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Gas–solid retention volumes of organic compounds on styrene–divinylbenzene and ethylvinylbenzene–divinylbenzene co-polymer sorbent beads

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Abstract

Reliable gas sampling with a sorbent requires a good knowledge of the gas–solid retention volumes of the analytes on the sorbent. Literature data on specific retention volumes at 20°C ($V_{g,293}$, l/g) are reviewed for a number of styrene–divinylbenzene (Sty–DVB) and ethylvinylbenzene–divinylbenzene (EVB–DVB) sorbents, namely XAD-2, Porapak P, Porapak Q, Chromosorb 101, and Chromosorb 102. New measurements are also made by gas–solid chromatography for a Sty–DVB polymer employed in one variety of Empore membrane extraction filters. For all of the data, the $\log V_{g,293}$ values are highly correlated with both $\log p_L^0$ (log of the liquid vapor pressure at 20°C) and with T_b (pure compound boiling point, K). The correlation equations allow the prediction of $\log V_{g,293}$ based on either $\log p_L^0$ or T_b . Equations that can be used for a wide range of compounds and a range of Sty–DVB and EVB–DVB sorbents are: $\log V_{g,293} = -1.16 \log p_L^0 + 3.51$, and $\log V_{g,293} = 0.0227T_b - 6.60$. Separate equations are recommended for aliphatic acids and alcohols. For the Sty–DVB beads used in one variety of Empore extraction filters, the correlation equations are $\log V_{g,293} = -0.99 \log p_L^0 + 3.04$, and $\log V_{g,293} = 0.0175T_b - 4.97$. Most of the available data support absorption into the resin matrix as the dominant gas–solid partitioning mechanism for organic analytes to Sty–DVB sorbent materials.

Keywords: Sorbents; Styrene–divinylbenzene sorbents; Ethylvinylbenzene–divinylbenzene sorbents; Retention volumes, specific; Retention prediction; Hydrocarbons

1. Introduction

Organic polymeric sorbent materials have been used extensively in the preconcentration of organic compounds in both air and water samples. In the prediction of the sample volume that can be passed through a sorbent bed without significant break-

through losses for a given compound (the “safe sampling volume”), a very important quantity is the specific retention volume V_g (l/g). Chromatographically, V_g is the volume of air required to elute the center of an incremental pulse of the analyte of interest through the sorbent bed at a temperature of interest such as 293 K (20°C). At 293 K, the specific retention volume is represented as $V_{g,293}$ (l/g). Available retention volume data for both Tenax-GC/

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TA and polyurethane foam (PUF) have been reviewed by Pankow [1,2].

Styrene–divinylbenzene (Sty–DVB) is one class of synthetic resins that have been demonstrated to be effective in collecting a wide variety of volatile organic compounds (VOCs) in air. Some advantages of Sty–DVB are that (1) it is inexpensive; (2) it is available in a variety of particle sizes, and small Sty–DVB particles (e.g., 3–8 μm in diameter) have favorable mass transfer characteristics; (3) sorbed analytes are relatively easy to recover after sampling; (4) different functionalities can be added to such resin particles.

The purpose of this paper is to examine the available gas–solid $V_{g,293}$ data for two different types of co-polymer sorbent beads, Sty–DVB and ethylvinylbenzene–divinylbenzene (EVB–DVB). Included in this effort is an experimental study of the retention volumes of several compounds on Sty–DVB co-polymer beads utilized by 3M Corp. (St. Paul, MN, USA) in one type of Empore extraction membrane. The considerable utility of Empore filters has been clearly established in the sampling and analysis of water [3–15], and these filters are now part of an accepted US Environmental Protection Agency method for organic pollutants in water [3].

2. Prior studies and general considerations

A number of studies of $V_{g,293}$ values have been carried out for Sty–DVB- and EVB–DVB-type co-polymer sorbents. Of the Sty–DVB type, the sorbents studied include XAD-2, Porapak P, Chromosorb 101, and Chromosorb 102. Of the EVB–DVB type, there is Porapak Q. Table 1 summarizes the available retention data, including the boiling-point and vapor-pressure values for the compounds studied. Since the sorbents mentioned retain all but the most volatile organic compounds to some significant degree at 20°C, all of the data in Table 1 were obtained by extrapolation from higher temperatures in a $\log V_g$ versus $1/T$ format where T is the temperature (K). In some of the studies examined, the extrapolation equations were given; for others, we carried out the extrapolations based on the published $\log V_g$ versus $1/T$ data.

The potential error associated with a $\log V_g$ versus

$1/T$ extrapolation to 20°C increases as the distance of the extrapolation increases. Thus, an extrapolation to 20°C from temperatures in the 125°C range for a less volatile compound will yield a less reliable $V_{g,293}$ value than will an extrapolation to 20°C from the 40°C range for a relatively more volatile compound. Nevertheless, because the actual slope of the $\log V_g$ versus $1/T$ plot is directly proportional to the heat of desorption from the sorbent, and because that heat always decreases as T increases, the bias present in such extrapolations always leads to underestimates of the true $V_{g,293}$ values. This means that there will always be a built-in safety factor when extrapolated $V_{g,293}$ values are used to predict safe sampling volumes.

