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Short Communication

Determination of specific retention volumes at 20°C for hydrocarbons on microporous carbons

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ABSTRACT

Gas chromatography was used to determine the specific retention volumes at 20°C, V_g(20°C), for various hydrocarbons on different microporous carbons. It was found that all microporous carbons can be used for the diffusive sampling of hydrocarbons with more than four carbon atoms. Those hydrocarbons with more than seven carbon atoms have extremely high V_g(20°C) values on these adsorbents, whereas the V_g(20°C) values for very light hydrocarbons ($\leqslant C_3$) are almost all less than 100 l/g, which shows that diffusive sampling may not be suitable for them. It was also found that the adsorption of molecules occurs readily in those micropores which give the highest isosteric heats of adsorption.

INTRODUCTION

The uptake rate of a diffusive sampler (DA/L) [1] should be constant in an ideal case before the saturation of adsorbents, as it depends only on the geometry of the sampler (cross-sectional area, *A*, and diffusion length, *L*) and the individual pollutant vapour which has a particular diffusion coefficient in air, *D*. However, this is true only for an optimized adsorbent–adsorbate system. In practice, non-constant sampling rates were observed [2,3], which are related to the characteristics of the adsorption of the adsorbate–adsorbent system concerned. Therefore, in diffusive sampling, the optimum adsorbent has to be selected for a particular analyte in order to keep the analyte concentration at the adsorbent surface as low as possible.

The adsorbent for diffusive sampling can be selected by determining the experimental uptake rate [4], which should be similar to the ideal uptake rate for the optimized adsorbate–adsorbent system. It can also be selected by a much simpler method as suggested by Brown and Walkin [3]. They proposed that the strength of an adsorbent should be expressed as the retention volume of a particular analyte at 20°C per gram of adsorbent, *i.e.*, the specific retention volume at 20°C. If this value exceeds 100 l/g, the adsorbent should prove satisfactory for diffusive sampling.

Microporous carbons are potential adsorbents for diffusive sampling, especially for the sampling of light hydrocarbons. In this paper, the results of the specific retention volumes at 20°C for various hydrocarbons on different microporous carbons are reported; these can be used as a guide for the selection of adsorbents in the future diffusive sampling work.

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EXPERIMENTAL

Gas chromatographic measurements were made using a Perkin-Elmer F30 gas chromatograph fitted with a flame ionization detector. The carrier gas was nitrogen (supplied by British Oxygen) at a flow-rate of 35 cm^3/min, which was controlled by the make-up needle valve throughout the course of the experiments. The column inlet pressure was measured by a septum pressure gauge and the outlet pressure was measured to be atmospheric. Retention measurements were made over the temperature range 40–380°C. The gas hold-up time (t_0) was determined by the homologus series method [5].

The hydrocarbons used were 1% calibration standards for *n*-alkanes (methane to *n*-butane) and *n*-alkenes (ethylene to *n*-butylene) from Phase Separations and *n*-pentane to *n*-nonane, cyclohexane, benzene, isopentane, 2-methylpentane and 2,2-dimethylbutane from Aldrich. The details of the sample preparation have been described previously [6].

The adsorptive vapours were injected into the carrier gas stream by means of a gas-tight syringe. The on-line computer was started simultaneously with injection. Sequences of injections were made until retention volumes were reproducible to within 2% for at least three consecutive injections. The specific retention volume, V_g, was calculated from the following equation:

$$V_g = 273\,(t_R - t_0)\,F_c/T\,w \qquad (1)$$

where t_R is the retention time of the adsorptive (min), t_0 is the gas hold-up time (min), T is the absolute temperature (K), w is the weight of adsorbent in the column (g) and F_c is the volumetric carrier gas flow-rate reduced to column temperature and mean pressure (cm^3/min).

