Journal of Chromatography, 627 (1992) 294–299
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 701

Short Communication

Hydrogen bonding

XXIII. Application of the new solvation equation to log V_g values for solutes on carbonaceous adsorbents

Michael H. Abraham and David P. Walsh

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (UK)

(First received June 30th, 1992; revised manuscript received October 20th, 1992)

ABSTRACT

Truncated versions of our new solvation equation can be used to correlate and to predict log V_g values for solutes on adsorbents such as Carbotrap, Carbosieve and charcoal cloths. The two truncated equations are log $V_g = c + rR_2 + l \log L^{16}$ and log $V_g = c + l \log L^{16}$, where V_g is the retention volume for a series of solutes on a given carbon, R_2 is the solute excess molar refraction, L^{16} is the solute gas–liquid partition coefficient on hexadecane at 298 K and *c*, *r* and *l* are constants. The equation in R_2 and log L^{16} is shown to be very much better in the correlation of log V_g values than previous equations in log (vapour pressure) or in normal boiling point and can reproduce log V_g to within 0.4 to 0.9 log units when V_g covers a range of up to 15 orders of magnitude. The above two equations can be used to select the adsorbent giving rise to the largest V_g values for any particular adsorbate for which R_2 and log L^{16} are known.

INTRODUCTION

We have recently shown how phases such as common gas–liquid chromatographic stationary phases [1,2], ionic salts [1], candidate phases for piezo-electric chemical sensors [3] and polymers [4] can be characterised through our new solvation equation (eqn. 1). In this equation, *SP* represents a set of retention data for a series of solutes on a given phase: *SP* can be *L* (the gas–liquid partition coefficient), or V_g (the specific retention volume) or τ (the adjusted relative retention time). All these quantities as *SP* will yield the same constants in eqn. 1, except for the *c* constant.

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

The solute parameters used as descriptors or explanatory variables in eqn. 1 are R_2 (an excess molar refraction [5]), π_2^H (our new solute dipolarity/polarisability parameter [6]), α_2^H and β_2^H (the effective hydrogen-bond acidity and basicity [6]) and log L^{16}, where L^{16} is the solute gas–liquid partition coefficient on hexadecane at 298 K [7]). The various constants (*c*, *r*, *s*, *a*, *b* and *l*) in eqn. 1 that serve to characterise the particular phase are found by the method of multiple linear regression analysis.

In a recent paper, Pankow [8] attempted to corre-

Correspondence to: M. H. Abraham, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK.

late log V_g values for 38 solutes on the graphitised material Carbotrap, with vapour pressure (as log P in Torr at 293 K; 1 Torr = 133.322 Pa) and with normal boiling point (T_b, in K). Although Pankow obtained some correlations of log V_g by rather arbitrarily selecting four different regression lines in each case, there was but little overall correlation of log V_g with either log P or with T_b Since adsorption of gaseous solutes by materials such as Carbotrap is of considerable practical importance, we have investigated the applicability of eqn. 1 to the Carbotrap results, in the hope that we might be able to generate better equations for the prediction of log V_g values.