3. Experimental

Gas–solid chromatography was used to measure retention volumes as a function of temperature for a range of compounds. Retention volumes were extrapolated to 293 K (20°C) in a $\log V_g$ versus $1/T$ format as outlined above. The measurements were made using a Varian 3400 gas chromatograph with a flame ionization detector. The nitrogen carrier gas pressure of ca. 40 p.s.i.g. (1 p.s.i.=6894.76 Pa) yielded flow-rates through the column of ca. 2 ml/min. The glass columns used were ca. 4.5 cm long, and had an inner diameter (I.D.) of 2 mm. Each column was packed with ca. 50 mg of a Sty–DVB sample. Prior to packing, the beads were dried and pre-conditioned at 80°C for ca. 24 h. After packing, each column used was conditioned for another 24 h at 90°C, which caused about a 1% weight loss for the beads. Two types of Sty–DVB were used: (a) the type used in Empore membrane extraction filters (“3M(a)”, 350 m^2/g); and (b) a second, higher surface area sample (“3M(b)”, 880 m^2/g).

The V_g values were calculated according to the following standard gas chromatography equations:

$$F_{\text{col}} = jF_{\text{fm}} \frac{T}{T_{\text{fm}}} \frac{P_{\text{out}} - P_{\text{w,fm}}^0}{P_{\text{out}}} \quad (1)$$

$$j = \frac{3}{2} \left(\frac{(P_{\text{in}}/P_{\text{out}})^2 - 1}{(P_{\text{in}}/P_{\text{out}})^3 - 1} \right) \quad (2)$$

Table 1
Compound property and specific retention volume data at 20°C for various compounds sorbing to styrene–divinylbenzene (Sty–DVB) and ethylvinylbenzene–divinylbenzene (EVB–DVB) co-polymer sorbents

Compound information		Sorbent properties				Retention		Ref.	
Type and name	Boiling point T_b (K)	Vapor pressure $\log p_v^0$ at 20°C (Torr)	Sorbent type	Brand name	Specific surface area a (m ² /g)	Mesh range	$\log V_{R,293}$ (l/g)	$\log V_{R,293}$ (l/m ³) (calculated) ^a	
<i>Aliphatics</i>									
<i>n</i> -Pentane	309.4	2.57	EVB–DVB	Porapak Q	524	60–80	0.89	–1.83	Djordjevic and Laub [16]
			Sty–DVB	3M(a)	350	>400	0.65	–1.92	this work
			Sty–DVB	3M(b)	880	>400	0.74	–2.20	this work
<i>n</i> -Hexane	341.9	2.03	Sty–DVB	XAD-2	364	20–50	0.62	–1.94	Gallant et al. [17]
			Sty–DVB	3M(a)	350	>400	1.33	–1.21	this work
			Sty–DVB	3M(b)	880	>400	1.52	–1.42	this work
Cyclohexane	345.6	1.82	EVB–DVB	Porapak Q	524	60–80	1.74	–0.98	Djordjevic and Laub [16]
<i>n</i> -Heptane	371.6	1.52	EVB–DVB	Porapak Q	524	60–80	1.80	–0.92	Djordjevic and Laub [16]
Methylcyclohexane	373.5	1.53	EVB–DVB	Porapak Q	524	60–80	2.33	–0.39	Djordjevic and Laub [16]
<i>n</i> -Octane	398.2	1.02	Sty–DVB	XAD-2	364	20–50	2.25	–0.47	Djordjevic and Laub [16]
<i>n</i> -Decane	447.3	0.11	Sty–DVB	XAD-2	364	20–50	1.81	–0.75	Gallant et al. [17]
<i>Halogenated aliphatics</i>									
Dichloromethane	313.3	2.54	EVB–DVB	Porapak Q	524	60–80	0.77	–1.95	Djordjevic and Laub [16]
			EVB–DVB	Porapak Q	510	80–100	0.17	–2.54	Vidal-Madjar et al. [18]
			Sty–DVB	3M(a)	350	>400	0.35	–2.19	this work
			Sty–DVB	3M(b)	880	>400	0.50	–2.44	this work
Chloroform	334.5	2.14	EVB–DVB	Porapak Q	524	60–80	1.43	–1.29	Djordjevic and Laub [16]
			EVB–DVB	Porapak Q	510	80–100	0.79	–1.92	Vidal-Madjar et al. [18]
Carbon tetrachloride	349.7	1.90	EVB–DVB	Porapak Q	524	60–80	1.68	–1.04	Djordjevic and Laub [16]
			EVB–DVB	Porapak Q	510	80–100	1.09	–1.62	Vidal-Madjar et al. [18]
			Sty–DVB	3M(a)	350	>400	1.15	–1.39	this work
			Sty–DVB	3M(b)	880	>400	1.11	–1.83	this work
1,1-Dichloroethane	330.6	2.20	Sty–DVB	3M(a)	350	>400	0.76	–1.78	this work
			Sty–DVB	3M(b)	880	>400	0.93	–2.01	this work
1,2-Dichloroethane	356.7	1.78	Sty–DVB	XAD-2	364	20–50	1.29	–1.27	Gallant et al. [17]
			Sty–DVB	3M(a)	350	>400	1.11	–1.43	this work
			Sty–DVB	3M(b)	880	>400	1.32	–1.62	this work
1,1,1-Trichloroethane	347.3	1.98	Sty–DVB	3M(a)	350	>400	1.10	–1.44	this work
			Sty–DVB	3M(b)	880	>400	1.10	–1.84	this work
1,1-Dichloroethylene	310.2	2.71	EVB–DVB	Porapak Q	510	80–100	0.96	–1.75	Vidal-Madjar et al. [18]
			Sty–DVB	3M(a)	350	>400	0.39	–2.15	this work
			Sty–DVB	3M(b)	880	>400	0.60	–2.34	this work
<i>trans</i> -1,2-Dichloroethylene	320.7	2.35	Sty–DVB	3M(a)	350	>400	0.66	–1.88	this work
			Sty–DVB	3M(b)	880	>400	0.82	–2.12	this work
Trichloroethylene (TCE)	360.2	1.76	Sty–DVB	XAD-2	364	20–50	1.49	–1.08	Gallant et al. [17]
			Sty–DVB	3M(a)	350	>400	1.41	–1.13	this work
			Sty–DVB	3M(b)	880	>400	1.66	–1.28	this work
			EVB–DVB	Porapak Q	510	80–100	1.07	–1.64	Vidal-Madjar et al. [18]
<i>Aromatics</i>									
Benzene	353.3	1.76	Sty–DVB	XAD-2	364	20–50	1.72	–0.84	Gallant et al. [17]
			EVB–DVB	Porapak Q	524	60–80	1.85	–0.87	Djordjevic and Laub [16]
			Sty–DVB	Chromosorb 101	358	0–100	1.75	0.21	Butler and Burke [19]
			Sty–DVB	Chromosorb 102	350	80–100	1.95	–0.59	Butler and Burke [19]
			Sty–DVB	Porapak P	75	100–120	1.80	–0.075	Butler and Burke [19]
			Sty–DVB	Porapak P	75	80–100	1.57	–0.30	Vejrosta et al. [20]
			EVB–DVB	Porapak Q	600	100–120	2.03	–0.74	Butler and Burke [19]
			EVB–DVB	Porapak Q	600	50–80	2.15	–0.63	Vejrosta et al. [20]
			Sty–DVB	3M(a)	350	>400	1.21	–1.33	this work
			Sty–DVB	3M(b)	880	>400	1.32	–1.62	this work

