Journal of Chromatography, 555 (1991) 183–190
Elsevier Science Publishers B.V., Amsterdam

CHROM. 23 382

Study of microporous carbons by gas chromatographic determination of heats of physisorption

X. L. CAO*
Environmental Science Division, Lancaster University, Lancaster LA1 4YQ (UK)
and
B. A. COLENUTT and K. S. W. SING
Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH (UK)
(First received December 27th, 1990; revised manuscript received April 15th, 1991)

ABSTRACT

Gas chromatography has been used to measure low-coverage isosteric heats of adsorption (q^{st}) of *n*-alkanes (C_1 to C_9), *n*-alkenes (C_2 to C_4), isopentane, cyclohexane, benzene, 2-methylpentane and 2,2-dimethylbutane on different microporous carbons. The similar q^{st} values between *n*-alkanes and *n*-alkenes, cyclohexane and benzene show the non-polar or slight polar surfaces of these adsorbents. The q^{st} values of the molecules with branch chains or bulky shapes are smaller than those of corresponding straight-chain molecules, which may indicate the molecular sieving properties of these slit-shaped microporous carbons. It is also shown that there may be an enhancement of adsorption energy for adsorption of some molecules in wider micropores.

INTRODUCTION

Gas chromatography (GC) can be used not only as a means of chemical analysis, but also as a means of physicochemical measurement. Over the past twenty years GC has become an unique means of studying the adsorption characteristics of surface by the determination of isosteric heats of adsorption (q^{st}) at very low surface coverage [1], provided that certain conditions are fulfilled. By using saturated molecules of different size and shape, for example alkanes, it is possible to investigate the non-specific adsorbate–adsorbent interactions and avoid any specific effects which may contribute to the energitics of adsorption of polar molecules [2,3]. The magnitude of the specific adsorbate–adsorbent interaction can be estimated by the differences between the corresponding values for unsaturated and saturated linear hydrocarbons [4,5].

GC can also be used to study the enhancement of adsorption energy associated with the physisorption of molecules in very narrow pores [2,3], *i.e.*, the process of primary micropore filling [6]. It is known that the energy of adsorption is considerably enhanced when physisorption takes place in very narrow pores, and the maximum enhancement is given when the width of the pore is slightly larger than the diameter of the adsorbed molecule [7]. Thus the determination of the enhancement of adsorption energy at very low surface coverage should provide an effective method for the estimation of the width of narrow pores of a given shape [8]. Carrott and Sing [3] found that the isosteric heats of adsorption are weighted in favour of the narrowest pores in the adsorbent, the observed differences in the values of isosteric heats of adsorption given by different microporous carbons can be regarded as reflecting not only differences in pore width, but also differences in the homogeneity of the micropore structure.

In this paper, the results of a study of isosteric heats of adsorption of molecular probes with different sizes, shapes and polarity on different microporous carbons were reported in order to have a better understanding of the relationships between the isosteric heats of adsorption and the microporous carbons' pore structures and the surface properties. The q^{st} values of these molecular probes on these adsorbents were compared with those on the non-specific adsorbent, graphitized carbon black (GCB).

EXPERIMENTAL

GC measurements were made using a Perkin-Elmer F30 gas chromatograph fitted with a flame ionization detector. The carrier gas was nitrogen at a flow-rate of 35 cm^3/min which was controlled by the make-up needle valve throughout the course of the experiment. The column inlet pressure was measured by a septum pressure gauge and the outlet pressure was assumed 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 homologous series method.

The adsorptive vapours were injected into the carrier gas stream by means of a gas-tight syringe. The on-line computer was started simutaneously when injecting. The specific retention volume, V_g, was calculated from the equation

$$V_g = 273\,(t_R - t_0)F_c/(Tw) \tag{1}$$

where t_R is the retention time of the adsorptive, t_0 is the gas hold-up time, T is the column temperature, w is the weight of adsorbent in the column, and F_c is the volumetric flow-rate reduced to column temperature and mean pressure.

