid or soft beads with different properties to be prepared, in narrow particle size ranges, from non-porous to about 600 nm pores, surface areas from about 2 to 1000 m² g⁻¹, and with different monomer chemistries. It is this range of properties that enables them to be used for so many divergent applications in analytical chemistry.

There are a number of empirical guides that can be used to match the sorption properties of individual porous polymers to particular applications and a very large applications data base is available.[1] Modified versions of the McReynolds' phase constants system, Snyder's selectivity triangle, and the relative retention of ethylene, acetylene and carbon dioxide, have been proposed as methods to standardize sorbent selectivity of porous polymers.[2–4] These methods are inadequate on theoretical and practical grounds.[5,6] More recently, Abraham and co-workers have used the solvation parameter model to characterize the sorption properties of carbon,[7,8] and Poole and co-workers the sorption properties of Tenax sorbents.[9] Poole and Poole used the solvation parameter model to explain the influence of solvent effects on the breakthrough volume of porous polymer particle-loaded membranes, used for the solid-

phase extraction of organic compounds from water containing 1% (v/v) of various organic solvents which were added to improve sample processing properties.[10] Only recently has experimental data for porous polymers of the styrene–divinylbenzene type, suitable for analysis by the solvation parameter model, become available, and is the subject of this communication.[11,12]

Results and Discussion

The form of the solvation parameter model suitable for characterizing the retention properties of porous polymer sorbents with sorption occurring from the gas phase is given by eqn. (1):[6–9]

$$SP = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \tag{1}$$

where *SP* is some free energy related property of the system, such as the specific retention volume, distribution constant, or the breakthrough volume; R_2 is the solute's excess molar refraction; π_2^H is the ability of the solute to stabilize a neighbouring dipole by virtue of its capacity for orientation and induction interactions; α_2^H and β_2^H are parameters characteristic of the solute's effective hydrogen-bond acidity and hydrogen-bond basicity, respectively; and $\log L^{16}$ is the distribution constant for the solute between a gas and *n*-hexadecane at 298 K. The solute's excess molar refraction is usually available by simple arithmetic calculation; the other solute descriptors are parameters derived from equilibrium measurements for complexation and partition processes with values available for over 2000 compounds.[13,14] The system constants in equation (1) are unambiguously defined: the *r* constant refers to the capacity of the sorbent for interaction with solute n- or π-electrons; the *s* constant to the sorbent's capacity for dipole–dipole and dipole-induced dipole interactions; the *a* constant characterizes the sorbent's hydrogen-bond basicity (because a basic sorbent will interact with an acidic solute); the *b* constant characterizes the sorbent's hydrogen-bond acidity; and the *l* constant incorporates contributions from solvent cavity formation and dispersion interactions. The system constants are determined from experimental values for the observed parameter, *SP*, for a group of solutes of known properties, sufficiently varied to define all interactions in eqn. (1), and of sufficient number to establish the statistical validity of eqn. (1), by multiple linear regression analysis.

Table 1 summarizes the fit of the solvation parameter model to several sets of experimental data taken from the references indicated in the table. The data of Pankow *et al.*[12] is the most useful for styrene–divinylbenzene sorbents and allows the system constants to be determined as a function of temperature. The system constants vary linearly with temperature over the range 70 to 90 °C, but if the data point at 20 °C is included, a

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quadratic fit is superior [R^2 is generally >0.99 except for the a constant on sorbent 3M(a)] and is similar to trends observed in the temperature dependence of the system constants in GLC, for which more extensive data over wider temperature ranges are available.[19,20] The data at 20 °C is typical of normal sorbent trapping conditions and will be all that is interpreted here.

The styrene–divinylbenzene polymers differ primarily in surface area (and therefore presumably pore structure) with the 3M(a) polymer having a surface area of 350 m^2 g^{-1}, 3M(b) 880 m^2 g^{-1}, and Chromosorb 106 700–800 m^2 g^{-1}. The main contribution to retention is dispersion, as represented by the l constant with lone pair–lone pair electron repulsion reducing retention (the r constant is negative for three of the four sorbents). Dipole-type interactions are not significant (the s constant is zero). The general structure of the sorbent contains no functional groups to act as a hydrogen-bond acid, yet some capacity for hydrogen-bond interactions is identified by the model. All four styrene–divinylbenzene sorbents are weak hydrogen-bond acids (b constant) while all but the 3M(a) polymer are weak hydrogen-bond bases (a constant). This would suggest that the polymers contain unanticipated polar impurities in their structure introduced during synthesis or during thermal conditioning and use. Their general influence on retention will be discussed subsequently.