Table 1 (Continued)

Compound information			Sorbent properties			Retention		Ref.	
Type and name	Boiling point T_b (K)	Vapor pressure $\log p_L^0$ at 20°C (Torr)	Sorbent type	Brand name	Specific surface area a (m ² /g)	Mesh range	$\log V_{g,293}$ (l/g)	$\log V_{g,s,293}$ (l/m ³) (calculated) ^a	
Toluene	383.8	1.32	Sty-DVB	XAD-2	364	20–50	2.41	-0.15	Gallant et al. [17]
			Sty-DVB	3M(a)	350	>400	1.75	-0.79	this work
			Sty-DVB	3M(b)	880	>400	2.02	-0.92	this work
<i>p</i> -Xylene	411.5	0.81	Sty-DVB	XAD-2	364	20–50	2.96	0.40	Gallant et al. [17]
Ethylbenzene	409.4	0.87	Sty-DVB	XAD-2	364	20–50	2.75	0.19	Gallant et al. [17]
<i>n</i> -Propylbenzene	432.4	0.41	Sty-DVB	XAD-2	364	20–50	3.66	1.10	Gallant et al. [17]
Fluorobenzene	358.3	1.75	Sty-DVB	XAD-2	364	20–50	1.50	-1.07	Gallant et al. [17]
Chlorobenzene	405.2	0.96	Sty-DVB	XAD-2	364	20–50	2.39	-0.18	Gallant et al. [17]
			Sty-DVB	Chromosorb 101	35	NA	2.89	1.35	Eiceman and Karasek [21]
Bromobenzene	429.2	0.50	Sty-DVB	XAD-2	364	20–50	2.81	0.24	Gallant et al. [17]
<i>p</i> -Dichlorobenzene	447.2	0.17	Sty-DVB	XAD-2	364	20–50	3.37	0.81	Gallant et al. [17]
			Sty-DVB	Chromosorb 101	35	NA	3.77	2.23	Eiceman and Karasek [21]
1,2,4-Trichlorobenzene	491.7	-0.54	Sty-DVB	Chromosorb 101	35	NA	4.45	2.91	Eiceman and Karasek [21]
<i>Ketones</i>									
Acetone	329.5	2.21	EVB-DVB	Porapak Q	524	60–80	0.90	-1.82	Djordjevic and Laub [16]
			Sty-DVB	3M(a)	350	>400	0.47	-2.07	this work
			Sty-DVB	3M(b)	880	>400	0.60	-2.34	this work
Methylethylketone (MEK)	352.8	1.88	Sty-DVB	XAD-2	364	20–50	0.64	-1.92	Gallant et al. [17]
			Sty-DVB	Chromosorb 101	35	80–100	1.76	0.22	Butler and Burke [19]
			Sty-DVB	Chromosorb 102	350	80–100	1.83	-0.71	Butler and Burke [19]
			Sty-DVB	Porapak P	75	100–120	1.61	-0.26	Butler and Burke [19]
EVB-DVB	Porapak Q	600	100–120	2.07	-0.71	Butler and Burke [19]			
2-Heptanone	424.6	0.004	Sty-DVB	XAD-2	364	20–50	3.16	0.60	Gallant et al. [17]
4-Heptanone	417.2	0.075	Sty-DVB	XAD-2	364	20–50	3.18	0.62	Gallant et al. [17]
Cyclohexanone	428.8	0.54	Sty-DVB	XAD-2	364	20–50	2.56	0.00	Gallant et al. [17]
3-Methyl-2-butanone	367.7	1.33	Sty-DVB	XAD-2	364	20–50	1.40	-1.16	Gallant et al. [17]
3,3-Dimethyl-2-butanone	379.2	1.19	Sty-DVB	XAD-2	364	20–50	1.93	-0.63	Gallant et al. [17]
2,6-Dimethyl-4-heptanone	441.2	-0.002	Sty-DVB	XAD-2	364	20–50	4.21	1.65	Gallant et al. [17]
Acetophenone	475.8	-0.45	Sty-DVB	XAD-2	364	20–50	3.89	1.33	Gallant et al. [17]
<i>Amines</i>									
<i>n</i> -Butylamine	351.0	1.86	Sty-DVB	XAD-2	364	20–50	1.26	-1.31	Gallant et al. [17]
<i>n</i> -Amylamine	377.6	1.34	Sty-DVB	XAD-2	364	20–50	2.11	-0.45	Gallant et al. [17]
<i>n</i> -Hexylamine	403.2	0.81	Sty-DVB	XAD-2	364	20–50	2.68	0.12	Gallant et al. [17]
Benzylamine	458.2	-0.24	Sty-DVB	XAD-2	364	20–50	3.90	1.33	Gallant et al. [17]
Di- <i>n</i> -butylamine	432.2	0.30	Sty-DVB	XAD-2	364	20–50	3.84	1.28	Gallant et al. [17]
<i>Alcohols</i>									
Methanol	337.9	1.94	Sty-DVB	3M(a)	350	>400	-0.23	-2.77	this work
			Sty-DVB	3M(b)	880	>400	-0.38	-3.32	this work
Ethanol	351.7	1.62	Sty-DVB	XAD-2	364	20–50	0.24	-2.32	Gallant et al. [17]
			Sty-DVB	3M(a)	350	>400	0.19	-2.35	this work
			Sty-DVB	3M(b)	880	>400	0.13	-2.81	this work
			Sty-DVB	XAD-2	364	20–50	0.97	-1.59	Gallant et al. [17]
2-Propanol	355.5	1.49	Sty-DVB	3M(a)	350	>400	0.74	-1.80	this work
			Sty-DVB	3M(b)	880	>400	0.80	-2.14	this work
<i>n</i> -Butanol	390.4	0.75	Sty-DVB	XAD-2	364	20–50	1.32	-1.25	Gallant et al. [17]
<i>sec.</i> -Butanol	372.7	1.11	Sty-DVB	XAD-2	364	20–50	1.31	-1.25	Gallant et al. [17]
<i>tert.</i> -Butanol	356.1	1.43	Sty-DVB	XAD-2	364	20–50	0.20	-2.36	Gallant et al. [17]
			Sty-DVB	Chromosorb 101	35	80–100	-0.16	-1.70	Butler and Burke [19]
			Sty-DVB	Chromosorb 102	350	80–100	1.76 ^b	-0.78 ^b	Butler and Burke [19]
			Sty-DVB	Porapak P	75	100–120	0.44	-1.44	Butler and Burke [19]
EVB-DVB	Porapak Q	600	100–120	2.31	-0.47	Butler and Burke [19]			