TABLE I

SPECIFIC RETENTION VOLUME (V_g) FOR ORGANIC COMPOUNDS ON CARBOTRAP AT 293 K, AND COMPOUND PARAMETERS

Compound	log P (293 K) (Torr)	log V_g (293 K) (l/g)[a]	T_b (°C)	R_2	log L^{16}
Ethane	4.47	−1.76	−88	0.000	0.492
Propane	3.81	−1.26	−42	0.000	1.050
n-Butane	3.18	−0.39	0	0.000	1.615
n-Pentane	2.63	0.77	36	0.000	2.162
n-Hexane	2.08	1.90	69	0.000	2.668
n-Octane	1.04	4.21	126	0.000	3.677
n-Decane	0.43	6.68	174	0.000	4.686
n-Dodecane	−0.52	11.21	216	0.000	5.696
n-Tetradecane	−1.57	13.92	252	0.000	6.705
1,2-Dichloroethane	1.78	0.29	84	0.416	2.573
1,1,1-Trichloroethane	1.78	1.10	87	0.369	2.733
1,1,2-Trichloroethane	1.28	1.39	114	0.499	3.290
Butanone	1.88	0.58	80	0.166	2.287
Heptan-4-one	−0.08	3.39	149	0.113	3.705
Cyclohexanone	0.60	3.31	157	0.403	3.792
n-Butylamine	1.86	3.32	78	0.224	2.618
Acetic acid	1.07	−0.15	118	0.265	1.750
Propanoic acid	0.46	0.22	141	0.233	2.290
Pentanoic acid	−0.82	2.63	187	0.205	3.380
Ethanol	1.64	−0.31	78	0.246	1.485
Butan-1-ol	0.64	1.28	118	0.224	2.601
2-Methylpropan-2-ol	1.49	0.81	83	0.180	1.963
Benzene	1.88	1.07	80	0.610	2.786
Toluene	1.34	2.81	111	0.601	3.325
Ethylbenzene	0.85	4.31	136	0.613	3.778
p-Xylene	0.81	4.63	138	0.613	3.839
n-Propylbenzene	0.40	6.24	159	0.604	4.230
Isopropylbenzene	0.51	5.23	153	0.602	4.084
n-Butylbenzene	−0.05	6.77	183	0.600	4.730
n-Hexylbenzene	−1.16	9.85	226	0.591	5.720
n-Octylbenzene	−2.15	12.12	262	0.579	6.714
Biphenyl	−1.41	9.57	258	1.360	6.063
Chlorobenzene	0.94	3.20	132	0.718	3.640
1,4-Dichlorobenzene	−0.22	4.13	173	0.825	4.446
Acetophenone	−0.46	4.81	202	0.818	4.483
Benzylamine	−0.24	4.35	184	0.829	4.319
Phenol	−0.70	2.79	182	0.805	3.897
p-Cresol	−1.40	4.31	202	0.820	4.307

[a] Data from Pankow [8].

RESULTS AND DISCUSSION

The log V_g values at 293 K, together with vapour pressures as log P with P in Torr at 293 K, and normal boiling points were all taken from Pankow [8] except that we include two extra log P values for hexylbenzene and octylbenzene to complete the set. These are all given in Table I, together with values of R_2 and log L^{16} to which we shall refer below. Units of R_2 are (cm^3/mol)/10, whilst L^{16} is dimensionless [5,7]. Application of the full eqn. 1 to the 38 log V_g values showed that most of the explanatory variables were not statistically significant, as judged by Student's t-test, and we were left with eqn. 2, or the abbreviated eqn. 3.

$$\log V_g = -4.73 - 2.27R_2 + 2.65 \log L^{16} \quad (2)$$
$$n = 38, \rho = 0.9737, \text{S.D.} = 0.88, F = 318$$

$$\log V_g = -4.82 + 2.41 \log L^{16} \quad (3)$$
$$n = 38, \rho = 0.9570, \text{S.D.} = 1.10, F = 392$$

These may be compared with the corresponding equations in T_b/K or in log P, again for all 38 solutes,

$$\log V_g = -12.64 + 0.040\, T_b/\text{K} \quad (4)$$
$$n = 38, \rho = 0.8262, \text{S.D.} = 2.14, F = 77$$

$$\log V_g = 5.14 - 2.00 \log P \quad (5)$$
$$n = 38, \rho = 0.7869, \text{S.D.} = 2.34, F = 59$$

In eqns. 2–5, n is the number of solutes, ρ is the overall correlation coefficient, S.D. is the standard deviation in log V_g and F is the Fisher F-statistic. It is clear that log L^{16} is a very much better descriptor than either T_b/K or log P; this is shown rather well in Figs. 1–3.

Pankow [8] pointed out that some of the V_g values at 293 K had been obtained by extrapolation from higher temperatures, and this probably accounts for the rather large S.D. values in eqns. 2–5. Nevertheless, either eqn. 2 or eqn. 3 could be used to estimate log V_g values for any solute from R_2 and log L^{16}. The former can be calculated from the liquid refractive index at 293 K as described before [5], or can be estimated quite reliably, whilst the latter can be obtained experimentally relatively easily [7], and in any case is known for a large number of compounds, already [6,7].

Although the S.D. value in eqn. 2 is 0.88 log units, it should be remembered that the spread in the experimental log V_g values covers over 15 log units. The rather large S.D. value is unlikely to originate from errors in our R_2 and log L^{16} parameters, at least to any extent, because even for the n-alkanes (for which we have very reliable parameters) application of eqn. 3 leads to an S.D. of 0.94 log units.

