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Short Communication

Gas phase retention volume behavior of organic compounds on Carbotrap graphitized carbon

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ABSTRACT

The graphitized carbon material Carbotrap is often used for sampling gaseous organic compounds. Knowledge of the retention volumes of the compounds of interest on Carbotrap is required to design sampling protocols. Published data are examined here to develop correlation equations between retention volume and both vapor pressure and boiling point. The 38 compounds considered included ethane, butane, 1,2-dichloroethane, benzene, trichloroethene, 1,1,2-trichloroethane, phenol, toluene, chlorobenzene, *n*-butylamine, 4-heptanone, *p*-dichlorobenzene, decane, *n*-butylbenzene, biphenyl, *n*-dodecane, *n*-tetradecane. The correlation equations are examined in terms of gas–solid adsorption theory. They allow prediction of retention behavior for compounds for which experimental retention data are not yet available.

INTRODUCTION

Interest is increasing in using the graphitized carbon material Carbotrap for sampling gas phase organic compounds. Recently, retention volumes on Carbotrap at 293 K were released by Supelco [1] for a wide range of compounds. However, that work did not examine how those data may be used to predict retention values for other compounds of interest. As Pankow [2] has discussed for the sorbent Tenax-GC, useful correlation equations can be developed in gas–solid chromatography between retention volumes and physical constants such as vapor pressure and boiling point.

THEORY

The specific gas phase retention volume ($V_{g,T}$) of a compound on a sorbent at a given temperature T (K) is defined as

$$V_{g,T} = V_{R,T}/w \qquad (1)$$

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where $V_{R,T}$ is the actual net gas phase retention volume at temperature T, and w is the weight of sorbent (g). The standard units for $V_{R,T}$ and $V_{g,T}$ are l and l/g, respectively. Both $V_{R,T}$ and $V_{g,T}$ depend on T as well as the enthalpy of desorption ΔH_s (kcal/mol) from the sorbent surface [3].

When the number of sites for sorption is limited, the sorption process is Langmuirian in character. When the system is not being overloaded chromatographically, such sorption occurs in a "linear" manner, and Pankow [2] obtains

$$\log V_{g,T} = 5.79 + \log fN_sAT + (\Delta H_s - \Delta H_v)/0.0046T - \log p_T^0 \quad (2)$$

where f is a dimensionless constant that depends on the difference between the compound's entropy of desorption from the surface and the entropy of vaporization of the pure compound, N_s is the moles of sites per cm^2 of surface, A is the specific surface area of the sorbent (m^2/g), ΔH_v is the enthalpy of vaporization of the pure compound (kcal/mol), and p_T^0 is the vapor pressure (Torr) of the pure compound at temperature T.

The value of f is often assumed to be equal to ≈ 1, though in many cases that may not in fact be the case [4]. Using an equation described by Pankow [5], one can show that $N_s \approx 5 \cdot 10^{-10}$ mol/cm^2 for the types of compounds for which Carbotrap is suited. The value of A released by Supelco [1] for Carbotrap is about 100 m^2/g. Taking these values and assuming that f is in fact equal to 1, at $T = 293$ K, eqn. 3 becomes

$$\log V_{g,293} = 0.96 + 0.745\,(\Delta H_s - \Delta H_v) - \log p_{293}^0 \quad (3)$$

For Tenax-GC, the corresponding equation ($T = 293$ K) is

$$\log V_{g,293} = -0.15 + 0.745\,(\Delta H_s - \Delta H_v) - \log p_{293}^0 \quad (4)$$

The smaller constant in eqn. 4 *vs.* that in eqn. 3 is due to the comparatively small value of A for Tenax-GC ($\approx$6.4 m^2/g, Pankow [2]). On Carbotrap at $T = 293$ K, for "liquid-like" sorption (*i.e.*, $f = 1.0$ and $\Delta H_s - \Delta H_v$), eqn. 3 becomes

$$\log V_{g,293} = 0.96 - \log p_{293}^0 \quad (5)$$

To the extent that fN_s and $(\Delta H_s - \Delta H_v)$ remain constant from compound to compound, eqn. 2 indicates that at a given value of T, a correlation of log $V_{g,T}$ data *vs.* log p_T^0 should yield a straight line with a slope of -1.00. For a compound that is normally a solid at the temperature of interest, the value of the vapor pressure in eqns. 2–5 should be that of the sub-cooled liquid, *i.e.*, $p_{L,T}^0$. The reason is that the sorbed state is likely to be more similar to the liquid state than it is to the ordered crystalline solid state [6]. Bidleman [6] describes how to calculate $p_{L,T}^0$ values.