Table 1 (Continued)

Compound information			Sorbent properties				Retention		Ref.
Type and name	Boiling point T_b (K)	Vapor pressure $\log p_L^0$ at 20°C (Torr)	Sorbent type	Brand name	Specific surface area a (m ² /g)	Mesh range	$\log V_{g,293}$ (l/g)	$\log V_{g,s,293}$ (l/m ³) (calculated) ^a	
Isobutanol	381.2	0.97	Sty–DVB	XAD-2	364	20–50	1.11	–1.45	Gallant et al. [17]
<i>Phenols</i>									
Phenol	454.9	–0.35	Sty–DVB	XAD-2	364	20–50	3.57	1.00	Gallant et al. [17]
<i>o</i> -Cresol	464.2	–0.52	Sty–DVB	XAD-2	364	20–50	4.12	1.56	Gallant et al. [17]
<i>m</i> -Cresol	475.4	–0.91	Sty–DVB	XAD-2	364	20–50	4.19	1.63	Gallant et al. [17]
<i>p</i> -Cresol	475.1	–0.95	Sty–DVB	XAD-2	364	20–50	4.18	1.62	Gallant et al. [17]
<i>m</i> -Chlorophenol	487.2	–0.65	Sty–DVB	Chromosorb 101	35	NA	4.68	3.14	Eiceman and Karasek [21]
2,4,6-Trichlorophenol	519.2	–1.68	Sty–DVB	Chromosorb 101	35	NA	5.20	3.66	Eiceman and Karasek [21]
<i>Acids</i>									
Acetic acid	391.1	1.07	Sty–DVB	XAD-2	364	20–50	0.85	–1.71	Gallant et al. [17]
Propionic acid	414.2	0.37	Sty–DVB	XAD-2	364	20–50	1.60	–0.96	Gallant et al. [17]
<i>n</i> -Butanoic acid	438.7	–0.08	Sty–DVB	XAD-2	364	20–50	1.89	–0.67	Gallant et al. [17]
<i>n</i> -Pentanoic acid	459.2	–0.69	Sty–DVB	XAD-2	364	20–50	2.46	–0.10	Gallant et al. [17]
<i>Miscellaneous compounds</i>									
Acetonitrile	354.8	1.85	Sty–DVB	Chromosorb 101	35	80–100	0.67	–0.87	Butler and Burke [19]
			Sty–DVB	Chromosorb 102	350	80–100	0.74	–1.80	Butler and Burke [19]
			Sty–DVB	Porapak P	75	100–120	0.71	–1.17	Butler and Burke [19]
			EVB–DVB	Porapak Q	600	100–120	0.94	–1.83	Butler and Burke [19]
			Sty–DVB	3M(a)	350	>400	0.26	–2.28	this work
			Sty–DVB	3M(b)	880	>400	0.35	–2.59	this work
Ethyl acetate	350.3	1.81	Sty–DVB	3M(a)	350	>400	1.24	–1.30	this work
			Sty–DVB	3M(b)	880	>400	1.51	–1.43	this work
Tetrahydrofuran	339.2	2.11	EVB–DVB	Porapak Q	524	60–80	1.70	–1.02	Djordjevic and Laub [16]
Thiophene	357.3	1.75	EVB–DVB	Porapak Q	524	60–80	1.72	–1.00	Djordjevic and Laub [16]

^a While the calculation of $\log V_{g,s,293}$ values by Eq. 3 places the retention volume information on a surface-area normalized basis, doing so does not by itself argue that the sorption mechanism is exclusively adsorptive in nature.