The molecular probes used were *n*-alkanes (methane to *n*-nonane), *n*-alkenes (ethene to *n*-butylene), cyclohexane, benzene, 2-methylpentane, 2,2-dimethylbutane and isopentane. Two 1% calibration standards (from Phase Separations) for *n*-alkanes (methane to *n*-butane) and *n*-alkenes (ethene to *n*-butylene) were used after diluting them to 1–10 ppm in nitrogen. The other samples were prepared by injecting 1 μl liquid of each into a 1-l Pyrex glass flask which had been purged with dry nitrogen. The range of masses of molecular probes injected was 1–80 ng.

The following adsorbents were studied. Carbosieve B is a polymer-based molecular sieve carbon, obtained from JJ's Chromatography, Hardwick Trading Estate (King's Lynn, UK). The two charcoal cloths, CC1, a high burn off charcoal cloth 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 the adsorbents are summarized in Table I.

The Carbosieve B column was made of glass tube with dimensions of 35 cm × 2

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 from nitrogen α_s-plot, respectively.

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

mm I.D., which was filled with glass beads (80–100 mesh) and Carbosieve B (80–100 mesh). The charcoal cloth columns were constructed using the method mentioned in Carrott and Sing's work [3]. Before use, columns were heated overnight at 380°C in an nitrogen flow of 35 cm^3/min.

RESULTS AND DISCUSSION

It was found that under the conditions employed almost all molecular probes gave nearly symmetrical chromatographic peaks with specific retention volumes independent of flow-rate or sample size, except a few cases, such as 2,2-dimethylbutane on Carbosieve B and *n*-octane and *n*-nonane on Carbosieve B and CC2. Thus it could be

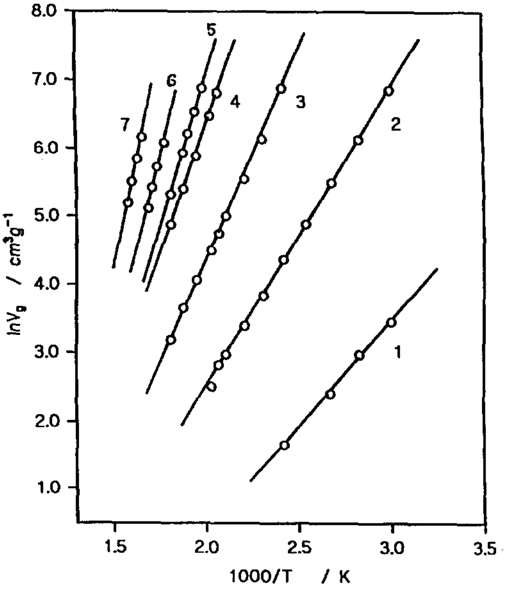


Fig. 1. Variation of specific retention volume with temperature for *n*-alkanes on Carbosieve B. Numbers on lines indicate number of carbon atoms.

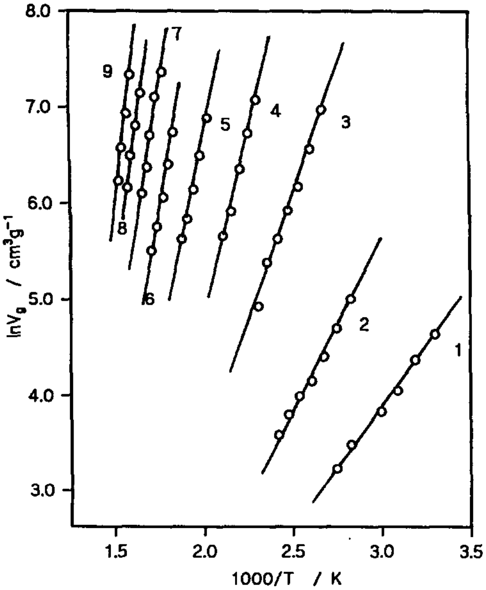


Fig. 2. Variation of specific retention volume with temperature for *n*-alkanes on CC1. Numbers on lines indicate number of carbon atoms.