The following microporous carbons were used. Carbosieve B is a polymer-based molecular sieve carbon, obtained from JJ's Chromatography (King's Lynn, Norfolk, UK). Two charcoal cloths, CC1, a high burn-off charcoal with a much wider range of pore size, and CC2, a low burn-off charcoal cloth, were kindly supplied by Dr. J. J. Freeman of Brunel University. The surface properties of these carbons are given in Table I. The details of the column preparation and conditioning have been described previously [6].

TABLE I

SURFACE PROPERTIES OF ADSORBENTS

A_{BET} = BET specific surface area; A_s = external area; V_p and V_s = primary and secondary micropore volumes respectively, from nitrogen α_s plot. For definition of α_s see ref. 9.

Adsorbent	A_{BET} (m^2/g)	A_s (m^2/g)	V_p [cm^3(liq.)/g]	V_s [cm^3(liq.)/g]
Carbosieve B	1174	51.5	0.45	0
CC1	2074	60.5	0.23	0.98
CC2	1039	16.5	0.41	0

RESULTS AND DISCUSSION

It was found that under the conditions employed almost all hydrocarbons gave nearly symmetrical chromatographic peaks, except in a few instances, such as 2,2-dimethylbutane on Carbosieve B and *n*-octane and *n*-nonane on Carbosieve B and CC2.

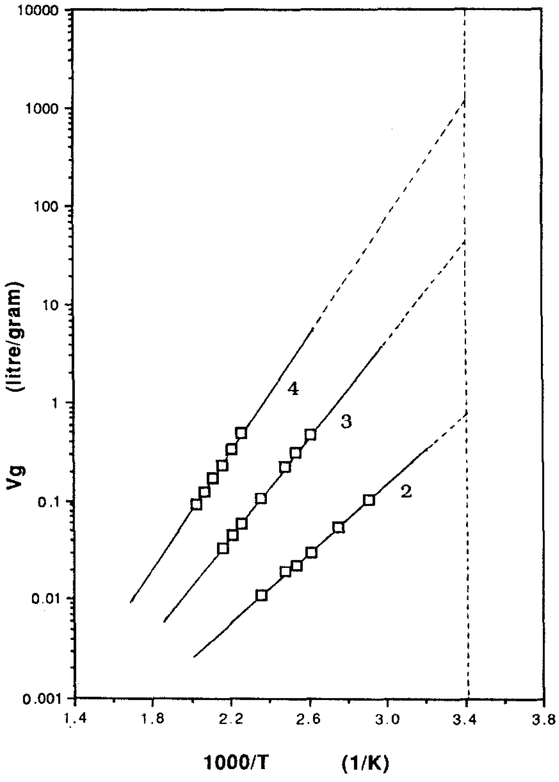

Fig. 1. Plots of log V_g against $1/T$ for *n*-alkenes on Carbosieve B. Numbers on lines indicate number of carbon atoms.

The specific retention volumes were calculated according to eqn. 1 from the retention times. The logarithms of the derived specific retention volumes (l/g) were then plotted against the reciprocal of the absolute column temperature. Representative log V_g *vs.* $1/T$ plots of different hydrocarbons for Carbosieve B, CC1 and CC2 are shown in Figs. 1–5. These plots are almost all linear over a wide range of temperature, although there is a slight curvature in some instances.

The specific retention volumes at 20°C were obtained for each hydrocarbon by extrapolating the slope of each line in the log V_g *vs.* $1/T$ plots. The derived values of the specific retention volumes at 20°C for each hydrocarbon are given in Table I. The V_g (20°C) values for 2,2-dimethylbutane on Carbosieve B and *n*-octane and *n*-nonane on Carbosieve B and CC2 cannot be determined because of the severe asymmetry of the chromatographic bands (tailing) and the problem of irreproducible retention data.