^b This datapoint is considered an outlier for this compound on Sty–DVB sorbents.

$$V_n = (t_r - t_m)F_{col} \quad (3)$$

$$V_g = V_n/m \quad (4)$$

where F_{col} is the corrected average column flow-rate; j the compressibility factor; F_{fm} the flow-rate measured at the bubble flow meter; T the temperature (K) of the column; T_{fm} the temperature of the flow meter; P_{out} the total pressure at the outlet of the column; P_{in} the total pressure at the inlet of the column; $p_{w,fm}^0$ the vapor pressure of water at the temperature of the bubble flow meter; V_n the net retention volume; t_r the measured retention times of the analyte of interest; t_m the measured retention time of an unretained species (e.g., methane); and m the mass of sorbent in the column.

4. Experimental results

The $\log V_g$ (l/g) versus temperature data obtained

in this study are given in Table 2 for 3M(a), and in Table 3 for 3M(b). For the more strongly retained compounds (e.g. benzene and toluene), $\log V_g$ values could only be measured at temperatures which are significantly higher than ambient. Regression equations of $\log V_g$ versus $1/T$ were used as described above to obtain extrapolated estimates of $\log V_{g,293}$ for all compounds. The regression parameters are given in Table 4 and Table 5 together with the resulting $\log V_{g,293}$ values. In general, the 3M data agree well with the data for other similar Sty–DVB sorbent materials.

5. Correlations of $\log V_{g,293}$ with $\log p_L^0$ and with boiling point

If p_L^0 (Torr) and T_b (K) represent the vapor pressure and standard boiling point (1 atm of overlying pressure; 1 atm=101 325 Pa), respectively, then Pankow [1,2] has shown why $\log V_{g,293}$ values will

Table 2

log V_g (l/g) versus temperature for 3M(a) styrene–divinylbenzene (Sty–DVB) co-polymer sorbent beads (350 m²/g)

Compound	Boiling point (°C)	Boiling point T_b (K)	log p_L^0 at 20°C (Torr)	log V_g (l/g)							
				40°C	50°C	60°C	70°C	75°C	80°C	85°C	90°C
				(meas.)	(meas.)	(meas.)	(meas.)	(meas.)	(meas.)	(meas.)	(meas.)
<i>Alkanes, haloaliphatics, and aromatics</i>											
<i>n</i> -Pentane	36.1	309.4	2.57	0.14	-0.11	-0.36	-0.54	-0.65	-0.76	-0.83	-0.91
1,1-Dichloroethylene	37	310.2	2.71	-0.07	-0.30	-0.54	-0.72	-0.79	-0.89	-0.98	-1.04
Methylene chloride	40	313.3	2.54	-0.09	-0.33	-0.58	-0.73	-0.81	-0.91	-0.98	-1.05
<i>trans</i> -1,2-Dichloroethylene	47.5	320.7	2.35	0.16	-0.09	-0.30	-0.53	-0.61	-0.69	-0.79	-0.89
1,1-Dichloroethane	57.3	330.6	2.20		0.08	-0.13	-0.39	-0.45	-0.55	-0.65	-0.73
<i>n</i> -Hexane	68.7	341.9	2.03			0.23	0.02	-0.09	-0.21	-0.29	-0.44
1,1,1-Trichloroethane	74.1	347.3	1.98			0.18	-0.04	-0.11	-0.23	-0.30	-0.39
Carbon tetrachloride	76.5	349.7	1.90			0.19	0.00	-0.11	-0.24	-0.28	-0.39
Benzene	80.1	353.3	1.76			0.23	0.04	-0.05	-0.19	-0.24	-0.36
1,2-Dichloroethane	83.5	356.7	1.78			0.11	-0.09	-0.24	-0.32	-0.42	-0.48
Trichloroethylene	87	360.2	1.76			0.38	0.10	0.01	-0.10	-0.17	-0.28
Toluene	110.6	383.8	1.32				0.54	0.45	0.34	0.26	0.14
<i>Oxygenates</i>											
Acetone	56.3	329.5	2.21	-0.05	-0.27	-0.40	-0.63	-0.79	-0.87	-0.94	-1.04
Methanol	64.7	337.9	1.94	-0.63	-0.82	-0.99	-1.13	-1.21	-1.31	-1.33	-1.47
Ethyl acetate	77.1	350.3	1.81		0.40	0.14	-0.05	-0.20	-0.29	-0.40	-0.52
Ethanol	78.5	351.7	1.61	-0.26	-0.44	-0.61	-0.79	-0.94	-1.02	-1.04	-1.14
Acetonitrile	81.6	354.8	1.84	-0.20	-0.47	-0.65	-0.84	-0.99	-1.07	-1.11	-1.20
2-Propanol	82.3	355.5	1.49		0.00	-0.31	-0.43	-0.54	-0.65	-0.78	-0.85

tend to correlate with both log p_L^0 and T_b . The log $V_{g,293}$ versus log p_L^0 correlations can be expected to have slopes near -1, and log $V_{g,293}$ versus T_b correlations can be expected to have slopes near 0.02 [1].