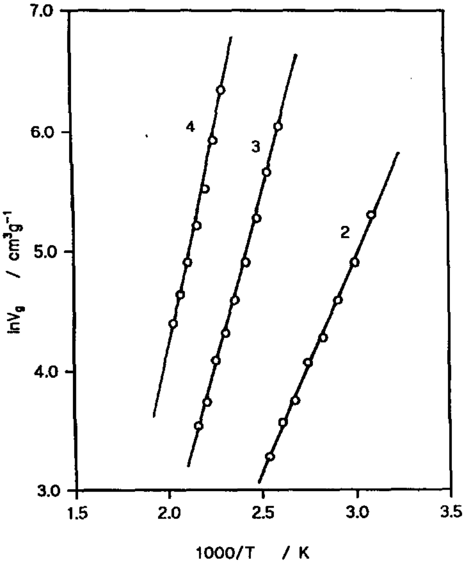


Fig. 3. Variation of specific retention volume with temperature for *n*-alkenes on CC2. Numbers on lines indicate number of carbon atoms.

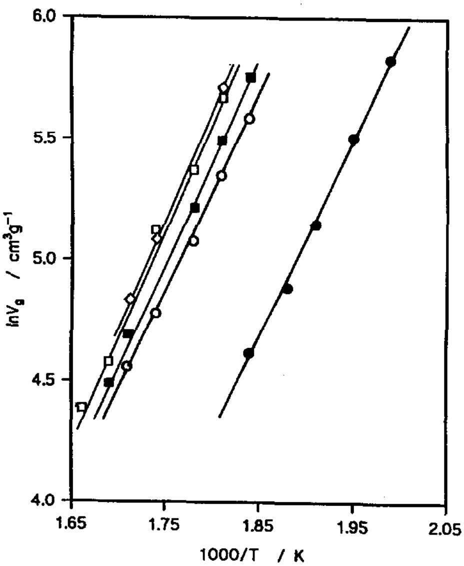


Fig. 4. Variation of specific retention volume with temperature for hydrocarbons on CC2. ○ = 2,2-Dimethylbutane; ● = isopentane; □ = benzene; ■ = cyclohexane; ◇ = 2-methylpentane.

assumed that adsorption occurred at very low surface coverage, and use may then be made of the equation

$$q^{st} = R\,d(\ln V_g)/d(1/T) \qquad (2)$$

in order to calculate q^{st}, the isosteric heats of adsorption at zero uptake, from the variation of $\ln V_g$ with $1/T$ (R is the universal gas constant).

Representatives $\ln V_g$ *vs.* $1/T$ plots of different molecular probes for Carbosieve B, CC1 and CC2 are shown in Figs. 1–4, respectively. These plots are almost all linear over a wide range of temperature, although there is a slight curvature in some cases.

The derived values of q^{st} for each adsorbent are listed in Table II, and the q^{st} vs. n_c (the number of carbon atoms in the *n*-alkanes or *n*-alkenes adsorptive molecules) plots for *n*-alkanes and *n*-alkene are shown in Figs. 5 and 6. The estimated uncertainty in the values of q^{st} is about ± 1 kJ/mol. The q^{st} 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 problems of irreproducible retention data.

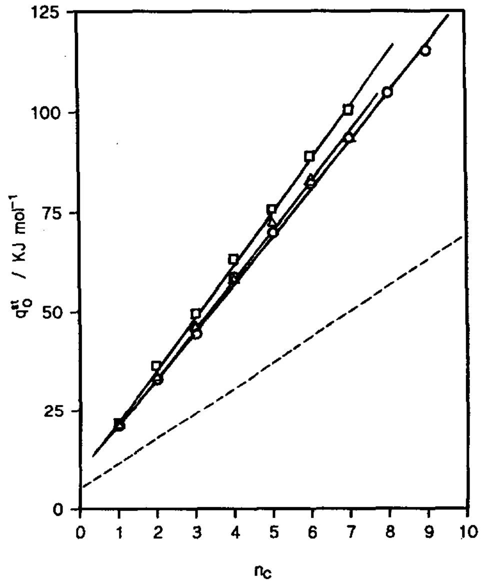
The linearity of the plots of q^{st} *vs.* n_c for *n*-alkanes and *n*-alkenes show that there is a fairly steady increase in the adsorbent–adsorbate interaction energy with increase in chain length of *n*-alkanes and *n*-alkenes. The values of q^{st} for *n*-alkanes, given by microporous samples, are considerably higher than the corresponding values given by GCB, which is an indication of porous nature or polar surface of these adsorbents.