As mentioned in the Introduction, Pankow used different regression lines, against both T_b/K and log P, when discussing the log V_g values. Lines were obtained by arbitrarily dividing up the data into

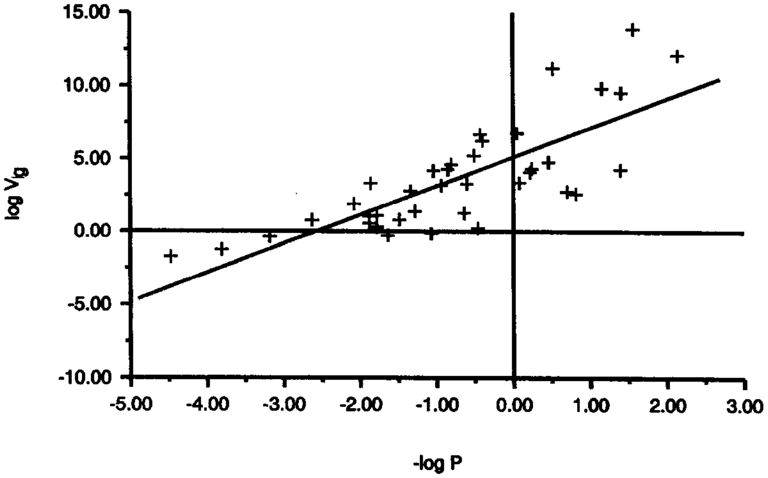

Fig. 1. Log V_g vs. $-\log P$ for compounds on Carbotrap at 293 K.

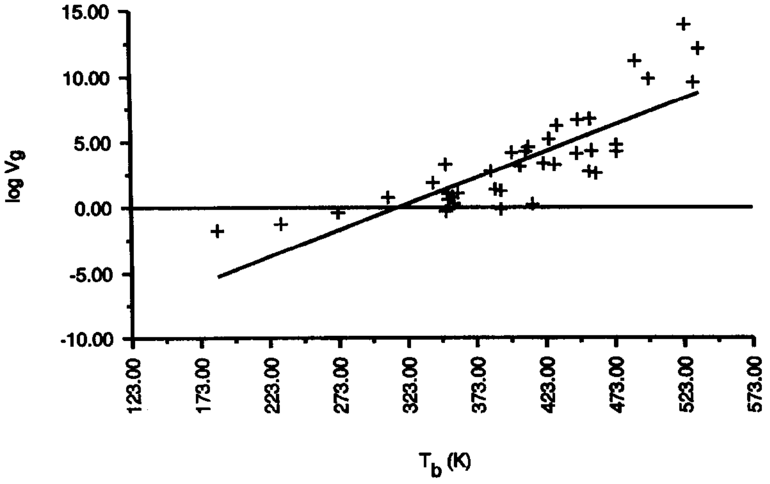

Fig. 2. Log V_g *vs.* T_b (K) for compounds on Carbotrap at 293 K.

sets for which log $P < 1.6$ and $T_b/K > 373$ and log $P > 1.6$ and $T_b/K < 373$, and by taking acids and phenols separately, alcohols being excluded. The only compound-specific linear equations listed by Pankow were for the five acids and phenols in Table I, for which he obtained eqns. 6 and 7,

$$\log V_g = -20.9 + 0.0522\ T_b/K \quad (6)$$
$$n = 5,\ \rho = 0.9732,\ S.D. = 0.50,\ F = 54$$

$$\log V_g = 1.45 - 1.83 \log P \quad (7)$$
$$n = 5,\ \rho = 0.9831,\ S.D. = 0.40,\ F = 87$$

However, judging by the *F*-statistic, there is not much to choose between eqns. 6 and 7 and eqns. 4 and 5, whilst eqns. 6 and 7 are definitely inferior to the "all-solute" eqns. 2 and 3. Our conclusion is that the "all-solute" equations are to be preferred, especially since these are likely to be the most useful in predictions of log V_g values.