Fig. 1 plots the data from Table 1 in a log $V_{g,293}$ versus log p_L^0 format, and Fig. 2 plots the data in a log $V_{g,293}$ versus T_b format. For both figures, the data point from Butler and Burke [19] for *tert*-butanol was considered to be an outlier for this compound, and was not plotted. In Fig. 1, many of the points plot along a diagonal band, and yield the correlation equation $\log V_{g,293} = -1.16 \log p_L^0 + 3.51$. As expected, the slope is near -1. The datasets for the alkanolic acids and the alcohols, both rather polar compound classes, were regressed individually. (Similar compound-class dependency in retention volume data has been observed for the sorbent Tenax-GC/TA [1].) Table 6 gives the regression parameters for the correlation lines in Fig. 1 and Fig. 2, as well as those for 3M(a). Table 6 will allow the prediction of log $V_{g,293}$ for compounds of interest that have not yet been studied experimentally.

A clear, negative correlation of log p_L^0 with T_b exists for most groups of organic compounds. This is illustrated in Fig. 3, which is a log p_L^0 versus T_b correlation for the compounds in Table 1. The result is $\log p_L^0 = -0.01952 T_b + 8.67$. When this equation is substituted into the correlation for "most compounds" in Fig. 1 ($\log V_{g,293} = -1.16 \log p_L^0 + 3.51$, see Table 6), then, as expected, we essentially obtain the Fig. 2 correlation for the same compounds ($\log V_{g,293} = 0.0227 T_b - 6.60$, see Table 6). The two are not exactly the same because all of the compounds are included in the Fig. 3 correlation. The overall conclusion is that log p_L^0 and T_b are equally useful as predictive correlating parameters for log $V_{g,293}$.

6. Making use of the retention data and the correlation equations

For TCE sorbing to XAD-2 (Sty–DVB), Table 1 indicates that log $V_{g,293} = 1.49$; for TCE sorption to Porapak Q (EVB–DVB), Table 1 indicates

Table 3
 $\log V_g$ (l/g) versus temperature for 3M(b) styrene–divinylbenzene (Sty–DVB) co-polymer sorbent beads (880 m²/g)

3M(b), 880 m ² /g									
Compound	Boiling point (°C)	Boiling point T _b (K)	$\log p^0$ at 20°C (Torr)	$\log V_g$ (l/g)					
				50°C	60°C	70°C	80°C	85°C	90°C
<i>Alkanes, haloaliphatics, and aromatics</i>									
<i>n</i> -Pentane	36.1	307.4	2.57		-0.20	-0.40	-0.58	-0.68	-0.77
1,1-Dichloroethylene	37	310.2	2.71	-0.12	-0.35	-0.54	-0.72	-0.83	-0.91
Methylene chloride	40	313.3	2.54	-0.20	-0.38	-0.57	-0.74	-0.86	-0.94
<i>trans</i> -1,2-Dichloroethylene	47.5	320.7	2.35	0.07	-0.14	-0.35	-0.55	-0.65	-0.74
1,1-Dichloroethane	57.3	330.6	2.20		-0.03	-0.22	-0.39	-0.52	-0.61
<i>n</i> -Hexane	68.7	341.9	2.03		0.40	0.17	-0.04	-0.18	-0.27
1,1,1-Trichloroethane	74.1	347.3	1.98			0.08	-0.07	-0.18	-0.24
Carbon tetrachloride	76.5	349.7	1.90			0.09	-0.07	-0.16	-0.23
Benzene	80.1	353.3	1.76			0.16	-0.04	-0.14	-0.21
1,2-Dichloroethane	83.5	356.7	1.78			0.07	-0.11	-0.24	-0.32
Trichloroethylene	87.0	360.2	1.76			0.30	0.06	-0.04	-0.15
Toluene	110.6	383.8	1.32			0.71	0.54	0.38	0.31
<i>Oxygenates</i>									
Acetone	56.3	329.5	2.21	-0.14	-0.38	-0.58	-0.76	-0.89	-0.96
Methanol	64.7	337.9	1.94	-0.99	-1.21	-1.40	-1.51		
Ethyl acetate	77.1	350.3	1.81	0.58	0.39	0.05	-0.13	-0.26	-0.37
Ethanol	78.5	351.7	1.61	-0.53	-0.67	-0.90	-1.04		
Acetonitrile	81.6	354.8	1.84	-0.34	-0.59	-0.74	-0.92	-1.03	-1.11
2-Propanol	82.3	355.5	1.49	0.03	-0.27	-0.53	-0.66	-0.78	-0.87

Table 4
 Regression parameters for $\log V_g$ (l/g) = $m/T + b$ for 3M(a) styrene–divinylbenzene (Sty–DVB) co-polymer sorbent beads (350 m²/g)

3M(a), 350 m ² /g			
Compound	<i>m</i>	<i>b</i>	$\log V_{g,293}$ (l/g)
<i>n</i> -Pentane	2402	-7.55	0.65
1,1-Dichloroethylene	2220	-7.18	0.39
Methylene chloride	2172	-7.06	0.35
<i>trans</i> -1,2-Dichloroethylene	2365	-7.41	0.66
1,1-Dichloroethane	2366	-7.31	0.76
<i>n</i> -Hexane	2661	-7.75	1.33
1,1,1-Trichloroethane	2277	-6.67	1.10
Carbon tetrachloride	2354	-6.88	1.15
Benzene	2374	-6.89	1.21
1,2-Dichloroethane	2459	-7.28	1.11
Trichloroethylene	2591	-7.43	1.41
Toluene	2427	-6.53	1.75
Acetone	2282	-7.32	0.47
Methanol	1838	-6.50	-0.23
Ethyl acetate	2667	-7.85	1.24
Ethanol	2040	-6.76	0.19
Acetonitrile	2263	-7.45	0.26
2-Propanol	2419	-7.51	0.74