The corresponding q^{st} values for *n*-alkanes generally have the following order: Carbosieve B > CC2 ≥ CC1, *i.e.*, Carbosieve B which possesses a homogeneous pore structure gives higher q^{st} values than CC1 which has a much broader range of pore

TABLE II

ISOSTERIC HEATS OF ADSORPTION FOR VARIOUS HYDROCARBONS ON ADSORBENTS

Adsorptive	q^{st} (kJ/mol)		
	Carbosieve B	CC1	CC2
Methane	22.2	20.9	21.4
Ethane	36.6	33.0	33.8
Propane	49.5	44.3	46.2
n-Butane	62.9	58.6	57.6
n-Pentane	75.4	69.7	71.8
n-Hexane	88.9	82.1	82.7
n-Heptane	100.4	93.6	93.4
n-Octane	–	104.7	–
n-Nonane	–	115.2	–
Ethylene	36.4	29.4	33.9
Propylene	48.9	45.2	47.4
n-Butylene	60.3	59.4	61.3
Isopentane	69.2	66.5	68.3
Cyclohexane	75.7	73.9	69.7
Benzene	74.9	72.6	70.7
2-Methylpentane	83.3	79.4	75.8
2,2-Dimethylbutane	–	75.1	68.4



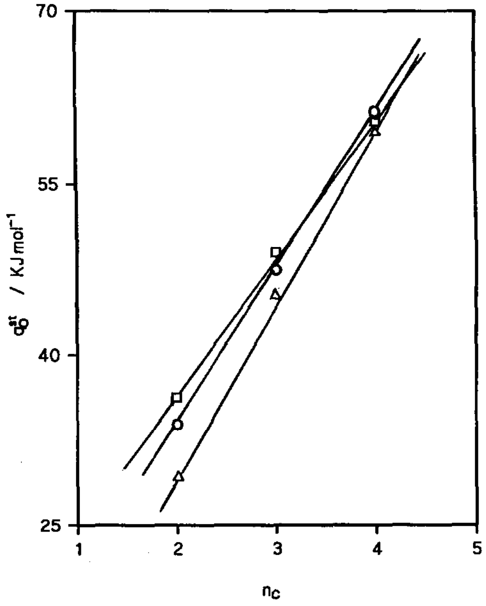


Fig. 5. Variation of q^{st} with *n*-alkane chain length for various adsorbents. ○ = CC1; □ = Carbosieve B; △ = CC2. Dashed line: GCB [9].

Fig. 6. Variation of q^{st} with *n*-alkene chain length for various adsorbents. ○ = CC2; □ = Carbosieve B; △ = CC1.

TABLE III

DIFFERENCES BETWEEN THE q^{st} VALUES OF *n*-ALKANES AND *n*-ALKENES ON ADSORBENTS

Adsorbents	Δq^{st} (kJ/mol)		
	Ethylene and ethane	Propylene and propane	*n*-Butylene and *n*-butane
Carbosieve B	−0.1	−0.5	−2.5
CC1	−3.6	0.9	0.7
CC2	0.2	1.3	1.6

sizes. This results show, as Carrott and Sing [3] reported, that the isosteric heats of adsorption are weighted in favour of the narrowest pores in the adsorbent. It is interesting to note that the q^{st} values of *n*-alkanes on CC1 which has much broader range of pores are similar to those on CC2, but the q^{st} values for molecular probes with branched or bulky shapes on CC1 are higher than those on CC2. 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.