We can also test our general equation using the data of Cao [9] who obtained V_g values for a variety of hydrocarbons on three microporous carbons, *viz.* Carbosieve B (Carb B), and two charcoal cloths, CC1 and CC2. The log V_g values recorded by Cao

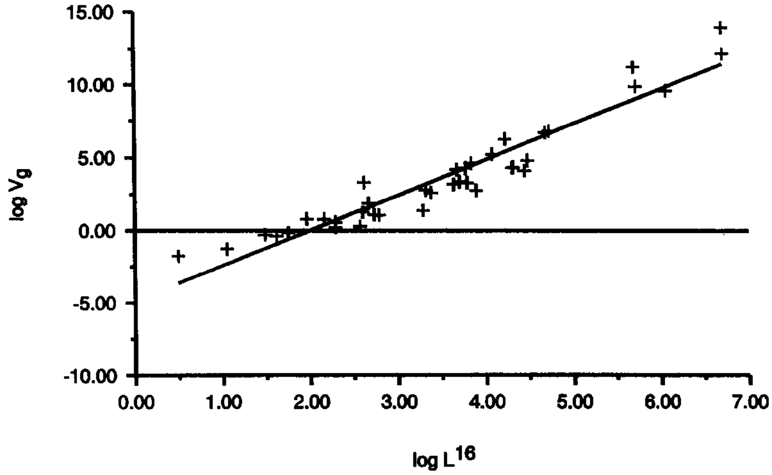

Fig. 3. Log V_g *vs.* log L^{16} for compounds on Carbotrap at 293 K.

TABLE II

SPECIFIC RETENTION VOLUMES (V_g, l/g) FOR ORGANIC COMPOUNDS ON VARIOUS ADSORBENTS AT 293 K, AND COMPOUND PARAMETERS

Compound	log V_g (293 K) (l/g)[a]			R_2	Log L^{16}
	Carbosieve B	CC1	CC2		
Methane	−0.92	−0.89	−1.30	0.000	−0.323
Ethane	0.76	0.04	0.08	0.000	0.492
Propane	2.52	1.70	1.72	0.000	1.050
n-Butane	4.28	3.71	3.26	0.000	1.615
n-Pentane	5.70	5.23	4.45	0.000	2.162
2-Methylbutane	5.36	4.57	4.62	0.000	2.013
n-Hexane	6.88	6.79	6.08	0.000	2.668
2-Methylpentane	6.45	6.52	5.41	0.000	2.503
2,2-Dimethylbutane		6.34	5.20	0.000	2.352
n-Heptane	9.60	8.59	7.62	0.000	3.173
n-Octane		10.26		0.000	3.677
n-Nonane		13.18		0.000	4.182
Cyclohexane	5.41	6.00	5.08	0.305	3.007
Ethene	−0.10	−0.17	−0.21	0.107	0.289
Propene	1.65	1.52	1.53	0.103	0.946
But-1-ene	3.08	3.04	3.00	0.100	1.491
Benzene	5.45	5.96	5.30	0.610	2.786

[a] Data obtained from Cao [9].

at 293 K, together with the corresponding solute R_2 and log L^{16} values, are in Table II. With no data exclusion at all, we can construct the following equations:

$$\log V_g\,(\text{Carb B}) = -0.41 - 4.46R_2 + 2.82 \log L^{16} \qquad (8)$$

$n = 14$, $\rho = 0.9834$, S.D. $= 0.58$, $F = 162$

$$\log V_g\,(\text{Carb B}) = -0.40 + 2.59 \log L^{16} \qquad (9)$$

$n = 14$, $\rho = 0.9523$, S.D. $= 0.94$, $F = 117$

$$\log V_g\,(\text{CC1}) = -1.05 - 3.35R_2 + 3.06 \log L^{16} \qquad (10)$$

$n = 17$, $\rho = 0.9868$, S.D. $= 0.66$, $F = 260$

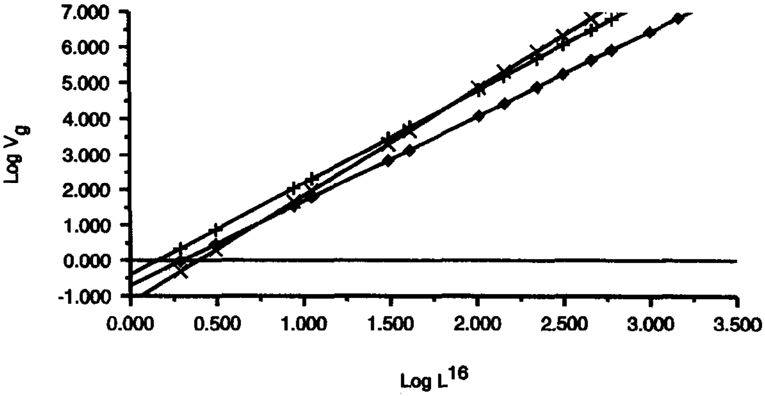

Fig. 4. Log V_g *vs.* log L^{16} for (+) Carbosieve B, (×) CC1 and (◆) CC2 at 293 K.