Table 5
 Regression parameters for $\log V_g$ (l/g) = $m/T + b$ for 3M(b) styrene–divinylbenzene (Sty–DVB) co-polymer sorbent beads (880 m²/g)

3M(b), 880 m ² /g			
Compound	<i>m</i>	<i>b</i>	$\log V_{g,293}$ (l/g)
Pentane	2287	-7.07	0.74
1,1-Dichloroethylene	2287	-7.21	0.60
Methylene chloride	2164	-6.89	0.50
<i>trans</i> -1,2-Dichloroethylene	2375	-7.28	0.82
1,1-Dichloroethane	2327	-7.01	0.93
Hexane	2723	-7.77	1.52
1,1,1-Trichloroethane	2037	-5.85	1.10
Carbon tetrachloride	2043	-5.86	1.11
Benzene	2331	-6.64	1.32
1,2-Dichloroethane	2494	-7.19	1.32
Trichloroethylene	2754	-7.74	1.66
Toluene	2606	-6.87	2.02
Acetone	2380	-7.52	0.60
Methanol	2001	-7.20	-0.37
Ethyl acetate	2857	-8.24	1.51
Ethanol	2015	-6.75	0.13
Acetonitrile	2220	-7.23	0.35
2-Propanol	2568	-7.96	0.80

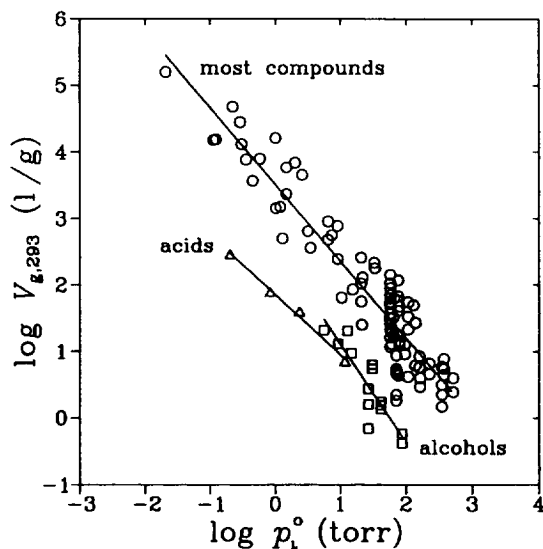


Fig. 1. $\log V_{g,293}$ (l/g) versus $\log p_L^0$ (Torr) at 293 K for data from Table 1 (1 Torr=133.322 Pa).

$\log V_{g,293} = 1.07$. For some compounds, however, Table 1 includes different values for $\log V_{g,293}$ for the same sorbent (e.g., dichloromethane on Porapak Q). In this circumstance, it might be best to take advantage of the averaging effects of the equations in Table 6, and use $\log V_{g,293} = -1.16 \log p_L^0 + 3.51$, or $\log V_{g,293} = 0.0227T_b - 6.60$ to obtain a general estimate of $\log V_{g,293}$ for dichloromethane on EVB-DVB/Sty-DVB-type sorbents.

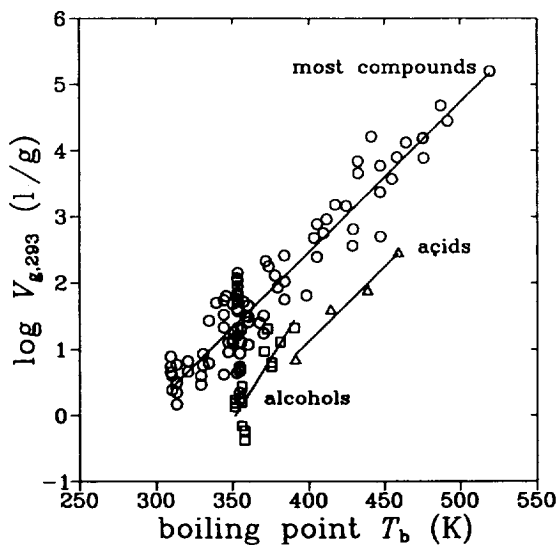


Fig. 2. $\log V_{g,293}$ (l/g) versus T_b (K) for data from Table 1.

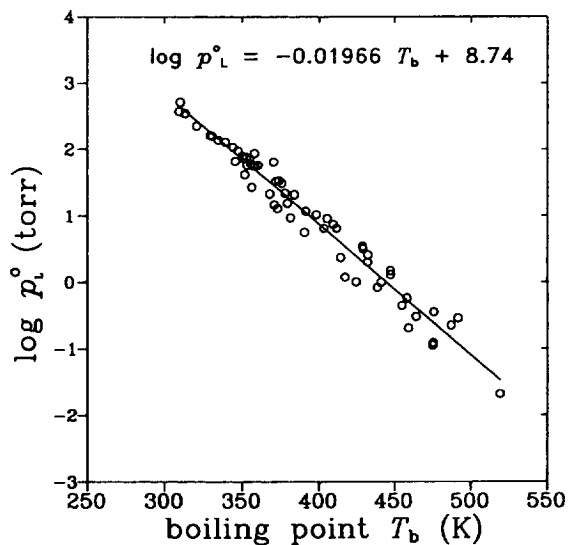


Fig. 3. $\log p_L^0$ (Torr) at 293 K versus T_b (K) for compounds in Table 1 (1 Torr=133.322 Pa).