Table III shows differences between the isosteric heats of adsorption of *n*-alkanes and *n*-alkenes on the adsorbents. It can be seen that for each adsorbent the q^{st} values of *n*-alkanes are similar to those obtained with the corresponding *n*-alkenes, which shows the non-polar or slightly polar surfaces of these adsorbents, and that the adsorption of *n*-alkenes was dependent primarily on non-specific dispersion forces. The non-polarity of these adsorbents can also be shown by the similar q^{st} values of benzene and cyclohexane for these adsorbents.

The differences between the q^{st} values of different-shape molecular probes are shown in Table IV. It can be seen that the q^{st} values of straigth-carbon-chain hydrocarbons are higher than those of hydrocarbons with branch chains or bulky shape, which may show the molecular sieving properties of these adsorbents. For all adsorbents, the q^{st} values obey the following order: *n*-pentane > isopentane, hexane > 2-methylpentane > 2,2-dimethylbutane > cyclohexane ≈ benzene. This may be explained by assuming that generally a linear conformation will allow greatest inter-

TABLE IV

DIFFERENCES BETWEEN THE q^{st} VALUES OF DIFFERENT-SHAPE MOLECULES

Adsorptive	Δq^{st} (kJ/mol)		
	Carbosieve B	CC1	CC2
Between *n*-hexane and			
2-methylpentane	5.5	2.7	6.9
2,2-dimethylbutane	–	6.9	14.3
cyclohexane	13.2	8.1	12.9
benzene	13.9	9.5	11.9
Between *n*-pentane and			
isopentane	6.2	3.2	3.6

actions between surface and adsorbate, while in branched structure the interaction between surface and adsorbate is weakened because some carbon atoms are relatively far away from the surface. It may also be an indication of slit-shaped micropores in these adsorbents to which the straight-chain molecules will be more accessible than those with bulky shapes.

CONCLUSIONS

GC has been shown to be useful for characterizing adsorbents by the determination of isosteric heats of adsorption at low surface coverage. For all adsorbents, the derived values of isosteric heats of adsorption of *n*-alkanes and *n*-alkenes generally increase linearly with the increase of the carbon number. The q^{st} values of *n*-alkenes are similar to those obtained with the corresponding *n*-alkanes, which shows the non-polar or slightly polar surface of these adsorbents. The q^{st} values of the molecules with branch chains or bulky shapes are smaller than those of corresponding straight-chain molecules, which may indicate the molecular sieving properties and the slit-shaped microporous structures of these adsorbents. The q^{st} values of hydrocarbons on these adsorbents were higher than those on GCB. The results also show that there may be an enhancement of adsorption energy for adsorption of some molecules in wider micropores.

REFERENCES

1 A. V. Kiselev, *Adv. Chromatogr.*, 4 (1967) 113.
2 P. J. M. Carrott and K. S. W. Sing, *Chem. Ind.*, (1986) 360.
3 P. J. M. Carrott and K. S. W. Sing, *J. Chromatogr.*, 406 (1987) 139.
4 T. Ahsan, B. A. Colenutt and K. S. W. Sing, *J. Chromatogr.*, 464 (1989) 416.
5 T. Ahsan, B. A. Colenutt and K. S. W. Sing, *J. Chromatogr.*, 479 (1989) 17.
6 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 2nd ed., 1982.
7 D. H. Everett and J. C. Powl, *J. Chem. Soc., Faraday Trans. 1*, 72 (1976) 619.
8 D. H. Everett, in S. J. Gregg, K. S. W. Sing and H. F. Stoeckli (Editors), *Characterization of Porous Solids*, Society of Chemical Industry, London, 1979, p. 99.
9 N. N. Avgul and A. V. Kiselev, in P. L. Walker (Editor), *Chemistry and Physics of Carbon*, Marcel Dekker, New York, 1965, p. 1.