$$\log V_g\,(\mathrm{CC1}) = -1.17 + 3.00 \log L^{16} \qquad (11)$$
$n = 17$, $\rho = 0.9769$, S.D. $= 0.84$, $F = 313$

$$\log V_g\,(\mathrm{CC2}) = -0.71 - 2.23R_2 + 2.48 \log L^{16} \qquad (12)$$
$n = 15$, $\rho = 0.9897$, S.D. $= 0.40$, $F = 287$

$$\log V_g\,(\mathrm{CC2}) = -0.70 + 2.38 \log L^{16} \qquad (13)$$
$n = 15$, $\rho = 0.9800$, S.D. $= 0.53$, $F = 315$

Bearing in mind the spread of data, some 14 log units for CC1, eqns. 8–13, especially the double regressions in R_2 and log L^{16}, do provide a useful means of estimating further log V_g values.

In addition, eqns. 8–13 are especially valuable in the characterisation of adsorbents. Plots according to eqns. 9, 11 and 13 are shown in Fig. 4 and illustrate how difficult it is to define what is the "best" adsorbent, even for *n*-alkanes. For rather small compounds, *i.e.* those with low log L^{16} values, Carbosieve B is the best adsorbent, but for larger compounds CC1 is the best. For the *n*-alkanes illustrated in Fig. 4 the cross-over point is between ethane and propane for CC1 and CC2 and between hexane and heptane for CC1 and Carbosieve B.

We can also compare Carbotrap with Carbosieve B, through eqns. 3 and 9. It is now clear that V_g values on Carbosieve B are always greater than on Carbotrap by factors upwards of 10^4, no matter what the size of the solute is, *i.e.* no matter what is the solute log L^{16} value.

CONCLUSIONS

Our new solvation equation, eqn. 1, can usefully be applied to analyses of log V_g values for solutes on adsorbents such as Carbotrap, Carbosieve B and charcoal cloths. Not only can log V_g values be estimated to around 0.4 to 0.9 log units when V_g covers a range of up to 15 orders of magnitude, but equations in R_2 and log L^{16}, and particularly the simple equation in log L^{16} can be used to select the adsorbent that will yield the largest V_g value for a solute of a given log L^{16} value.

ACKNOWLEDGEMENTS

We thank Dr. M. J. Wilkinson for his interest in this work, and the Ministry of Defence for support under Agreement No. 2047/140.

REFERENCES

1 M. H. Abraham, G. S. Whiting, R. M. Doherty and W. J. Shuely, *J. Chromatogr.*, 587 (1991) 229.
2 M. H. Abraham, G. S. Whiting, J. Andonian-Haftvan and J. W. Steed, *J. Chromatogr.*, 588 (1991) 361.
3 M. H. Abraham, I. Hamerton, J. B. Rose and J. W. Grate, *J. Chem. Soc., Perkin Trans. 2*, (1991) 1417.
4 M. H. Abraham, G. S. Whiting, R. M. Doherty, W. J. Shuely and P. Sakellariou, *Polymer*, 33 (1992) 2162.
5 M. H. Abraham, G. S. Whiting, R. M. Doherty and W. J. Shuely, *J. Chem. Soc. Perkin Trans. 2*, (1990) 1451.
6 M. H. Abraham, G. S. Whiting, R. M. Doherty and W. J. Shuely, *J. Chromatogr.*, 587 (1991) 213.
7 M. H. Abraham, P. L. Grellier and R. A. McGill, *J. Chem. Soc., Perkin Trans. 2*, (1987) 797.
8 J. F. Pankow, *J. Chromatogr.*, 547 (1991) 488.
9 X.-L. Cao, *J. Chromatogr.*, 586 (1991) 161.