7. Retention volumes normalized by specific surface area: $V_{g,s,293}$ versus $V_{g,293}$

Two mechanisms are possible for the sorption of an organic compound to an Sty-DVB or EVB-DVB resin bead: (1) adsorption to the available surface area of the bead; and/or (2) absorption into the organic polymer matrix of the bead. Both of these sorption mechanisms may be operative in a given

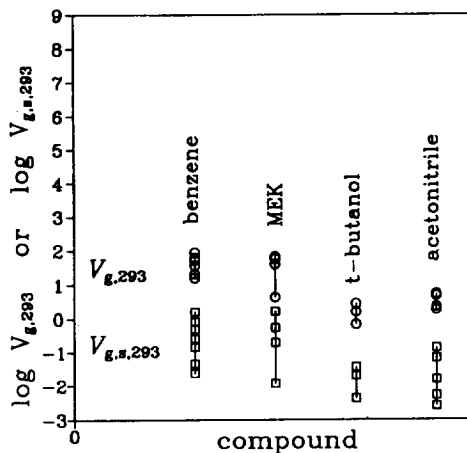


Fig. 4. $\log V_{g,293}$ (○) and calculated $\log V_{g,s,293}$ (□) for four compounds on Sty-DVB sorbents.

Table 6

Correlation equations for $\log V_{g,293}$ versus $\log p_L^0$ and $\log V_{g,293}$ versus T_b (K) for styrene–divinylbenzene (Sty–DVB) and ethylvinylbenzene–divinylbenzene (EVB–DVB) co-polymer sorbent beads

Comments	Equations
Most compounds on Sty–DVB and EVB–DVB sorbents, excluding alcohols and acids	$\log V_{g,293} = -1.16 \log p_L^0 + 3.51$ ($R^2 = 0.88$, Fig. 1) and $\log V_{g,293} = 0.0227T_b - 6.60$ ($R^2 = 0.88$, Fig. 2)
Alcohols on Sty–DVB sorbents	$\log V_{g,293} = -1.48 \log p + 2.59$ ($R^2 = 0.77$, Fig. 1) and $\log V_{g,293} = 0.0337T_b - 11.61$ ($R^2 = 0.78$, Fig. 2)
Acids on Sty–DVB sorbents	$\log V_{g,293} = -0.90 \log p + 1.85$ ($R^2 = 0.99$, Fig. 1) and $\log V_{g,293} = 0.0223T_b - 7.80$ ($R^2 = 0.97$, Fig. 2)
Data from this study for 3M(a) Sty–DVB beads (excluding oxygenates)	$\log V_{g,293} = -0.99 \log p + 3.04$ ($R^2 = 0.90$) and $\log V_{g,293} = 0.0175T_b - 4.97$ ($R^2 = 0.90$)

situation. For a series of otherwise similar resin sorbents, the relative importance of *absorption* versus *adsorption* will likely increase as the degree of cross-linkage (i.e., the percent DVB) within the resin decreases: uptake into the resin matrix is then less opposed by bead rigidity.

If adsorption were the dominant sorption mechanism for a given compound, then it would be logical to compute a surface-area-normalized specific retention volume $V_{g,s,293}$ (l/m^2) according to

$$V_{g,s,293} (l/m^2) = V_{g,293} / a \quad (5)$$

where a (m^2/g) is the specific surface area of the sorbent material. If one then had $\log V_{g,293}$ values for a single compound on several sorbents that were chemically similar but that possessed different a values, then one would expect that the scatter in the resulting $\log V_{g,s,293}$ values would be less than the scatter in the original $\log V_{g,293}$ values.

An examination of Table 1 reveals that there are four compounds which have been studied on multiple Sty–DVB sorbents, namely benzene, methylethylketone (MEK), *tert.*-butanol, and acetonitrile. The $\log V_{g,293}$ values and the calculated $\log V_{g,s,293}$ values for these compounds are presented in Fig. 4. As can be seen from the figure, normalizing by a does not decrease, but rather increases the scatter for three of the compounds; the scatter does not change significantly for *tert.*-butanol. We view these results as supportive of absorption as the dominant gas–solid partitioning mechanism to Sty–DVB resin beads of the type considered here.

A consideration of the 3M(b)/3M(a) datasets by themselves provides another way to compare $V_{g,293}$

values. Since the surface area ratio for these two otherwise similar Sty–DVB sorbents is $880/350 = 2.5$, then if adsorption was the dominant partitioning mechanism, the ratio of the $V_{g,293}$ values should also be ca. 2.5. The average of the measured ratio is, however, only 1.3, with a standard deviation of 0.33. This result also supports absorption as the important partitioning mechanism for the types of Sty–DVB resin beads considered here.

8. Conclusions

The sorption properties of Sty–DVB and EVB–DVB sorbent materials are well correlated with both $\log p_L^0$ and T_b . This observation applies to: (1) data that already exists in the literature; (2) new data obtained here for the Sty–DVB material used in Empore extraction membranes (“3M(a)”); and (3) new data obtained here for a high surface area Sty–DVB sorbent (“3M(b)”). Most of the available data support absorption as the dominant sorption mechanism for the gas–solid partitioning of most organic analytes to Sty–DVB sorbent materials.

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