Available data for Porapak R, and some representative data for Tenax polymers,[9] is included in Table 1 for comparison with the styrene–divinylbenzene sorbents. Porapak R is a poly-(vinylpyrrolidone) polymer with a high selectivity for hydrogen-bond acids (large a constant), as would be anticipated from its structure, although the fit of the data to the model is only modest, in part due to the limited variety and number of the solutes reported. Retention on Tenax GC is dominated by dispersion, but in contrast to the styrene–divinylbenzene sorbents, a significant contribution results from dipole-type interactions (large s constant). This shows a fundamental difference in the capacity of the styrene–divinylbenzene and Tenax sorbents for polar interactions and is an illustration of their complementary sorbent properties.

The contribution of the various intermolecular interactions to the retention of four varied solutes on the two styrene–divinylbenzene polymers 3M(a) and 3M(b) and Tenax GC is summarized in Table 2. The (c + $l$log L^{16}) term is taken as a rough measure of the cavity and dispersion contributions to retention and is clearly dominant and sensibly increases with the surface area for the two styrene–divinylbenzene sorbents. The very significant contribution of dipole-type interactions on Tenax is represented by the large contribution of $s\pi_2^H$ to the retention of benzyl cyanide and benzyl alcohol. The sorbent

Table 1 System constants for porous polymer sorbents at different temperatures

Sorbent	Temperature/°C	System constants*						Statistics†				Reference for data
		c	r	s	a	b	l	R	SE	F	n	
Styrene–Divinylbenzene—												
3M(a)	20	−1.92 (0.13)	−0.70 (0.13)	0	0.54 (0.19)	0.85 (0.12)	1.21 (0.05)	0.994	0.067	238	16	12
	70	−2.73 (0.10)	−0.38 (0.10)	0	0.57 (0.16)	0.80 (0.10)	1.01 (0.04)	0.993	0.06	224	17	
	75	−2.81 (0.12)	−0.32 (0.11)	0	0.64 (0.19)	0.68 (0.11)	1.00 (0.05)	0.991	0.07	171	17	
	80	−2.88 (0.11)	−0.32 (0.10)	0	0.61 (0.17)	0.69 (0.10)	0.98 (0.04)	0.993	0.06	214	17	
	85	−2.89 (0.12)	−0.26 (0.11)	0	0.61 (0.18)	0.66 (0.11)	0.95 (0.05)	0.991	0.06	164	17	
	90	−2.92 (0.09)	−0.22 (0.08)	0	0.56 (0.14)	0.63 (0.08)	0.93 (0.04)	0.995	0.05	273	17	
3M(b)	20	−1.87 (0.20)	−0.75 (0.22)	0	0	0.91 (0.22)	1.27 (0.08)	0.984	0.12	125	16	12
	70	−2.60 (0.07)	−0.33 (0.07)	0	0	0.59 (0.07)	1.03 (0.03)	0.997	0.04	717	17	
	80	−2.77 (0.09)	−0.33 (0.08)	0	0	0.62 (0.08)	1.02 (0.04)	0.996	0.05	400	17	
	85	−2.82 (0.08)	−0.29 (0.07)	0	0	0.60 (0.07)	0.99 (0.03)	0.996	0.04	416	16	
	90	−2.90 (0.08)	−0.26 (0.07)	0	0	0.60 (0.07)	0.98 (0.03)	0.995	0.04	363	15	
Gallant *et al.*	20	−2.46 (0.21)	0.44 (0.23)	0	0.85 (0.21)	0.65 (0.24)	1.29 (0.07)	0.978	0.26	175	37	12
Chromo-sorb 106	20	−1.69 (0.16)	−1.17 (0.13)	0	0.67 (0.25)	0.83 (0.17)	1.51 (0.05)	0.993	0.15	370	27	15
Poly(vinylpyrrolidone)—												
Porapak R	20	−1.75 (0.28)	−0.67 (0.27)	0.37 (0.21)	2.02 (0.51)	0	1.19 (0.10)	0.975	0.29	53	16	16
Poly(2,6-diphenylphenylene oxide)—												
Tenax GC	20	−2.54 (0.12)	−0.61 (0.19)	1.26 (0.21)	0	0	1.39 (0.04)	0.975	0.34	647	104	17
	20	−3.28 (0.11)	−0.36 (0.18)	0.70 (0.18)	0	0.43 (0.16)	1.41 (0.04)	0.990	0.20	513	51	18

* Numbers in brackets are the standard deviation in the coefficient. † R = correlation coefficient; SE = standard error in the estimate; F = F-statistic; n = number of solutes.