Application of Trouton's rule as described by Pankow [2] transforms eqns. 2 and 5 into

$$\log V_{g,T} = -1.91 + \log fN_sAT + (\Delta H_s - \Delta H_v)/0.0046T + 0.016\ T_b \quad (6)$$

$$\log V_{g,293} = -6.74 + 0.016\ T_b \quad (7)$$

TABLE I

SPECIFIC RETENTION VOLUME VALUES ($V_{g,293}$, l/g) FOR ORGANIC COMPOUNDS ON CARBOTRAP AT 293 K ALONG WITH BOILING POINTS AND LOG p^0_{293} VALUES

Compound	Boiling point (°C)	log p^0_{293} (Torr)	log $V_{g,293}$[a] (l/g)
Ethane	−88	4.47	−1.76
Propane	−42	3.81	−1.26
Butane	−0.5	3.18	−0.39
Ethanol	78	1.64	−0.31
Acetic acid	118	1.07	−0.15
Propionic acid	141	0.46	0.22
1,2-Dichloroethane	84	1.78	0.29
2-Butanone	80	1.88	0.58
Pentane	36	2.63	0.77
tert.-Butanol	83	1.49	0.81
Benzene	80	1.88	1.07
Trichloroethane	87	1.78	1.10
n-Butanol	118	0.64	1.28
1,1,2-Trichloroethane	114	1.28	1.39
Hexane	69	2.08	1.90
n-Pentanoic acid	187	−0.82	2.63
Phenol	182	−0.70	2.79
Toluene	111	1.34	2.81
Chlorobenzene	132	0.94	3.20
Cyclohexanone	157	0.60	3.31
n-Butylamine	78	1.86	3.32
4-Heptanone	149	−0.08	3.39
p-Dichlorobenzene	173	−0.22	4.13
Octane	126	1.04	4.21
Ethylbenzene	136	0.85	4.31
p-Cresol	202	−1.40	4.31
Benzylamine	184	−0.24	4.35
p-Xylene	138	0.81	4.63
Acetophenone	202	−0.46	4.81
Isopropylbenzene	153	0.51	5.23
n-Propylbenzene	159	0.40	6.24
Decane	174	0.43	6.68
n-Butylbenzene	183	−0.05	6.77
Biphenyl	258	−1.41	9.57
n-Hexylbenzene	226	NA[b]	9.85
n-Dodecane	216	−0.52	11.21
n-Octylbenzene	262	NA	12.12
n-Tetradecane	252	−1.57	13.92

[a] Data from Supelco [1].
[b] Not available.

where T_b (K) is the boiling point at 1 atm pressure. Thus, when fN_s and $(\Delta H_s - \Delta H_v)$ remain constant log $V_{g,293}$ will correlate with T_b as well as log p^0_{293}.

RESULTS AND DISCUSSION

The available gas phase retention data for Carbotrap are summarized in Table I

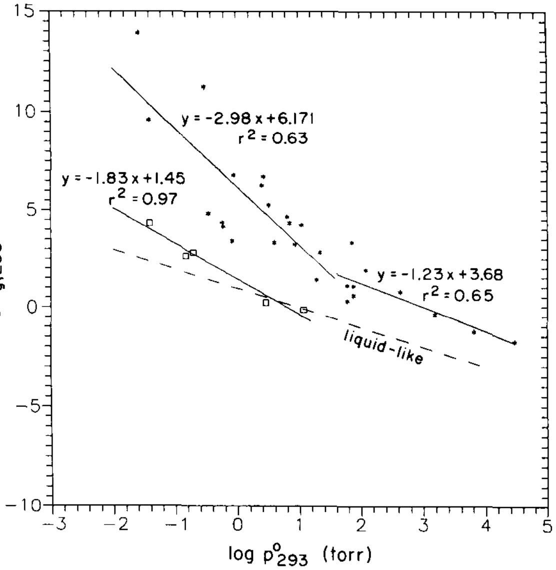

Fig. 1. Plots of log $V_{g,293}$ *vs.* log p^0_{293} for Table I data. Squares are for the acids and phenols. Dashed line is for liquid-like sorption (eqn. 5).

along with boiling points (in °C) and log p^0_{293} values. It should be pointed out that in obtaining the data for the strongly retained compounds, it was apparently necessary to extrapolate the retention data [as log ($V_{g,T}$/T) *vs.* 1/T, see ref. 3] from relatively high temperatures down to 293 K. If a given ΔH_s is not relatively constant over such a wide temperature range, the extrapolation will lead to an incorrect retention volume.