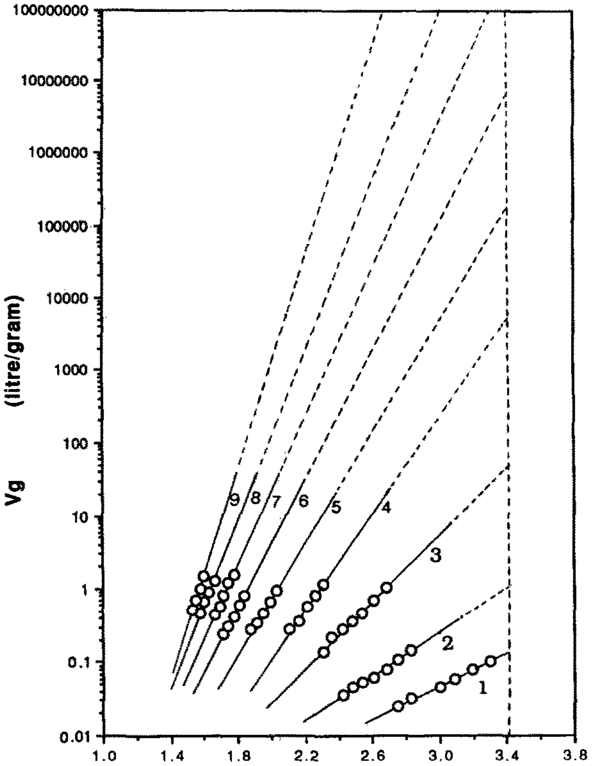

Fig. 2. Plots of log V_g against $1/T$ for *n*-alkanes on CC1. Numbers on lines indicate number of carbon atoms.

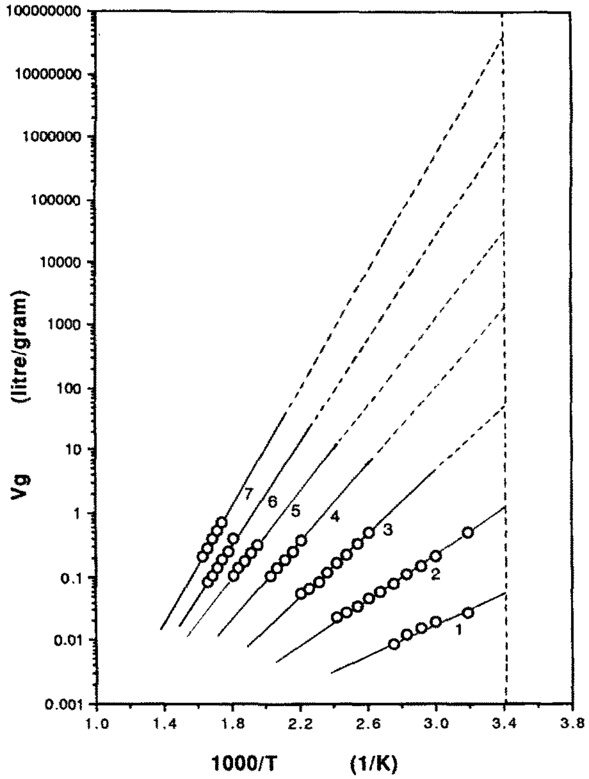

Fig. 3. Plots of log V_g against $1/T$ for *n*-alkanes on CC2. Numbers on lines indicate number of carbon atoms.

It can be seen from the results in Table II that the specific retention volumes at 20°C generally increase with increasing molecular weight of the hydrocarbons. The values of V_g (20°C) for hydrocarbons with more than four carbon atoms all exceed 100 l/g, which indicates that all these adsorbents can be used for the diffusive sampling of these hydrocarbons. However, owing to difficulies with desorption, polymer adsorbents that have much lower specific surface areas (such as Tenax) should be used for the diffusive sampling of hydrocarbons with more than seven carbon atoms instead of microporous carbons on which these hydrocarbons have extremely high V_g (20°C) values. In contrast, even for CC1, which has the highest specific surface area (2074 m^2/g) of the adsorbents, the values of V_g (20°C) for hydrocarbons with less than three carbon atoms, *i.e.*, methane