Table 2 Contribution of intermolecular interactions to retention on porous polymers at 20 °C

Solute	Polymer	Intermolecular interactions					Predicted log V_g/ l^{-1} g
		$c + l$ log L^{16}	rR_2	$s\pi_2^H$	$a\alpha_2^H$	$b\beta_2^H$	
Propylbenzene	3M(a)	3.189	−0.421	0	0	0.128	2.896
	3M(b)	3.508	−0.453	0	0	0.136	3.191
	Tenax GC	3.327	−0.366	0.631	0	0	3.592
Di-n-butyl ether	3M(a)	2.819	0	0	0	0.384	3.203
	3M(b)	3.118	0	0	0	0.409	3.527
	Tenax GC	2.903	0	0.316	0	0	3.219
Benzyl cyanide	3M(a)	2.958	−0.517	0	0	0.282	2.723
	3M(b)	3.265	−0.557	0	0	0.300	3.008
	Tenax GC	3.062	−0.450	1.401	0	0	4.013
Benzyl alcohol	3M(a)	3.178	−0.606	0	0.179	0.478	3.229
	3M(b)	3.496	−0.602	0	0	0.509	3.403
	Tenax GC	3.314	−0.487	1.098	0	0	3.925

Solute descriptors used in the calculation					
	Log L^{16}	R_2	π_2^H	α_2^H	β_2^H
Propylbenzene	4.230	0.604	0.50	0	0.15
Di-n-butylether	3.924	0	0.25	0	0.45
Benzyl cyanide	4.039	0.742	1.11	0	0.33
Benzyl alcohol	4.221	0.803	0.87	0.33	0.56

hydrogen-bond basicity of 3M(a) contributes to the retention of benzyl alcohol but at a level which is still quite small and less important than the hydrogen-bond acidity of the styrene–divinylbenzene sorbents. The results in Table 2 may seem contrary if a solute focus is used to explain retention properties, as is commonly the case. For example, in the case of benzyl alcohol, its capacity for hydrogen-bond interactions (particularly hydrogen-bond acidity) is of minor importance compared with other interactions, and viewing the properties of benzyl cyanide in terms of its dipolarity makes no sense in understanding its retention on the styrene–divinylbenzene sorbents, since these sorbents have no capacity for interactions of this kind. Sorbent selection must be based on first characterizing the capacity of the sorbent for specific intermolecular interactions and then using that information to predict solute retention, as we have done for a few compounds as an illustration in Table 2.

A comprehensive treatment of the retention properties of a styrene–divinylbenzene sorbent [similar to 3M(a)] for the extraction of solutes from water is available elsewhere.[10] Two features are of particular note: retention is dominated by the ease of cavity formation in the solvated sorbent and the strong hydrogen-bond acidity of water; and the uptake of the sample processing solvent by the sorbent produces large changes in the phase ratio and sorbent selectivity. Chambers and Fritz have recently provided retention data for a number of varied solutes on a styrene–divinylbenzene sorbent in non-aqueous solvents.[11] The solvation parameter model, eqn. (2), is fitted to this data in Table 3. For condensed phases solute transfer occurs with an approximate cancelling of dispersion interactions and thus eqn. (1) is modified to take account of this by using the characteristic volume (V_x) as the solute descriptor for the cavity term and m as the system constant representing the difference in the ease of cavity formation between the solvated sorbent and the solvent.[9,10,21,22] The fits to the model are reasonable given the

$$SP = c + mV_x/100 + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H \qquad (2)$$

small capacity factor values observed with the three solvents and the accepted experimental difficulty in making such measurements accurately. For acetonitrile, methanol and ethanol the ease of cavity formation in the solvated polymer (m constant) and the capacity of the solvated sorbent for electron lone pair–lone pair interactions (r constant) favour retention. Hydrogen-bond acid or base interactions diminish retention, and a major contribution to the selectivity difference between

Table 3 Sorption properties of a styrene–divinylbenzene sorbent in organic solvents

System constant	Acetonitrile*	Methanol*	Ethanol*
m	0.59 (0.07)	0.66 (0.06)	0.32 (0.06)
r	0.53 (0.08)	0.38 (0.05)	0.37 (0.07)
s	−0.46 (0.12)	0	0.27 (0.10)
a	−0.50 (0.06)	−1.03 (0.05)	−1.17 (0.05)
b	−0.76 (0.12)	−0.82 (0.08)	−0.87 (0.10)
c	−0.74 (0.12)	−0.44 (0.08)	−0.42 (0.07)
Statistics† —			
R	0.960	0.978	0.986
SE	0.08	0.07	0.07
F	58	146	154
n	30	30	28

* Numbers in brackets are the standard deviations in the coefficients.
† See Table 1 for description of terms.

the two alcohols and acetonitrile is seen in their different capacity to act as hydrogen-bond bases (a constant). Methanol and ethanol solvated sorbent has virtually identical r, b, and c constants, from which it can be inferred that the phase ratio of the solvated sorbents and capacity for hydrogen-bond acid and electron lone-pair interactions are about the same. The two solvents differ primarily in their cohesive density, hydrogen-bond basicity, and capacity for dipole-type interactions. Acetonitrile is most potent in its capacity to compete with the solvated sorbent in dipole-type interaction (s constant), while the solvated sorbent can compete effectively with methanol and ethanol for these interactions. Since pure organic solvents are commonly used to recover trapped analytes from porous polymer sorbents after extraction the solvation parameter model can be used to select the appropriate solvent to provide the largest concentration factor for an analyte.

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