The Table I data (except for the alcohols) are plotted *vs.* log p^0_{293} in Fig. 1 and *vs.* T_b in Fig. 2. For the few compounds that are solids at 293 K, there is little difference between the vapor pressures of the solids and that of the corresponding sub-cooled liquids, and so the former were used. Excluding the alcohols, acids and phenols from consideration for the moment, a break in behavior seems to occur at a log p^0_{293} value of ≈ 1.6 and at a T_b value of ≈ 373 K. The group of compounds for which log $p^0_{293} < 1.6$ is the same group for which $T_b > 373$ K. It is not known whether this break is real, or a result of artifacts due to obtaining the large $V_{g,293}$ values by extrapolation from high temperatures.

The four correlation lines that the two groups give *vs.* log p^0_{293} and *vs.* T_b are included in the figures. There is a fair amount of scatter around some of these correlation lines, more than was found in some cases by Pankow [2] for Tenax-GC. Therefore, in the case of the group for which log $p^0_{293} < 1.6$ and $T_b > 373$ K, it will not be possible to use the corresponding correlation lines to predict retention volume to better than perhaps ± 1.5 orders of magnitude. That degree of prediction will, nevertheless, still be useful. In the case of the acids and phenols, however, the degree of correlation is quite high, both when log p^0_{293} and T_b are used as the correlating parameters. Although not included in Figs. 1 and 2, the data for the alcohols are not out of line with the other data; the points deviate slightly negatively from the four correlation lines discussed above. An overall comparison of the Table I data with the

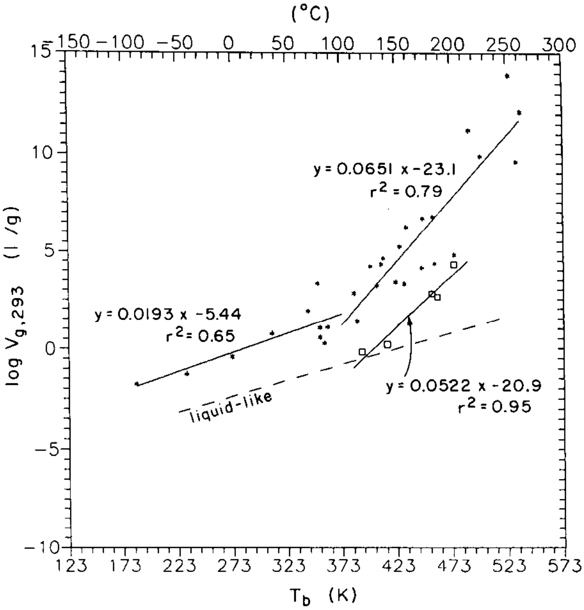

Fig. 2. Plots of log $V_{g,293}$ vs. T_b for Table I data. Squares are for the acids and phenols. Dashed line is for liquid-like sorption (eqn. 7).

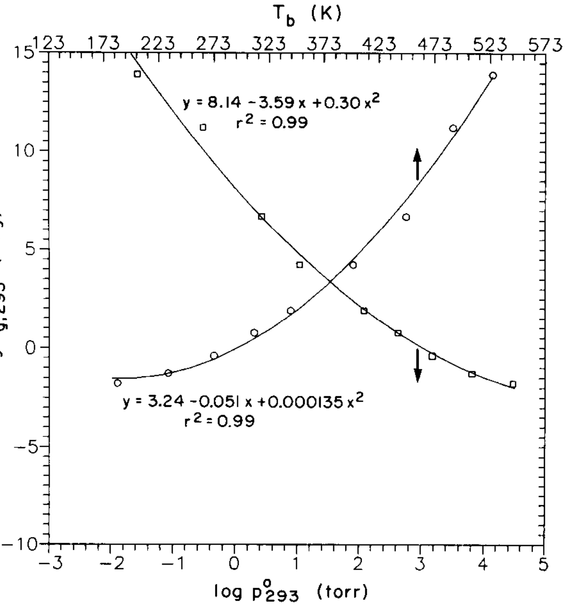

Fig. 3. Plots of log $V_{g,293}$ vs. log p^0_{293} and log $V_{g,293}$ vs. T_b for Table I alkanes.

plots of eqns. 5 and 7 given in the figures lead to the conclusion that sorption on Carbotrap is *not* very liquid-like for most compounds. Some of the correlation lines, however, have slopes approaching the theoretical values.

Fig. 3 presents the data for the alkanes alone. There is a definate curvature when log p^0_{293} and when T_b is used as the independent variable. As above, it is not known whether this curvature is real, or is an artifact of the extrapolations. The correlation parameters for the best-fit second order polynomial curves are given in the figure.

CONCLUSIONS

Gas–solid partitioning theory provides a useful framework in which to consider the gas phase retention volume behavior of organic compounds on Carbotrap. Correlation equations between specific retention volume and compound vapor pressure and boiling point with fair to very good r^2 values have been obtained. It is likely that these equations will be useful in predicting retention behavior for compounds for which experimental retention data are not yet available.

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