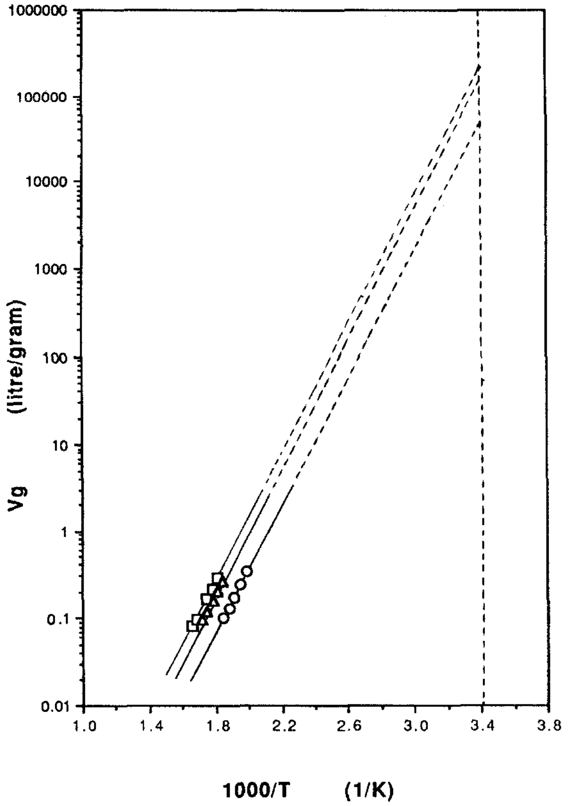

Fig. 4. Plots of log V_g against $1/T$ for hydrocarbons on CC2. ○ = Isopentane; □ = benzene; △ = 2,2-dimethylbutane.

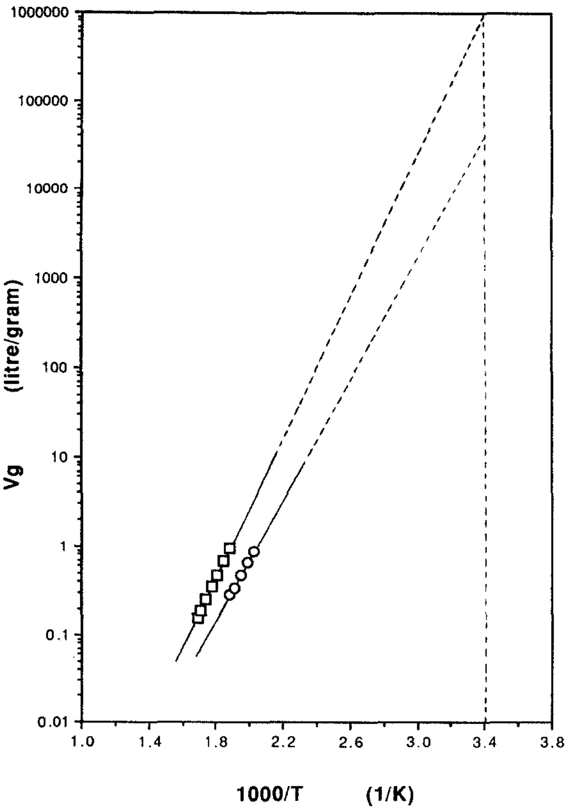

Fig. 5. Plots of log V_g against $1/T$ for hydrocarbons on CC1. ○ = Isopentane; □ = cyclohexane.

to propane, ethylene and propylene, are still far less than 100 l/g, except for propane on Carbosieve B, which shows that diffusive sampling may not be suitable for these very light hydrocarbons or the accuracy of their diffusive sampling measurement will be very poor compared with the pumped method.

It is interesting that, similarly to the findings for the isosteric heats of adsorption values, q^{st} [6], the corresponding V_g (20°C) values for *n*-alkanes and *n*-alkenes generally decrease in the order Carbosieve B > CC1 > CC2, *i.e.*, Carbosieve B, which possesses a homogeneous pore structure, gives higher V_g (20°C) values than CC1, which has a much broader range of pore sizes, which indicates that adsorption occurs readily in those micropores which give the highest isosteric heat of adsorption. In contrast, the V_g (20°C) values for hydrocarbons with branched chains or bulky shapes on CC1 are higher than those on the other two adsorbents. This may be due to the wider micropores in CC1, in which there may be an enhancement of the adsorption energy for adsorption of bulkier molecules, because the enhancement in q^{st} depends on the ratio of micropore width to molecular diameter [7], and the adsorptive molecules of different size will tend to adsorb preferentially in slightly different parts of the micropore structure [8].

The other phenomenon which is also similar to previous findings for q^{st} [6] is that the V_g (20°C) values of straight-chain hydrocarbons are higher than those of hydrocarbons with branched chains or bulky shapes, which may indicate the molecular sieving properties of these adsorbents. For all adsorbents, the V_g (20°C) values generally decrease in the order *n*-pentane > isopentane, *n*-hexane >

TABLE II

SPECIFIC RETENTION VOLUMES AT 20°C FOR HYDROCARBONS ON DIFFERENT ADSORBENTS

Hydrocarbon	V_g (20°C)		
	Carbosieve B	CC1	CC2
Methane	0.12	0.13	0.05
Ethane	5.8	1.1	1.2
Propane	330	50	52
n-Butane	$1.9 \cdot 10^4$	$5.1 \cdot 10^3$	$1.8 \cdot 10^3$
n-Pentane	$5.0 \cdot 10^5$	$1.7 \cdot 10^5$	$2.8 \cdot 10^4$
n-Hexane	$7.6 \cdot 10^6$	$6.1 \cdot 10^6$	$1.2 \cdot 10^6$
n-Heptane	$4.0 \cdot 10^9$	$3.9 \cdot 10^8$	$4.2 \cdot 10^7$
n-Octane	–	$1.8 \cdot 10^{10}$	–
n-Nonane	–	$1.5 \cdot 10^{13}$	–
Ethylene	0.80	0.68	0.62
Propylene	45	33	34
n-Butylene	$1.2 \cdot 10^3$	$1.1 \cdot 10^3$	$1.0 \cdot 10^3$
Benzene	$2.8 \cdot 10^5$	$9.2 \cdot 10^5$	$2.0 \cdot 10^5$
Cyclohexane	$2.6 \cdot 10^5$	$1.0 \cdot 10^6$	$1.2 \cdot 10^5$
Isopentane	$2.3 \cdot 10^5$	$3.7 \cdot 10^4$	$4.2 \cdot 10^4$
2-Methylpentane	$2.8 \cdot 10^6$	$3.3 \cdot 10^6$	$2.6 \cdot 10^5$
2,2-Dimethylbutane	–	$2.2 \cdot 10^6$	$1.6 \cdot 10^5$

2-methylpentane > 2,2-dimethylbutane > cyclohexane ≈ benzene, which may be explained by assuming that generally a linear conformation will allow the greatest interactions between surface and adsorbate, whereas with a branched structure the interaction between surface and adsorbate is weakened because some carbon atoms are relatively far away from the surface.

CONCLUSIONS

The specific retention volumes at 20°C provide a very simple method fo the selection of adsorbents for diffusive sampling. The results show that all microporous carbons can be used for the diffusive sampling of hydrocarbons with more than four carbon atoms. However, for hydrocarbons with more than seven carbon atoms, which have extremely high V_g (20°C) values, these adsorbents may not be suitable owing to the difficulties with desorption. The V_g (20°C) values for hydrocarbons with less than three carbon atoms are almost all less than 100 l/g, which indicates that diffusive sampling may not be suitable for these very light hydrocarbons. The results also show that the adsorption of molecules occurs readily in those micropores which give the highest isosteric heats of adsorption.

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